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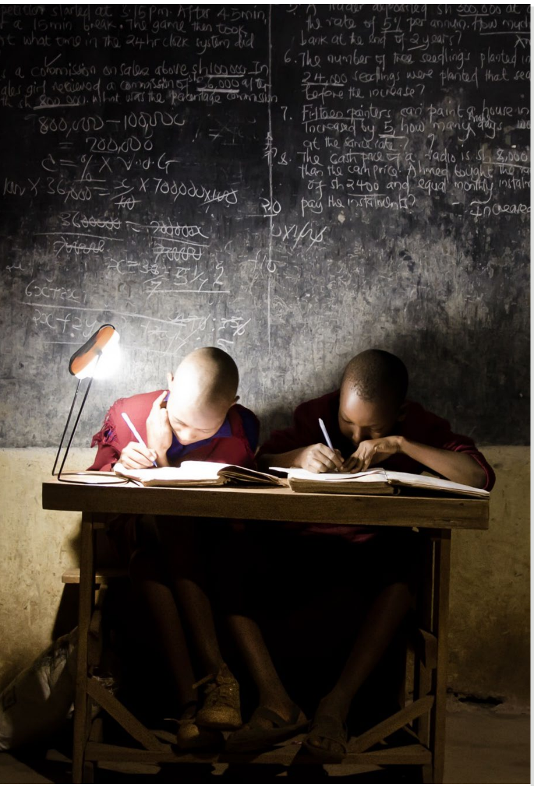
TECHNICAL NOTES



Lithium-ion Batteries Part II: Safety

Lithium-ion batteries are cost effective, high capacity, and capable of long cycle life when properly used in off-grid products. They can, however, present a serious safety hazard if poorly manufactured or improperly charged and discharged. Good design practices can mitigate the danger from these batteries and should always be used for off-grid products.

Introduction

Lithium-ion (Li-ion) batteries are often the battery of choice for mobile devices and off-grid products. Li-ion technology has a number of advantages over other battery chemistries including high energy density, excellent efficiency, competitive cost, and good cycle life. These qualities, coupled with ongoing improvements, will likely keep lithium as a dominant battery chemistry in off-grid products for years to come.

Safety, however, is one issue that is a concern with lithium-ion battery systems. Under certain conditions, Li-ion batteries can catastrophically catch fire or explode, potentially starting fires or causing serious injury or death.

Li-ion systems can, however, be made very safe with proper design features that incorporate well-known mechanical and electronic safety mechanisms. The billions of Li-ion batteries in use every day are a testament to the safety qualities of this technology.

Battery basics

A battery is an electrochemical energy storage device: this means that it stores and releases electrical energy using chemical reactions. Primary batteries have a chemical reaction that proceeds in one direction and are used only once. Secondary batteries use a reversible chemical reaction that stores and discharges energy for multiple cycles before the physical materials of the battery change and degrade, which eventually leads to battery failure.

In a Li-ion battery, lithium ions travel back and forth between the **anode** and **cathode** during charge and discharge (for Li-ion batteries, the negative electrode is labelled the anode and the positive electrode is the cathode). The ions move in an **electrolyte** and across a **separator** that sits between the two electrodes (Figure 1). The sequence involves reduction/oxidation (redox) reactions specific to the particular chemistry of the cathode, and the chemical energy of these reactions is harnessed to store and discharge electrical energy from the positive and negative terminals of the battery.

