Amionx™ SafeCore™ – Battery safety from the inside-out

Li-ion Battery Safety Landscape

In a growing age of information and electronics, the lithium-ion (Li-ion) battery has established itself as a ubiquitous power source for portable devices. The Li-ion battery, commercialized by the Sony Corporation in 1991, helped usher in the new era of mobile electronics like the laptop and the cell phone, but has since penetrated the transportation and utilities sectors, enabling revolutionary advancements like electric vehicles (EVs) and grid-scale energy storage for a smarter grid. The Li-ion battery was especially well-suited to provide power on the go because of its light weight and high capacity. According to a 2016 Transparency Market Research report, the global Li-ion battery market is poised to rise from $29.68 billion in 2015 to $77.42 billion in 2024.

A Li-ion battery is an electrochemical device that stores energy in a chemical form and then converts it to electricity when discharged. In Figure 1a, a typical Li-ion 18650 cylindrical cell and its components are shown. A Li-ion battery is comprised of five main parts: the negative electrode (anode), the positive electrode (cathode), the electrolyte, the separator, and the battery case. The electrodes are typically agglomerations of active particles (metal oxides in the cathode or graphite in the anode), conductive carbon, and binder which are coated onto metal foil substrates called current collectors. Current collectors ensure good charge balance in the cell and provide a low-resistance pathway for electrons to travel from the electrode to the external circuit. The electrolyte is typically a lithium salt dissolved in a carbonate-based organic solvent to provide good ionic conductivity and transport the Li^+ ions within the battery. During operation, Li^+ ions and electrons are generated by a reduction-oxidation (redox) reaction in the electrodes. The Li^+ ion is transported through the electrolyte, while the electron flows externally to provide current to a load. In a rechargeable battery, this reaction is reversible, and the opposite occurs to recharge the cell. Figure 1b,c show the Li-ion battery in its discharged and charged states, respectively.

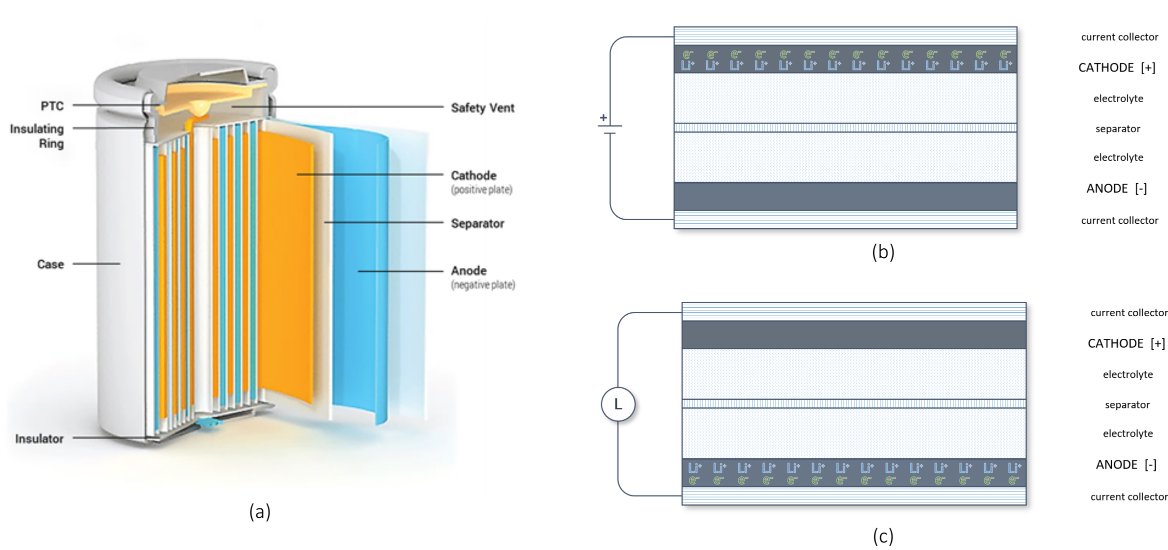


Figure 1. a) Cross-sectional image of a typical 18650 cell. b) Schematic of Li-ion battery in its discharged state. c) Schematic of a Li-ion battery in its charged state. Li^+ ions are represented as blue crosses and electrons are represented as green circles.

