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SimpliPhi Power Storage Solutions: Safety and Ecology

This paper is to outline the intrinsic safety of Lithium Ferro Phosphate (LFP) cells used in SimpliPhi batteries with a comparison to other types of Lithium Ion chemistries currently on the market.

Due to the extremely robust crystal structure of the Ferro (Iron) Phosphate, which does not break down under repeated packing and unpacking of the Lithium Ions during charging and discharging, SimpliPhi Lithium Ferro Phosphate batteries are among the longest lasting (10,000+ cycles) secondary battery types that are commercially available. Testing in the laboratory and field show up to >10,000 cycles or more depending on depth of discharge and environmental conditions.

The most common type of Li-Ion cell first made for commercial use was the $LiCoO_2$ or Lithium Cobalt Oxide, and while this chemistry offered a very high energy density, particularly as compared to the then industry standard lead acid, these cells had serious safety considerations. The low strength of the cobalt-oxygen bond in the $LiCoO_2$ chemistry led to the cell heating up and the bond breaking down, resulting in explosions and fires which can and have been extremely dangerous and with disastrous results in high pressure environments such as airplanes, large applications, or electric vehicles.

By contrast, in the LFP cell chemistry, the iron-phosphate-oxygen bond is much stronger than the cobalt-oxygen bond, so that when rigorously tested and utilized in field applications, (short circuited, overcharged, rapid charge and discharge, etc.), the oxygen atoms are more stable and much harder to dislodge. As a result, the LFP cells are not prone to overheating, explosion or the chemical property known as 'thermal runaway' and therefore do not over-heat or ignite in the event of rigorous mishandling and/or harsh environmental conditions.

A $LiCoO_2$ cell has an overcharge tolerance of about .1V over the charge plateau of 4.2V. Overcharge of as little as 4.3V per cell can lead to failure resulting in fire or explosion, whereas the LFP cell overcharge tolerance is about .7V, a much wider plateau that only results in heat being dissipated, rather than fire or explosion (thermal runaway). The exothermic heat of an overcharged LFP cell is only about 90 Joules/gram, but for an overcharged $LiCoO_2$ cell, it is well over 1600 J/g leading to explosion or fire that cannot be put out with conventional means, but rather managed until it self-extinguishes. To provide a comparative example, it only takes 30 Joules to weld a wire to a ball bearing (versus the 90 Joules/gram for an LFP cell).

'Thermal runaway' is a term used when a Li-ion cell fails in a catastrophic event. The following explains what happens during this event.

Several stages are involved in the build up to thermal runaway and each one results in progressively more permanent damage to the cell.

SimpliPhi Power, Inc. | 420 Bryant Circle | Ojai, CA 93023, USA | +1 (805) 640-6700 | info@simpliphipower.com | SimpliPhiPower.com

The first stage is the breakdown of the thin passivating SEI layer on the anode, due to overheating or physical penetration. This initial overheating may be caused by excessive currents, overcharging or in combination with high external ambient temperatures. The breakdown of the SEI layer starts at a relatively low temperature of 80ºC. But once this layer is breached, the electrolyte reacts with the carbon anode, just as it did during the formation process but at a higher, uncontrolled, temperature. This is an exothermal reaction which drives the temperature up still further.

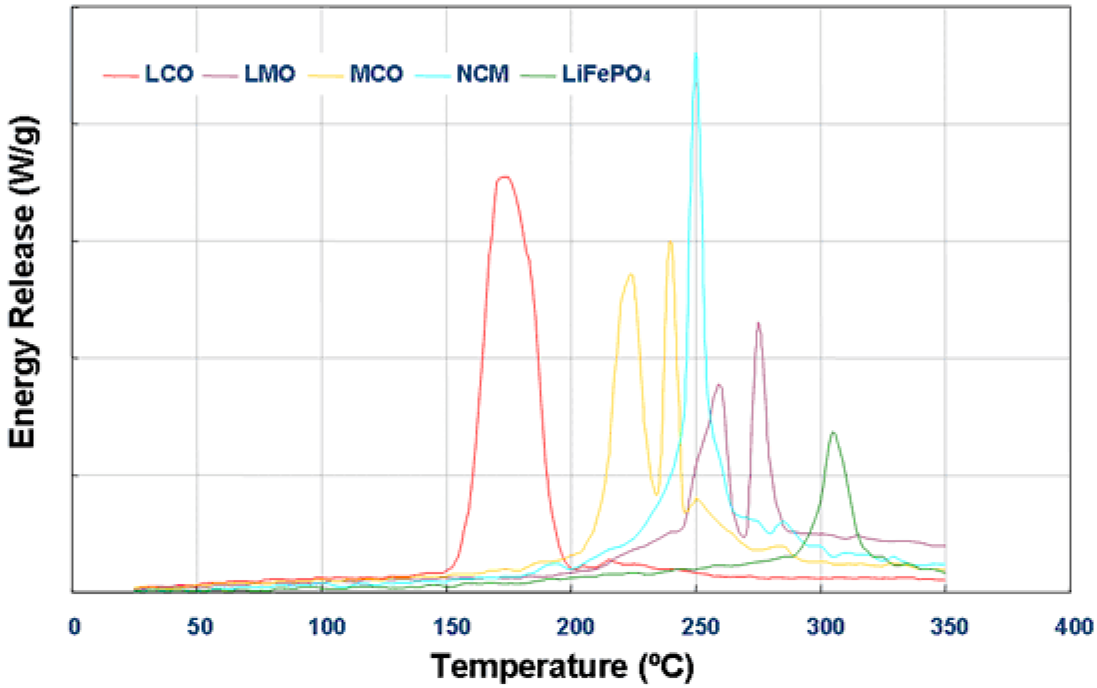
As the temperature builds up, heat from the anode reaction causes the breakdown of the organic solvents used in the electrolyte, releasing flammable hydrocarbon gases (Ethane, Methane and others) but no Oxygen. This typically starts at 110 ºC but with some electrolytes it can be as low as 70ºC. The gas generation due to the breakdown of the electrolyte causes pressure to build up inside the cell. Although the temperature increases to beyond the flashpoint of the gases released by the electrolyte, the gases do not burn because there is no free Oxygen in the cell to sustain a fire.
The cells are normally fitted with a safety vent which allows the controlled release of the gases to relieve the internal pressure in the cell, avoiding the possibility of an uncontrolled rupture of the cell - otherwise known as an explosion or more euphemistically "rapid disassembly" of the cell. Once the hot gases are released to the atmosphere they can of course burn in the air.