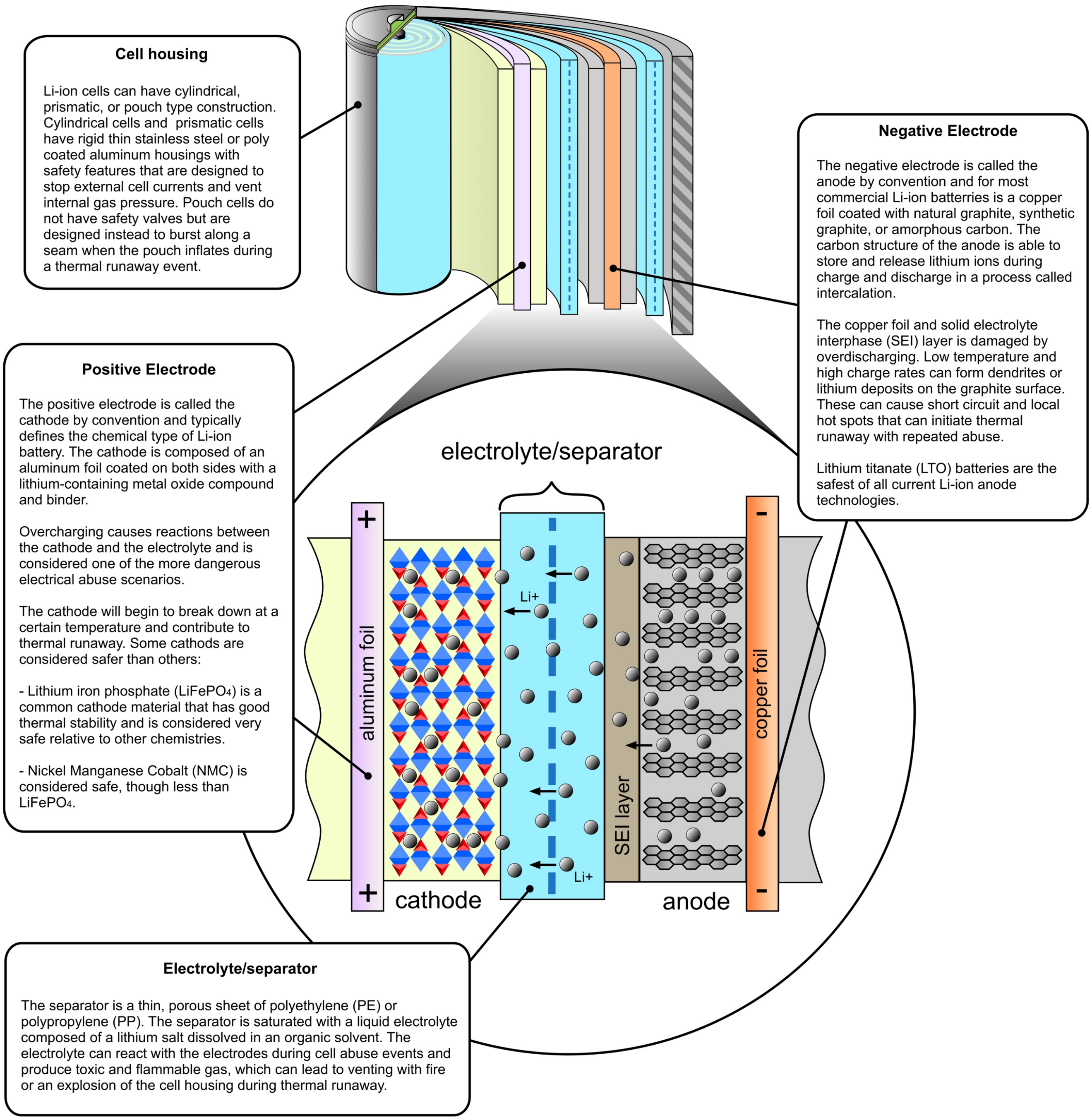


FIGURE 1. A SIMPLIFIED DIAGRAM OF AN 18650 LITHIUM IRON PHOSPHATE ($LIFEPO_4$) CYLINDRICAL CELL BATTERY DEPICTING THE PRIMARY FUNCTIONAL ELEMENTS: CATHODE (POSITIVE ELECTRODE), ANODE (NEGATIVE ELECTRODE), AND ELECTROLYTE/SEPARATOR.

NOTE: THE NEGATIVE AND POSITIVE ELECTRODES OF A BATTERY ARE REFERRED TO AS THE "ANODE" AND "CATHODE" RESPECTIVELY. THIS IS TECHNICALLY TRUE ONLY DURING BATTERY DISCHARGE. THIS CONVENTION IS USED CONSISTENTLY IN THE TECHNICAL LITERATURE.