The proliferation of consumer electronics and EVs has resulted in increased demand for batteries with higher energy density and power. Moreover, as devices increase in functionality and drivers of EVs expect longer ranges, the need for more power will continue to be the driving factor in Li-ion battery research. Such batteries are being realized through advancements in cell chemistries and architectures, however, efforts to safeguard these high-power batteries have had only limited success. The battery industry and regulatory agencies around the world have gone to great lengths and tremendous investment to improve Li-ion battery safety. Yet, batteries have still been known to fail when subjected to high voltage, high current, high temperature, high pressure, manufacturing defects, and many other hazards. These failures often result in catastrophic fires and explosions that cause injury, loss of property and even death. Li-ion battery failures have caused temporary grounding of a certain model of airplane; explosion and fires in EVs; recalls of hoverboards; recalls of notebook computers; fires causing burns to individuals from earbuds and e-cigarettes; and a recent recall of a cell phone model where the total cost exceeded $5 billion.

Why do Li-ion Batteries Fail?

- Raw material impurities and contaminations
- Manufacturing defects
- Battery management system defects
- Charger defects
- Environmental factors
- Cell and battery design errors
- User error
- Some combination of the factors above

The above scenarios can be the root cause of three main failure modes of batteries: overcharge, internal short, and high temperature.

- *Overcharge* occurs when the battery is charged beyond a safe voltage, and is often due to the failure of protection circuits in the charger or battery management system (BMS) and can take place at the cell or pack level. It can also be caused by a faulty cell, which would shift more demand to other cells in the pack in order to compensate. At this point, the metal oxides in the electrodes are oxidized beyond their stability window and begin to release huge amounts of heat and strong oxidizer O_2. Pressure builds within the cell and a massive amount of heat is generated which can lead to fires and explosions.

As heat is generated, flammable liquids and vapors can also quickly reach their flash point and ignite while the separator could melt down and lead to an internal short.

- *Internal shorting* occurs within the battery when there is an electronically-conductive pathway between the electrodes. The internal short can be due to user error like when punctured or crushed or simply due to a pre-existing manufacturing defect. It can also be formed over many cycles as lithium metal is deposited in needle-like structures, called dendrites, which grow and eventually bridge the electrodes to create a short circuit. In a shorted cell, the electrons do not flow through the external circuit to power a device. Instead, they travel rapidly through the cell generating large amounts of heat leading to a phenomenon known as thermal runaway.
- *Thermal runaway* is an uncontrolled cyclic reaction in which heat causes materials within the cell to decompose and generate more heat and so on until the cell eventually combusts. The electrolyte, a flammable organic liquid with a low flash point, is often complicit in thermal runaway. Because thermal runaway is cyclic in nature, there is no way to stop it once it has started. Moreover, in a multi-cell battery, an occurrence in one cell will likely propagate to neighboring cells until the whole battery pack is consumed. For this reason, it is critical to keep the cell under the onset temperature, which is about 150 °C (302 °F) in Li-ion batteries, but even cells that spend too much time at lower temperatures can be susceptible to a thermal runaway event. Thermal runaway can be activated directly by a heat source, or can be a byproduct of heat generated by overcharge or internal short.

Due to the severity of these failures, Li-ion batteries have not been suitable for certain applications and roughly a third of the cost and weight of current batteries comprises protection and packaging. This is necessitated by the nature of consumer applications, as manufacturers are best served by being conservative in their safety measures. Moreover in EV applications, where crashes and impacts can subject the battery pack to major trauma, packaging and safety devices account for more than half of the total pack weight. A completely safe battery, therefore has the potential to significantly extend EV range by replacing structural components with more batteries.

Making a Safe Battery (State-of-the-Art and Beyond)

Currently, a multifaceted approach has been employed to protect against a plethora of risks, in part because there is no universal solution available. A consumer off-the-shelf (COTS) 18650 cylindrical cell typically comes with as many as five individual forms of protection including external protection circuits and internal components designed to act as circuit breakers. Figure 2 illustrates the various combined strategies implemented to safeguard a cell.

