The Future of Battery Technologies – Part III
Risks/Safety Factors for Lithium Batteries

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This white paper is the third in our series on “The Future of Battery Technologies,” and provides an overview on the risks and safety factors associated with lithium batteries—common causes of external and internal battery faults, common issues to consider for primary and rechargeable batteries, and more. The white paper was authored by Dr Annika Ahlberg Tidblad, Intertek’s resident expert in battery testing. Her background is in research at KTH, the Swedish Royal Institute of Technology, with PhDs in applied electrochemistry and corrosion science, along with ten years of experience in battery technology.

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One of the lithium battery's major strengths is its high energy density, but that is also why the risks of lithium-based chemistry are greater than in other battery systems, should anything go wrong. Although the risks are directly linked to the specific cell chemistry, cell size and the number of cells in the battery, there are certain common factors. Lithium batteries contain inflammmable material in the form of organic electrolytes that have a low flash point and polymers that can maintain a fire and increase the risk of spreading to surrounding areas. The anode in primary lithium batteries consists of metallic lithium that melts at 180°C, and it reacts violently with water and air if the cell breaks or vents. The cells also contain several compounds that are toxic in themselves and which form harmful combustion products in the case of fire.

One should always try to avoid exposing batteries to heat. This is partly because the cell chemistry may become unstable if the temperature is too high, which can lead to venting, and in the worst case scenario, to explosion and fire. Partly because heat accelerates the normal chemical processes taking place in the battery cell, and thereby such reactions and processes that lead to aging and loss of capacity, i.e. decomposition of both electrode and electrolyte material. Heat can either be generated by the cell itself or come from an external source. This is especially problematic if a multi-cell battery is exposed to uneven thermal conditions, as the cells will age at different rates, which may lead to problems in cell balancing. Cell balancing means that battery cells that must interact in one and the same stack are chosen in such a way that the cell capacity has as little spread as possible. A battery stack is never stronger than the weakest cell.

Low temperatures can also pose a problem. Primary batteries generally only lose their function when it becomes too cold, which can be serious enough. Rechargeable batteries often have limited chargeability at low temperatures, and should not be charged if the ambient temperature is lower than the lowest recommended charge temperature, as it may lead to formation of metallic lithium which is precipitated as islands on the anode, so-called lithium plating, and forms dendrites that can cause interior short circuits in the cell.
Common External Causes of Battery Faults

Some of the most common causes of battery faults originating from the user or application include:

1. External short circuit of the battery
2. Too high discharge or charge current
3. Pole reversal, i.e. discharge of a cell below 0V
4. Charging primary batteries
5. Incorrect or insufficient charge control of chargeable batteries

All five of these conditions generate heat to a varying extent in the battery cell, which leads to increased aging or breakdown of the cell. As these risks are caused by external factors, it is possible to prevent and avoid them.

*External short circuit*

When battery poles are short circuited, the high short circuit current leads to generation of a lot of heat in the cell. The most efficient way of preventing this from happening is to employ smart battery design that ensures that the + and - poles are physically isolated from each other, by countersinking them into the battery casing and designing them in such a way that it is not possible to connect the battery incorrectly. In certain cases, it may be necessary to integrate further forms of protection in the form of a fuse, or a PTC (Positive Temperature Coefficient) component, which breaks the electrical circuit if the current or the temperature begins to run away. Certain cell manufacturers integrate PTCs in their cells.

It is also important to be aware of the risk of a short circuit when transporting individual cells or batteries. The rules that exist for packaging lithium cells and batteries, with or without equipment, are intended to prevent accidents from accidental short circuits.