Thermal runaway

The primary hazard from Li-ion batteries is a catastrophic event called ***thermal runaway*** in which the battery quickly and sometimes violently releases is stored electrochemical energy. During thermal runaway, the internal temperature of the battery cell exceeds temperatures of 500°C as the internal components react and ignite. Flammable gasses are generated inside the case, which will build up pressure and vent (often with the gases on fire) or even explode if the pressure relief mechanisms don't function properly. Depending on the size and design of the battery cell(s), cell cases, and battery pack, this can be extremely dangerous.

During thermal runaway, exothermic reactions become self-sustaining and uncontrolled.[1] Once the multi-stage process is started, it may or may not proceed to sudden catastrophic failure depending on many factors including the age and cycle history of the cell, the local temperature and environment, the specific cell chemistry, the construction of the battery pack, and any physical or electrical safety mechanisms that have been incorporated into the battery pack design.

Internal and external short circuits hazards

An internal short circuit is a common starting point for thermal runaway. Internal short circuits occur when current is allowed to flow between the cathode and anode layers inside the battery cell. [2] Internal short circuits involve a physical breach of the separator, allowing the anode and cathode layers to come into direct electrical contact with each other and discharge their electrochemical energy. Internal shorts cannot be controlled by electronics or fusing outside the cell.

External short circuits from circuit or wiring failures release energy quickly, generating resistive (ohmic) heating inside the cell. If the temperature rise is high and fast enough, it can shrink or melt the separator and initiate anode/cathode reactions with the electrolyte. This can directly initiate thermal runaway or, less critically, permanently damage the cell and possibly lead to subsequent failure with repeated abuse.

Separator tearing, melting, shrinkage, and collapse

The separator plays a central critical role in both normal cell operation and thermal runaway. Thermal runaway sequences all involve the compromise of the polymer separator as a critical step that allows events to accelerate to the point of catastrophic failure.[3]

Gas generation

Elevated temperature reactions between the anode, cathode and electrolyte can produce toxic and flammable gases which can build up pressure inside the case, ignite, and lead to explosion of the battery case. [1,4]

Electrolyte ignition

The electrolyte is typically a combination of lithium salts (e.g. $LiPF_6$) in a liquid organic solvent (a combination of ethylene carbonate (EC), dimethyl and/or diethyl carbonate (DMC and/or DEC)). The electrolyte is flammable and will produce toxic gases during thermal runaway when temperatures exceed ~200°C.[1,4]

Thermal runaway reaction temperatures

Thermal runaway can be initiated when a portion of the cell reaches a temperature as low as 100°C.[5] With the right cell type and under specific conditions, a series of chain reactions occur inside the cell. Each step takes place within a specific temperature window, and includes SEI decomposition/regeneration, electrode decomposition and electrolyte reactions, hazardous gas pressure buildup, and ignition of the electrolyte. For reactions to proceed, heat must build and release the cells' electrical and chemical energy fast enough to sustain and exceed the critical reaction temperatures of the cell components (Table 1). [1,4,6]

TABLE 1: THERMAL RUNAWAY REACTION TEMPERATURES[1]

CELL REACTION	REACTION TEMPERATURE
SEI layer decomposition	80-120 °C
SEI decomposition/regeneration	120-250 °C
separator melting (endothermic)	130-170 °C
anode collapse/decomposition	>250 °C
cathode collapse/decomposition	varies by chemistry
electrolyte ignition	200-250 °C

What causes thermal runaway?

Overcharge and external short circuit

Overcharging a Li-ion battery can generate heat, gas, and side reactions that can lead to cell damage and failure (Figure 2). Excessive de-intercalation of lithium ions from the cathode causes chemical reactions with the electrolyte that release gas, build up pressure within the cell case, and deposit lithium on the negative electrode. The cathode structure can collapse. Overcharging is often considered the worst type of cell abuse because of the multiple negative consequences and because the cell has a maximum amount of stored energy in this condition. Exceeding 150% state of charge (SOC) is particularly dangerous.[7]

An external short circuit also produces heat and gas if allowed to proceed unchecked, though electric current (and ion flow) will be in the opposite direction.