A positive thermal coefficient (PTC) current limiting switch and current-interrupting device (CID) are examples of internal protection which act as fuses that are invoked when under high temperature, pressure, or current. If the cell heats up, the PTC undergoes a phase transformation that increases its resistance by several orders of magnitude. The CID operates similarly to protect against high current surges, but is instead triggered by high pressure. While effective in some cases, the temperature inside the cell during a thermal runaway event can rise so rapidly that these measures don't have time to react and simply melt down.

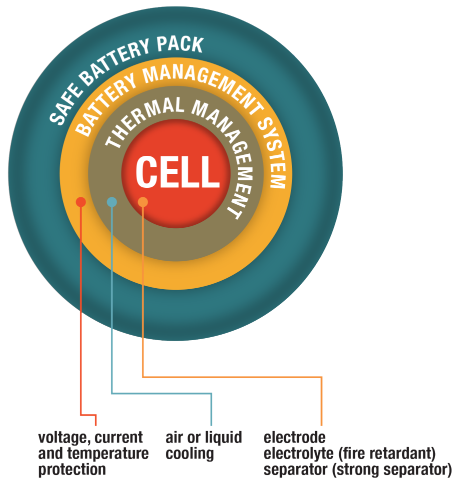


Figure 2. Layers of current state-of-the-art in battery safety comprised of several internal and external components that protect against heat, voltage, and current.

A battery management system (BMS) is an external printed circuit board (PCB) that keeps the cell within safe voltage ranges by protecting against overcharge and overdischarge. The cell is assembled into a pack with cooling systems and state-of-charge management and finally packaged in robust housing to protect against shock or trauma. These approaches have been somewhat effective, but are incomplete in providing robust safety.

Recent progress in battery materials has the potential to improve safety by removing flammable components and replacing them with inherently non-flammable, non-toxic materials. Experimentation with solid-state electrolytes is one promising area of research that aims to replace the flammable organic electrolytes with a safer inorganic glass or ceramic material that can also provide mechanical strength to the cell. Though the technology is not yet perfected and appears to be a few years from commercialization, solid electrolytes could improve both safety and energy density by enabling high-capacity, full-metal anodes to be used without the risk of Li dendrites. Solid-state could provide solutions for internal shorts by improving the mechanical strength of the cell and removing flammable electrolytes, but wouldn't protect against overcharge which manifests itself within the electrodes.

Nonflammable additives and co-solvents have also been investigated to reduce the electrolyte's flammability, and redox shuttles have been identified as a possible cell-level protection against overcharge. These approaches focus on modifications within the cell to stop the ionic flow, however there has been little effort by the battery industry to stop the electronic flow to prevent rapid discharge. Stopping the electronic flow is the fundamental objective of Amionx SafeCore.

Amionx SafeCore

Amionx is a spinout from American Lithium Energy Corporation (ALE), a company founded in 2006 in Carlsbad, CA. ALE has been designing, manufacturing, and supplying batteries to the Department of Defense for more than ten years. ALE began working on Li-ion safety technology while developing a PTC layer for military applications, and this technology was later revamped in an effort to make “bullet-safe” batteries for the Army. These batteries could be penetrated by a bullet without the risk of fire or explosion. The harsh environments experienced in the military were an optimal proving ground for the safety technology, and this heritage is critical to its high tolerance to hazards in commercial markets. The mission for Amionx is to transfer SafeCore technology for implementation in every Li-ion battery sold in commercial markets.

SafeCore was designed to combat the major hazards associated with batteries including overcharge, internal short, and high temperature. It is a layer within the cell that creates a delamination of the electrode from the current collector when triggered by a temperature, voltage, or current threshold. Because it works at the core of the battery, it remains a final line of defense even when other security measures fail. The working mechanism of the activated SafeCore layer is demonstrated in Figure 3. By creating a gap between the electrode and current collector, the internal resistance of the cell is effectively increased by several orders of magnitude. Because electrons no longer have access to the current collector which is a highly conductive metal foil, they crawl along the significantly less conductive electrode as the stored energy is released very slowly, rather than all at once. Because the rate of discharge is so low, minimal heat is generated and the cell is allowed to fail gracefully without experiencing thermal runaway.