*Too high discharge or charge current*

If the current is too high, the mass transport of the reactants for the main reactions is limiting, and the charge volume applied is partially consumed by other reactions in the cell, such as gassing and decomposition, which lead to increases in temperature. If the temperature increase is too high, it leads to further side reactions, which in turn generate even more heat. This increases the risk of venting and, in the worst-case scenario, uncontrolled cell reactions and thermal runaway.
When charging secondary cells, it is important not to exceed the recommended maximum charge current. If the charge current is too high, there is a risk of the lithium ions not managing to diffuse into the anode structure during charge, and instead being precipitated as lithium metal on the anode surface, which results in loss of capacity but also increases the risk of internal short circuits during subsequent use.

Apart from current limiters, it is important that there is a low voltage protection to prevent any cell discharging below the lowest recommended voltage limit of the cell. In rechargeable batteries, the low voltage protection prevents the anode's base metal, usually copper, from dissolving and contaminating the cell. Li-ion cells that are heavily discharged risk both irreversible loss of capacity and increased self-discharge in subsequent use. Rechargeable batteries also need to be fitted with an over-voltage protection to prevent early aging, lithium plating on the anode, because cathodes that consist of metal oxides form unstable phases and lose oxygen to the surrounding area. Depending on the application and the complexity of the battery, it is not always sufficient with over-voltage and low voltage protection at the stack level, and control may have to be implemented on an individual cell level within the battery stack.

**Pole reversal**

Pole reversal can take place in battery stacks that consist of multiple cells connected in series. It is important to make sure that the cells in a multi-cell battery stack are well matched to begin with, and they are exposed to mainly the same loads and other conditions, so that the capacity continues to be evenly distributed. Otherwise, in the worst case scenario, the weakest cell could risk being heavily discharged and forced to reverse its poles, which means that the cell would be charged by the other cells, which are still being discharged. Multi-cell battery stacks usually have a cell-balancing function that distributes the current between the cells in a suitable manner. If the battery stack is fitted with low voltage protection, this may help to prevent pole reversal.

**Charging primary batteries**

Primary lithium batteries are not constructed to be charged. If this takes place, gas is formed within the cell, causing its internal pressure to rise. This may result in venting, or most seriously, in explosion. Primary lithium cells connected in parallel, and thereby exposed to a potential source of charging, should be protected by diodes.

**Incorrect or insufficient charge control of rechargeable batteries**

Charging is the single most risky element in the battery cycle, as energy is permitted to flow into the system from an external source. It is extremely important to comply with the charge
recommendations of the cell and battery manufacturers, both with respect to current limitation, voltage limitation and temperature, in order to ensure a long and safe battery life. The risks involved in too high charge current, exceeding the voltage limits, and too high and low temperatures, have been discussed above.

Internal Causes of Battery Failure

In addition to external fault sources, there are risks that may be difficult to predict or prevent, and which are caused by unsuitable cell design, manufacturing faults or ageing mechanisms within the battery cell, such as:

1. Weak or faulty seals that can cause leakage or failure
2. Pollutants that can lead to gas-developing secondary reactions, resulting in aging or venting due to overpressure in the cell
3. Internal short circuits caused by formation of dendrites on the electrodes, metal particles or faulty insulation of conductors, etc.

Primary lithium batteries

Primary lithium batteries have a higher energy density than the rechargeable Li-ion and Li-polymer cells. Small primary cells, e.g. coin cells, often lack the integrated safety components at cell level. Slightly larger cylinder batteries and prismatic cells often have so-called safety valves, which is a form of fuse, or PTC.

The greatest safety risks are involved when a battery consists of several cells. In such cases, the cells should be soldered together in a battery stack to lower the risk of the user mixing different types of cell, and cell chemistries, when changing batteries. Even if the battery cells have integrated overheating protection, it is recommended that the battery is fitted with an external temperature limitation protector. The electrical protection must also include protection against charging, short circuit and a bypass connection protection that prevents pole reversal of an individual cell in a series, or a combination of serial and parallel connected cells.

In certain cases, a battery must be fully discharged before a used battery can be disposed of safely as waste. If required, this takes place using a resistive load that gives a very low current flow.