Overdischarge

Allowing the cell voltage to fall below the specified cutoff can cause the anode's copper foil to dissolve and redeposit (Figure 3). The SEI will also decompose and regenerate, releasing heat. If the cell continues to be discharged after it reaches 0% SOC (state-of-charge), copper dendrites can form conductive bridges from the anode to cathode. If the damaged cell can accept a recharge, these will cause weak internal short circuits (soft shorts). At a minimum, this causes capacity loss and increased internal resistance. Under extreme circumstances, this may initiate thermal runaway.[8]

Low temperature and high rate charging

Charging a lithium battery at low temperatures or high charge rates can hinder the ability of the graphite anode layer to accept lithium ions and leads to lithium deposition/plating on the anode surface (Figure 4). This lowers the capacity of the cell and favors the growth of thin dendrite structures that can pierce the separator and cause soft shorts. Subsequent charging does not remove the dendrites or plating, and the cell performance will suffer.[9] In extreme circumstances the dendrites can cause hard shorts that will heat the local area and lead to thermal runaway.

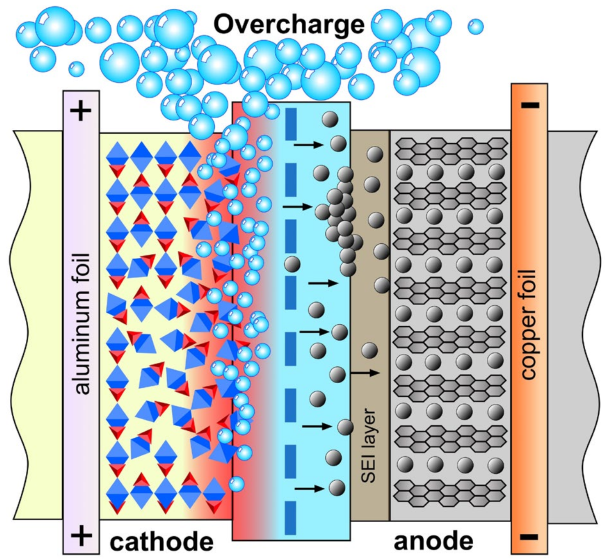


Figure 2. Overcharge releases heat and gas

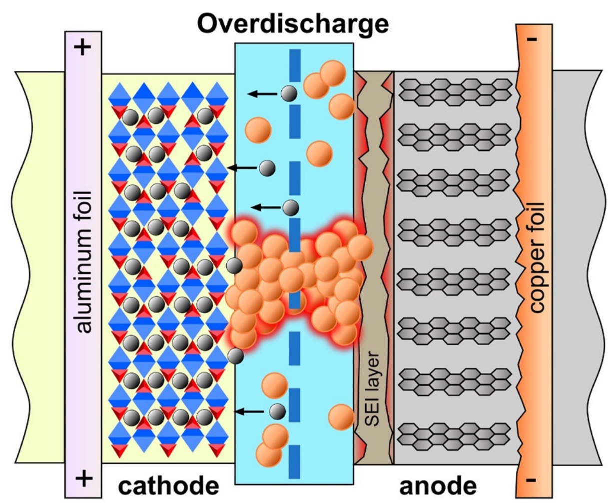


Figure 3. Overdischarge damages the copper anode

Low temperature charging or high charge rates

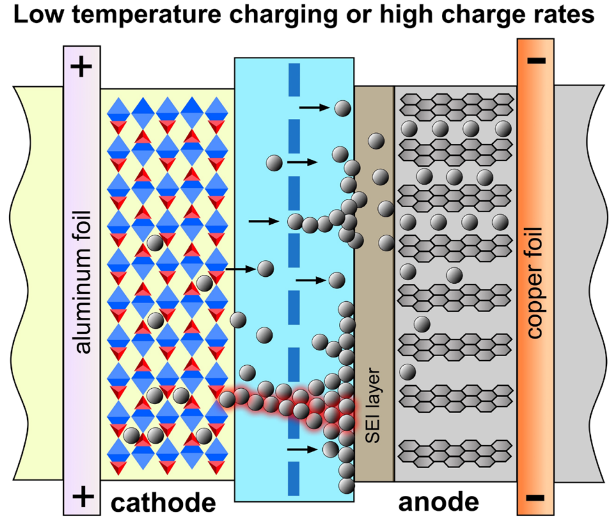


Figure 4. Low temp/high rate charging forms dendrites

Mechanical stress