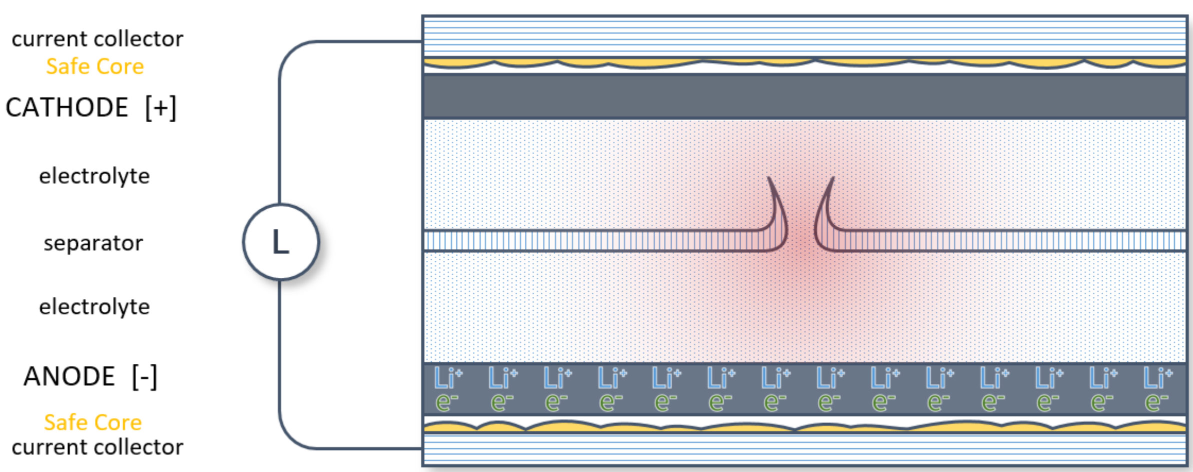
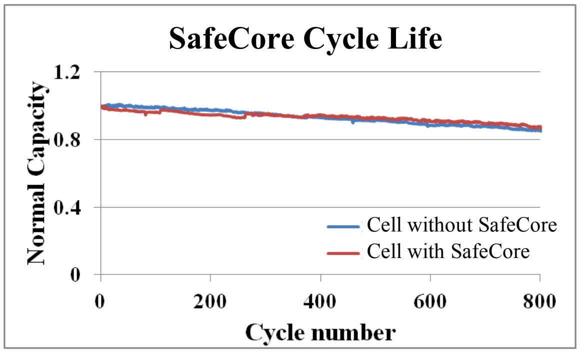


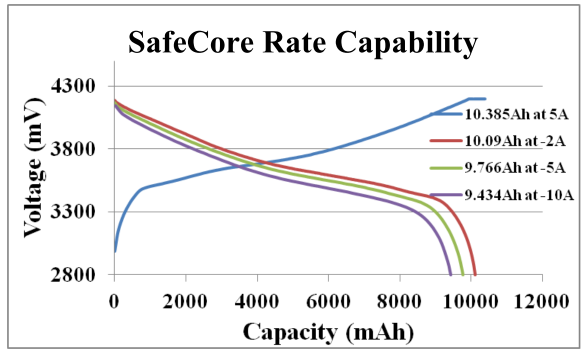
Figure 3. Schematic of a Li-ion cell with activated SafeCore layer.