At around 135 ºC the polymer separator melts, allowing the short circuits between the electrodes.

Eventually, heat from the electrolyte breakdown causes a subsequent breakdown of the metal oxide cathode material, releasing Oxygen which enables burning of both the electrolyte and the gases inside the cell.

The breakdown of the cathode is also highly exothermic, sending the temperature and pressure even higher. The cathode breakdown starts at around 200 ºC for Lithium Cobalt Oxide cells but at higher temperatures for other cathode chemistries.
By this time the pressure is also extremely high and the build-up in pressure within and across the cells inside a battery results in exoplosive events which are extremely dangerous, toxic and potentially lethal.

Below is a chart of the temperature characteristics of the cathode when it breaks down in various Li-ion cathode materials.



As the curves in the graph demonstrate, the green line in the graph, representing the Lithium Ferro Phosphate (LFP) chemistry (utilized by SimpliPhi), has the lowest energy release at the highest temperature resulting in a safer cell that does not go into thermal runaway.

The lithium manganese dioxide chemistry, or LiMn2O4 cell, is also one of the safer technologies, but with a much lower cycle life than the LFP. The lower cycle life makes it a less desireable candidate for energy storage. This chemistry is more commonly used in cordless tools.

NiMH chemistry and cells, with their low cycle life, low power to weight density and high cost make them a poor choice for large energy installations. One inherent risk with NiMH chemistry is that overcharging causes hydrogen gas to form, potentially rupturing the cell. Therefore, the NiMH cells have a vent to release the gas in the event of serious overcharging, which is noxious.

FEATURES	LiFePO4	LiCoO2	LiMn2O4	NiMH
SAFETY AND ENVIRONMENTAL CONCERNS	Safest: no explosion, no smoke, no fire under abusive working conditions, the most environmentally benign, non-toxic, no rare	Not stable; thermal management and runaway, very dangerous, health & environmental concerns due to Cobalt,	Acceptable but can also be explosive and prone to fire under abussive working conditions	Not stable, will catch fire even just under high temperature, noxious gases

	metal, fire resistant, easily disposed of	toxic, explosive		
CYCLE LIFE	Best among all the listed chemistries, cells rated @ 2000+ cycles	Acceptable (< 500 cycles)	Unacceptable (approx 300 cycles)	Below 500 cycles
POWER WEIGHT DENSITY	Acceptable 65% weight of NIMH	Best	Acceptable	Low
LONG TERM COST	Most Economical, low LCOE	High	Acceptable	High
THERMAL PERFORMANCE	Excellent (-45°C~ -70°C)	Decays beyond +55°C ~ -20°C	Decays extremely fast over +50°C	Decays faster in high temperature

SimpliPhi Power: Proprietary Architecture, Assembly Tequniques and Power Electronics Combined with the Safest, Most Environmentally Benign Chemistry - Advantages:

BMS:
- Over Charge Voltage Protection
- Over Discharge Protection
- Over Current Protection for Discharge Via Thermal Control
- Short Circuit Protection
- Cell Balancing

The (LFP) battery cell component is made with an intrinsically safe cathode material (iron phosphate). This creates a strong molecular bond, which withstands extreme conditions, prolongs cycle life, and maintains integrity with little or no maintenance over extended periods of time.

There is virtually no danger of thermal runaway, as there may be with Lead Acid, NiCd, and Lithium Cobalt type batteries. No active venting or cooling is required when built utilizing the proprietary architecture, materials and assembly methods.

SimpliPhi batteries do not vent dangerous gases, such as hydrogen and oxygen, because there are no chemicals used in the creation of the electrical energy, in contrast to Lead Acid and other battery chemistries. There are no dangers of exposure to sulfuric acid because SimpliPhi batteries do not have caustic electrolytes. Thermal runaway is not an issue with SimpliPhi products due to the basic stable and benign nature of the LFP cell chemistry utilized in all the PHI power storage products.

The LFP cells within the SimpliPhi batteries fully comply with the safety testing parameters of UL 1642.

The Lithium Ferrous Phosphate (LFP) cells utilized throughout the entire PHI and LibertyPak product lines are classified as non-hazardous by OSHA and WHMIS. They are non-toxic, unlike NiMH, NiCad or Lead Acid types of batteries (including AGM). SimpliPhi batteries contain the least amount of toxic metals, and are the most eco-friendly of all common battery types. Lithium easily combines into harmless compounds when disposed of. SimpliPhi batteries therefore present the most ecological, environmentally safe formats and chemistries in the most efficient architecture available in the power storage market today.