External pressure on the battery case wall puts pressure on the layers inside the cell (Figure 5). This can cause performance issues by causing soft shorts or concentrating current flow into hot spots, or in extreme cases can tear the separator and lead to a hard short and thermal runaway. Piercing the case wall with a foreign object is even more stressful and likely to lead to catastrophic failure.[1]

Thermal stress and high temperature use

Thermal stress can occur as external heat is applied to the battery cell case from the local environment or from one cell to another in a battery pack (Figure 6). The propagation of thermal runaway through a battery pack can exacerbate an already serious problem and increase the likelihood of battery fire and explosion.

High temperature charging above 45 °C will reduce the cycle life of the cell and may encourage the formation of defects. Electrode swelling and electrolyte reactions, SEI layer thickening, and gas generation all contribute to the degradation of the cell.[3] Integrated solar off-grid products may experience internal temperatures of 85 °C,[10] making this a particular concern for products with batteries designed to charge in the sun.

Manufacturing defects

Manufacturing defects are a major factor in the performance and safety of li-ion battery technology (Figure 7). Metal particle contamination, layer composition and uniformity, chemical impurities, deposition defects, and assembly procedures all play critical roles in determining battery cell capacity, output tolerances, cycle lifetimes, and resistance to thermal runaway. Defects are controlled at the cell and battery pack manufacturing level. [11,12]

Experience, proper manufacturing procedures, and good cell testing/matching are key elements that prevent manufacturing defects from causing problems, and potentially hazardous conditions in finished products.