SafeCore Characteristics

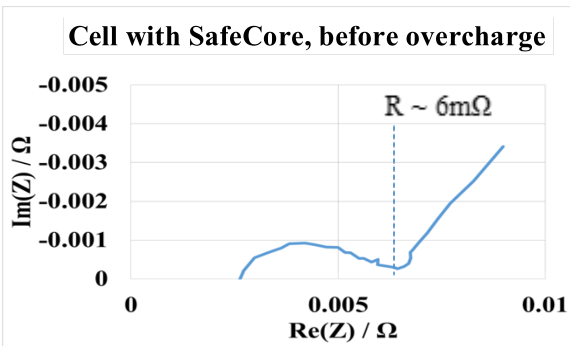
- SafeCore is a layer that can be applied to any Li-ion cell chemistry and any form factor (cylindrical or prismatic).
- SafeCore can be coated with the equipment used in a typical battery fabrication facility.
- SafeCore utilizes cheap, abundant materials that are easy to procure.
- Figure 4a shows the cell capacity at each cycle for a cell with SafeCore (red) and a cell without SafeCore (blue). Both cells show minimal decay with greater than 80% of the initial capacity retained after 800 cycles, and implementing SafeCore has no adverse effect on the lifetime of the cell. The cell with SafeCore has about 1-3% less initial capacity at the same size and weight, however, cells with SafeCore mitigate the cell's corrosive environment and therefore have the potential for a longer cycle life with better capacity retention.
- Figure 4b shows a cell with SafeCore discharged at low current (red), medium current (green), and high current (purple). At all three rates, the cell's capacity remains constant at about 10 Ah. A cell with SafeCore shows good power capability when discharged at various currents, as the discharge capacity is unaffected by the rate of discharge. SafeCore is does not hinder the cell performance in high power applications.
- Figure 4c shows the Nyquist plot (impedance measurement) of a cell with SafeCore at 4.2 V before an overcharge test. Before overcharging, the cell has an impedance of roughly 6 mΩ, which is competitive with commercial alternatives. When at rest, SafeCore does not affect the performance of the cell as the layer was designed with low impedance. For applications where power performance is vital, the SafeCore layer can be re-engineered to provide targeted protection at minimal impedance to enable rapid discharge functionality.
- Figure 4d shows the Nyquist plot of the cell with SafeCore after the overcharge test. Following the test, the cell is allowed to come back down to 4.2 V and the impedance is measured again. When SafeCore is invoked during the test, the impedance of the cell increases by approximately three orders of magnitude. The impedance of the cell is roughly 6Ω which restricts the flow of current and allows a safer, gradual discharge.
- SafeCore can be designed with specific thresholds in mind. For example, the onset of thermal runaway in a Li-ion cell is approximately 150 °C (302 °F). With that in mind, SafeCore's composition was designed with thermal trigger points at roughly 100 °C (212 °F).
- Safe Core is robust against overcharge, internal/external short circuit, and over-temperature.



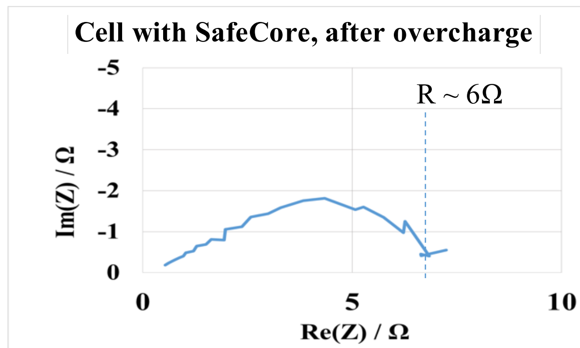
(a)



(b)



(c)



(d)

Figure 4. a) Cycle life of cells with (red) and without (blue) SafeCore. b) Rate capability of a 10 Ah SafeCore cell discharged at 0.2C, 0.5C, and 1C. c) Nyquist plot showing impedance of a cell with SafeCore in its resting state. d) Nyquist plot showing impedance of a cell with SafeCore when invoked.

Test Descriptions

Overcharge and internal short tests are two of many abuse tests created by compliance and safety boards such as UnderWriters Laboratories (UL) and United States Advanced Battery Consortium (USABC). These tests and other tests prescribed by these organizations mimic scenarios that typically cause a battery to fail in a commercial environment. SafeCore has been successfully demonstrated under more rigorous testing with more stringent requirements. The tests and data shown below are exemplary and do not demonstrate the full extent of the SafeCore technology.