Rechargeable lithium ion batteries

Most of us have seen and remember the scenes of burning laptops on the Internet, TV and in newspapers between 2006 and 2009. Studies of failures in the field showed that these were usually caused by an internal short circuit. The short circuit leads to the
cell's energy being discharged through a very limited volume, which leads to a rapid local temperature increase, reaching up to > 200°C in seconds. The heat induces the electrodes and electrolyte to begin to decompose, and these reactions add further heat, tipping the cell into so-called thermal runaway in which the cell temperature and pressure increase exponentially over time. The overpressure leads to the cell venting, which liberates electrolyte aerosol in the surrounding area, and can easily ignite. In extreme cases, the cell splits or explodes unless the overpressure can be ventilated out sufficiently quickly. Depending on the construction of the cell and the internal positioning of the cells in a battery pack, the ignited electrolyte from one cell may heat up the adjacent cells and causes the cascade effect.

Most Li-ion batteries on the market today indicate 60°C as their upper usage temperature. The majority of batteries currently on the market have graphite anodes. Graphite is not stable and can react chemically with the electrolyte in the cell. During manufacture and formation of the cell, a passive layer is formed on the anode surface, the SEI (Solid Electrolyte Interface) layer, which prevents continued reaction between the electrode and the electrolyte. As early as 90-120°C, the layer can begin to break down, allowing exothermal gas evolving reactions to begin. If a sufficiently large area of the SEI layer breaks down, the cell may enter thermal runaway.

Not all cells that develop an internal short circuit suffer thermal runaway. Factors that influence this include:

- The size and location of the short circuit
- The size and design of the cell
- The active material in the cell; cobalt oxide is, e.g. more reactive than manganese dioxide and iron phosphate
- Thermal properties of the various materials in the cells and the cells’ abilities to disseminate heat
- The cell’s state of charge, its age and history

Internal short circuits caused by production factors may occur in all types of Li-ion cells and it is unlikely that it will be possible to completely eliminate this type of fault. There are various types of integrated protection at cell level that attempt to prevent and counteract risks. Figure 1 shows a cut-through of a cylinder cell. At the top of the cell there are 2 mechanical protectors in the form of a CID (current interrupt device) that triggers at a pressure of around 10 bar, and a safety valve. Both of these are irreversible, and the cell no longer works if either of these protectors is triggered. In addition, there is usually a PTC that throttles the current at temperatures over 125°C. This PTC function is reversible and conduction restarts when the temperature falls. The separator between the anode and the cathode consists of 3 layers of polymer and is usually of the "shut-down" type, which means that when the cell temperature gets too high, around 165°C, the separator melts and the pores close. The consequence is that the electric circuit is broken as the ion conduction in the cell ceases to function. This effect is irreversible. A number of additives have also been added to the electrolyte in the form of
flame retardants or inhibitors and redox shuttles. The role of the redox shuttle is to manage and consume any overcharge effect so that the cell voltage does not get too high. The cell container is also a part of the total protection which secures the cell's integrity against its surroundings.

The increasingly more common "pouch" cells, i.e. cells with a soft coating that consists of a polymer-coated metal foil, lack many of the mechanical protection components that are found in cylindrical and prismatic cells with steel or aluminium casing. Pouch cells have no integral CID, PTC or safety valve, but are completely dependent on external protection circuits. In the case of a strong overpressure, the cell's welded seams split, generally in vicinity to the pole connectors where the weld is the weakest. Nor are pouch cells as resistant to impact or puncturing as cells with metal casing.

Figure 1  Cut-through of a Li-Ion cylinder cell

Intertek's expertise in battery testing & energy storage services ensures products meet performance, reliability and safety criteria. Intertek has expanded global energy storage testing facilities and advisory services. Throughout design, manufacturing & system deployment cycles, Intertek provides evaluations for performance, electrical safety, interoperability, fit for use, component selection and more. Please visit our website at www.intertek.com/energy-storage, contact icenter@intertek.com or call your regional lab:

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