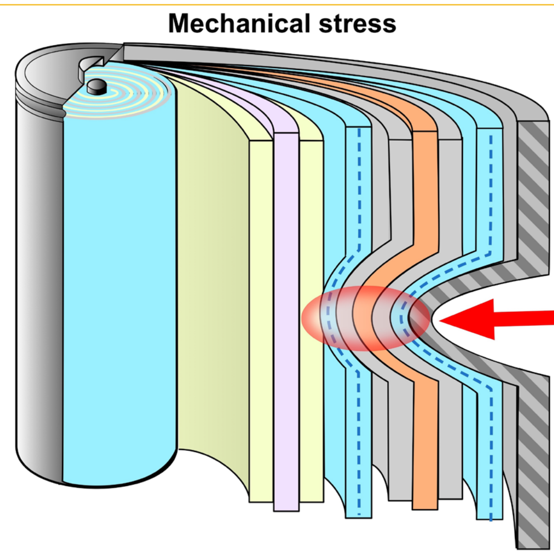


Figure 5. Mechanical stress damages internal layers

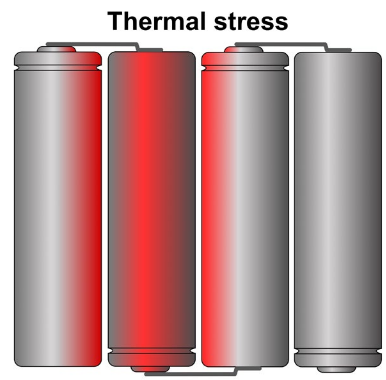


Figure 6. Thermal runaway can spread though the battery pack

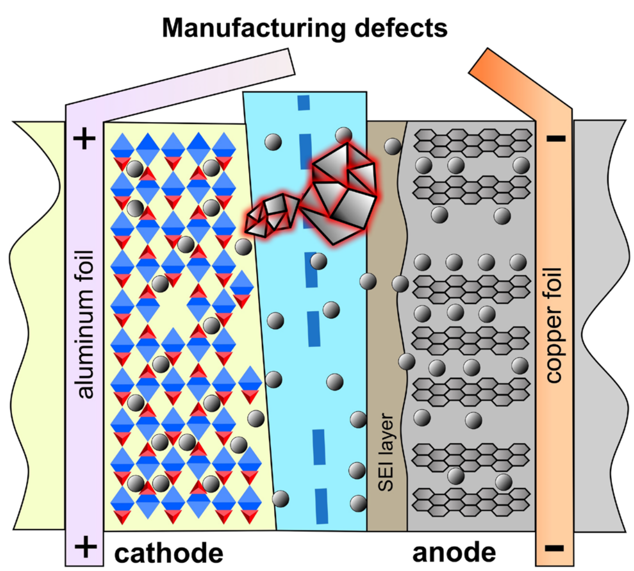


Figure 7. Manufacturing defects can take many forms and pose a serious risk to Li-ion based products

How to prevent thermal runaway

Cell manufacture, capacity matching, and battery pack assembly

Safe Li-ion battery design starts in the battery factory and includes carefully controlled manufacturing processes, contamination-free cell assembly, proper conditioning, and good cell matching.[13] The battery manufacturer should provide charge/discharge profiles, specific voltage and temperature limits, and cell output tolerances (capacity, voltage etc.) for the lot or cell type.

Cells used in battery packs should always be of the same type and from the same manufacturer, preferably from the same manufacturing lot. Cell capacities should be matched as closely as possible so that all the cells experience approximately the same voltage and state-of-charge cycle history. Older or used cells should never be used with new cells.

Built-in cell protection and venting

Li-ion batteries are designed with safety features that can shut down the cell current and release pressure from gas buildup before the case ruptures catastrophically (explodes) and ejects burning electrolyte and molten cell contents.[14] The most common and mature designs for venting are found in cylindrical cells, though battery manufacturers use a variety of designs. A positive temperature coefficient (PTC) switch is a conductive polymer disk that increases its electrical resistance with an increase in temperature. This decreases the current draw from the cell and is designed to reset when the temperature returns to normal. A current interrupt device (CID) is another disk that is designed to permanently disconnect the positive terminal with an increase in pressure and preferentially break to release that pressure (Figure 8).

Prismatic cells have metal cases and are similar to cylindrical cells, but pouch cells do not have rigid cell cases to resist pressure buildup. In normal operation pouch cells swell 5-10% by volume, but under abuse conditions the cells can build up a large volume of gas and are designed to break along one of the pouch seams with excessive gas pressure (Figure 9).