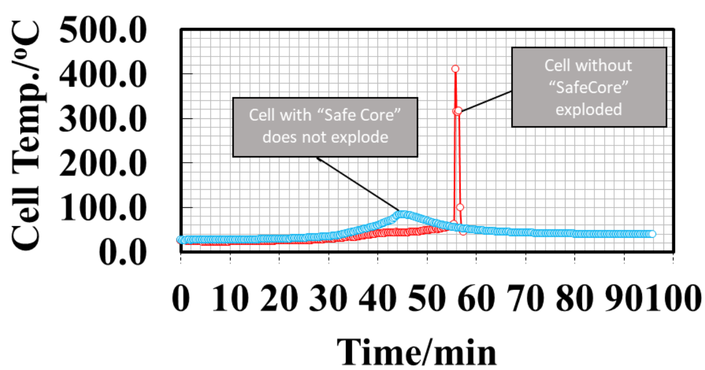
Overcharge

In the overcharge test, a cell is overcharged to 12 V and must sustain that voltage without fire or explosion. A cell charged to 4.2 V is used for these tests. The cell is then charged to 12 V at a 1C rate. C-rate is an effective metric for determining how long it will take to fully charge or discharge the entire cell's capacity. That is, for a 10 Ah cell being charged with a current of 5 A would take 2 hours to fully charge, so 5 A is a C/2 charge rate for a 10 Ah cell. For the overcharge test, cells are charged at a 1C rate instead of using the same current, because naturally bigger cells can sustain higher currents. This test serves to simulate what would happen if the charging circuitry failed or if there is a nonuniform state-of-charge across cells in a pack, causing an individual cell to be charged beyond its maximum voltage threshold.

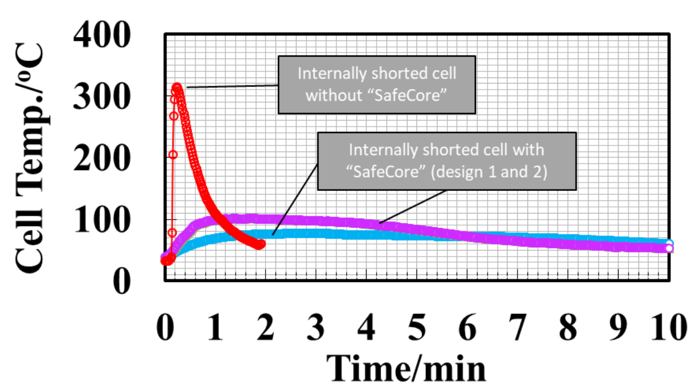
Two cells were evaluated, one with SafeCore and one without SafeCore, and the results are shown in Figure 5a. The cell without SafeCore was charged to about 6 V before the onset of thermal runaway, at which point there is a sharp spike in temperature exceeding 400 °C as the cell was completely incinerated. The cell with SafeCore instead charged all the way to 12 V and was monitored at 12 V for about an hour without any signs of explosion or fire. Instead the cell with SafeCore gradually heated to about 100 °C and then began to gradually cool back to room temperature.

Internal Short

In an internal short test, a cell is completely punctured by a nail to create a short-circuit. A cell charged to 4.2 V is used for these tests. In an internal short test, the reaction to the short is almost instantaneous as large amounts of energy surge through the short. Three cells were evaluated, two with SafeCore and one without SafeCore, and the results are shown in Figure 5b. In the cell without SafeCore, there is a rapid increase in temperature reaching higher than 300 °C, eventually leading to an explosion. This rapid heating occurs within the span of seconds, leaving little time for conventional measures to react and prevent. Two cells were tested with SafeCore, each with a different design. Neither cell eclipsed 100 °C nor were they above room temperature within 10 minutes of the short.



(a)



(b)

Figure 5. a) Overcharge test of cells with (blue) and without (red) SafeCore. b) Internal short test of cells with (purple and blue) and without (red) SafeCore.

The Amionx go-to-market strategy is to employ a technology transfer model. The implementation of SafeCore adds de minimis cost to the bill of materials for the battery, and requires no additional capital investment in modern battery factories. It is anticipated that SafeCore could be commercially available in batteries within six months of the commencement of the technology transfer process. Since the launch of the Company in mid-2017, Amionx has been engaged in discussions with numerous companies and regulatory agencies globally, and recently entered into evaluations for SafeCore with two global companies. Additionally, CONNECT recently awarded SafeCore the 2017 Most Innovative Product in the field of Cleantech, Sustainability, and Energy.

For more information please visit www.amionx.com or contact the company at info@amionx.com or on 1 (888) 473-8500.