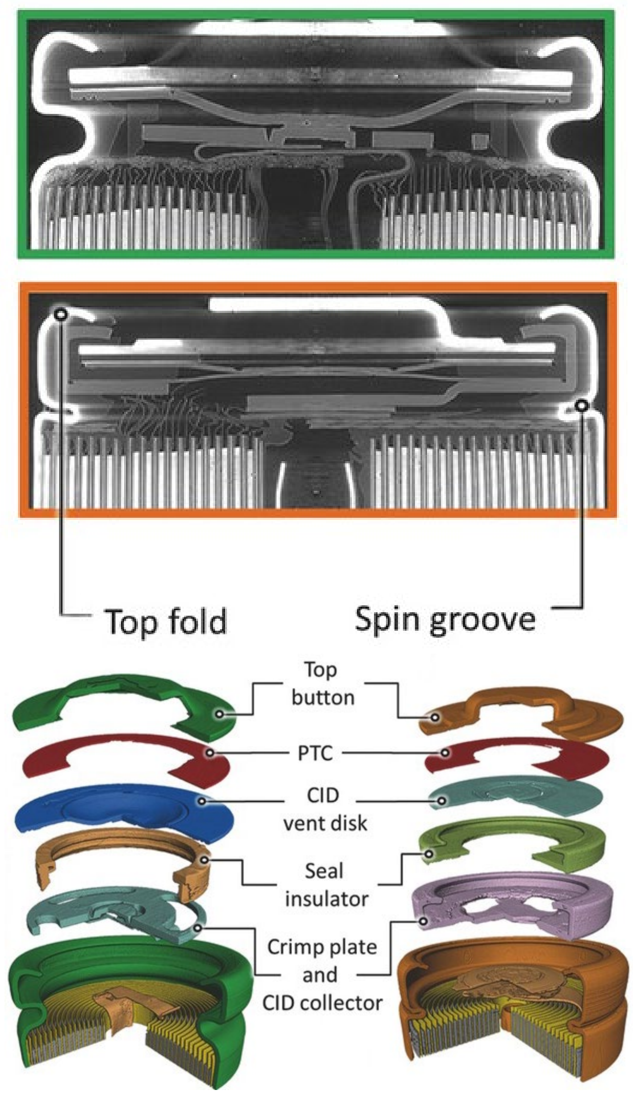


Figure 8. X-ray images and component drawings of two commercial Li-ion 18650 cylindrical cells.

Advanced Science, Volume: 5, Issue 1, First published: 27 Oct 2017, DOI: (10.1002/advs.201700369)

Figure 9. Swelling of a Li-ion pouch cell

Safer battery materials

Lithium Iron Phosphate ($LiFePO_4$)

Many off-grid products use Lithium Iron Phosphate ($LiFePO_4$, also abbreviated as LFP) for the cathode positive electrode. $LiFePO_4$ batteries exhibit many qualities that make them ideally suited for solar applications where safety, stability, and cycle life are primary requirements.[15] They have lower energy density than competing Li-ion chemistries, but this is acceptable for many off-grid applications.

The key advantage of $LiFePO_4$ as a cathode material lies in its chemical stability and the ability to withstand relatively high temperatures (Table 2). The molecular structure absorbs and releases lithium ions without a large change in volume, and is resistant to the growth of defects from daily charge and discharge cycles.

$LiFePO_4$ cells are NOT impervious to thermal runaway, however, and the same precautions for other chemistries also apply to them.

Lithium Nickel Manganese Cobalt Oxide (NMC)

NMC (also called NCM) Li-ion batteries are available with different ratios of nickel, manganese, and cobalt. These cathode blends take advantage of the properties that these elements provide while also mitigating some of their negative cost, safety, and performance attributes. The development of NMC battery technologies makes them increasingly attractive for use in off-grid products.

The safety of NMC electrodes is lower than $LiFePO_4$, but it is typically better than other cobalt based electrodes.

Lithium Titanate

Lithium titanate (LTO) can be used instead of graphite for the anode (negative electrode) of NMC or lithium manganese oxide (LMO) batteries. Lithium titanate batteries are considered very safe and have extremely long cycle lifetimes. If technology improvements lead to cost and energy density improvements, they would be excellent batteries for off-grid products.

TABLE 2. THERMAL STABILITY OF CATHODE MATERIALSERROR! REFERENCE SOURCE NOT FOUND.

Material	Abbr.	Decomposition temperature
Lithium cobalt oxide	LCO	150°C
Nickel cobalt aluminum	NCA	150°C
Nickel manganese cobalt	NMC	210°C
Lithium manganese oxide	LMO	265°C
Lithium iron phosphate	LFP	310°C

Enhanced safety separators and electrolytes

Separators with improved thermal properties exist for use with liquid electrolytes. Shutdown separators, for example, feature both PE and PP layers and are designed so that the pores in the film melt closed, and shut down current flow, when the cell overheats.

Ceramics, glass, and inorganic particles can also be incorporated into the separator to increase temperature resistance, and research continues to develop better performance and enhanced safety of this component.

Electrolyte research is focused on finding ways to replace liquid organic solvents, and their low associated flash points and high flammability, with safer options. This includes both liquid and non-liquid systems, as well as gelled electrolytes that contain a reduced liquid component but still retain good ionic conductivity. Some of these approaches currently exist for Li-metal primary batteries and are being studied for use with Li-ion secondary systems.[16]

Li-ion batteries in off-grid products

As the off-grid industry grows, system size and product complexity increases. Larger batteries in off-grid products generally pose an increased hazard due to the higher stored energy content in the system, but this does not mean that larger products are more or less dangerous. Small batteries can still start fires, and the driving factors of increased safety or risk are the same in all cases.

Battery pack design

Off-grid product manufacturers are increasingly buying individual cells and assembling their own battery packs. This requires extra training and attention to handling procedures to prevent the introduction of defects. Good Li-ion product design will always include:

- Quality cells with low defect rates, made in clean conditions with stringent manufacturing protocols and proper testing and cell qualification.
- Proper battery pack assembly. This includes good cell matching and pack assembly that does not mechanically abuse the cells.
- Battery pack handling and product assembly should not damage the cells.
- The off-grid product housing design should consider thermal events, cell venting, and heat exchange between cells and their environment.
- The product housing must protect and secure the pack, and prevent stress from clips and fasteners.
- Reliable battery management electronics. Proper charge and discharge is essential to good performance, long life, and safety.

Battery management systems

Battery management systems must be used with Li-ion batteries to control charging and protect the individual cells from electrical abuse (Figure 10). High and low voltages, high charge currents, external short circuits, and proper charging profiles are necessary to protect Li-ion cells from electrical abuse and provide adequate cycle lifetimes. Li-ion batteries can be badly damaged from just a single electrical abuse event or from longer term smaller scale cyclical abuse.

Battery protection circuitry can be incorporated directly into the battery cell, cell block, or pack, OR it can be integrated with the off-grid product's other control circuitry external to the battery. It must be capable of reliably regulating the battery within the specific tolerance range provided by the battery manufacturer.

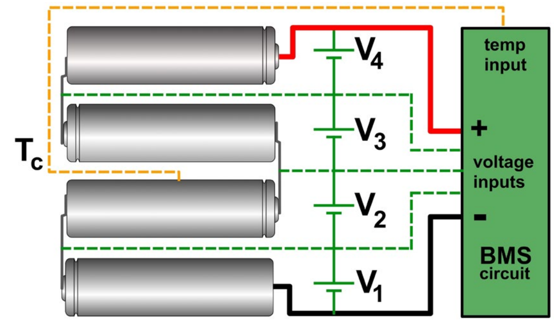


Figure 10. BMS schematic for a 4-series cell battery pack. In this example, the individual cells and the battery pack temperature are monitored. Advanced BMS topologies also include individual cell control and balancing, as well as multiple temperature monitoring inputs.

At a minimum, the BMS must:

- Prevent an external short circuit or excessive current draw
- Monitor the battery pack voltage
- Protect the battery pack against deep discharge
- Protect the battery pack against overcharge

Cells used in series are at particular risk of an imbalance developing between the strong and weak cells in the series. Lower capacity cells can be overcharged or deeply discharged before the other cells, and this can lead to capacity loss and possibly cell voltage reversal. These problems can be mitigated with advanced BMS features that include individual cell monitoring and control and are recommend for all series-cell packs.

Advanced BMS features:

- Monitor every individual cell in the battery pack
- Prevent deep discharge and overcharge of individual cells as well as the entire battery pack
- Perform cell balancing of individual cells to maintain pack consistency and prolong life
- Monitor the temperature of cells and battery packs, and cut off charge and discharge when needed
- Perform coulomb counting to assess state-of-charge and battery capacity

Conclusion

Li-ion battery technologies, when properly deployed, are safe, cost effective, durable, and well suited to off-grid applications. With certain lithium technologies under specific abuse conditions, however, they can enter thermal runaway and catastrophically release considerable amounts of energy in a very short amount of time. The resulting fire or explosions can be extremely dangerous to people and property.

Li-ion battery fires in consumer products, though rare, are high profile events that can cause significant harm and garner considerable attention. Understanding Li-ion hazards should be well understood by off-grid product manufacturers that use these technologies, and preventing catastrophic failures should be the highest priority for battery manufacturers, off-grid product manufacturers and stakeholders, and government regulators.

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