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Battery Technologies

A General Overview & Focus on Lithium-Ion

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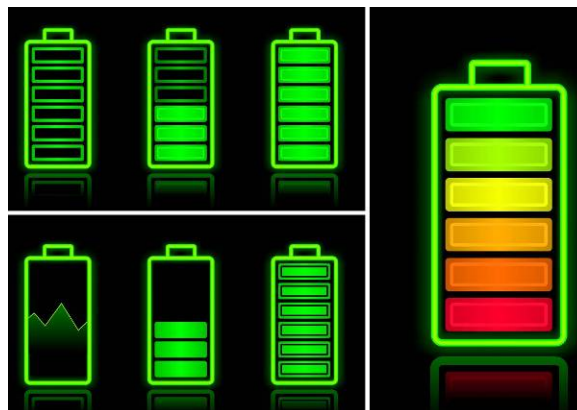
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Battery Technologies – Overview

A “battery” is the generic term for an electrochemical source of electricity, which stores energy in a chemically bound form until converting it directly into electric power. A battery may either be a single cell or multiple cells connected in a series or parallel configurations.

A battery cell consists of a container, electrodes (anode and cathode), separator material, electrolyte, and conductive current collectors. The container is the metal can, plastic case, or foil pouch housing of the cell. The anode (the negative electrode) is where the cell’s oxidation reaction takes place, generating electrons to the external circuit. The cathode (the positive electrode) is where the cell’s reduction reaction takes place, consuming electrons from the external circuit. The separator is a physical paper/non-woven film barrier which electrically insulates the anode from the cathode (preventing electrical internal short circuits but allowing anions/cations to freely pass). The electrolyte is the aqueous (non-aqueous for lithium batteries) medium providing the ionic conduction inside the battery. The conductive current collectors are typically the carrier metal substrates holding the anode/cathode active ingredients. In lithium-ion batteries these are copper foil for the anode, and aluminum foil for the cathode.

Batteries are categorized as being either primary or secondary systems. For instance, primary batteries are commonly known as disposable batteries and are not engineered for recharging (doing so may result in an explosion). Conversely, secondary batteries are engineered so they can be safely recharged. This is owed to the fact that the anode and cathode discharge reactions are reversible. During recharge, the *discharged* anode and cathode are returned to their original *charged* state. Much of the engineering involved in the design of rechargeable batteries involves the management of gasses generated during cycling - careful control of charge voltages and currents is critical in this management scheme, as is consideration of gas recombination mechanisms. Properly designed, a secondary battery can be recharged hundreds or thousands of times.



Primary Systems

The most popular primary battery used in portable consumer products is the 1.5 Volt standard alkaline battery (Zn/MnO₂), though the primary lithium metal battery has significant market penetration. In replacing Zn/MnO₂ with primary lithium, system voltage and cost becomes a factor. Of the many different types of primary lithium battery chemistries on the market, the most common is lithium/manganese dioxide (Li/MnO₂). These 3.0 Volt systems are primarily used for



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memory backup and in consumer products such as cameras and toys. Li/MnO₂ batteries have difficulty competing with alkaline batteries in many consumer products because of their price. The 1.5 Volt lithium/iron disulfide system (Li/FeS₂) is experiencing rapid market growth based on its high rate discharge performance and perfect voltage fit as an alkaline replacement. On high rate applications, the Li/FeS₂ provides a 5X to 10X service life advantage over Zn/MnO₂. However, on moderate to low rate applications, there is very little service advantage. It begs this question: *Does the 5X high rate performance justify the 3X price increase?* This simple example serves to highlight the performance/cost trade-off when considering various battery systems for specific applications.

Metal/air batteries – though another similar type of primary battery – possess an active cathode not contained within the cell which allows them to hold a huge volumetric energy density advantage over competing batteries. As a consequence, a much larger portion of the cell's internal volume can therefore be devoted to the anode, which occupies a far greater space than in a conventional primary battery and results in a very high energy density. A number of different metal/air systems have been the subject of research (with Li/Air being the most coveted), but only the primary zinc/air battery has achieved extensive use. In the consumer market, Zn/air button cells are used almost exclusively for hearing aid applications.

Battery Market in Change

The use of lead-acid batteries (Pb/Ac) began in the nineteenth century. Because of low manufacturing costs, good performance and long life, the lead-acid battery is still the most common rechargeable battery system in the world, with a market share of as much as 40 to 45%. The lead-acid battery has a wide field of applications, and new manufacturing methods, cell designs and application areas are still introduced. Its most common use is as a starter battery in cars, with additional applications in industrial trucks and as reserve power. In the Electric Vehicle arena, Pb/Ac is well positioned to capture much of the emerging micro-hybrid market (start/stop hybrids).

NiCd batteries are a mature and thoroughly tested battery technology that was patented in 1899 by Waldemar Jungner. NiCd batteries are used in a wide variety of stationary, mobile and portable applications, ranging from large-scale backup power and start batteries for aircraft to handheld power tools and toys. Due to stricter EU environmental legislation, NiCd batteries are expected to be gradually phased out in Europe, at least in consumer electronics applications. However, NiCd batteries are expected to retain a strong position on several niche markets.

The NiMH battery uses relatively new battery technology developed in the early 1990s. NiMH batteries offer the same cell voltage as NiCd batteries, and can therefore replace them in many applications without modification. Cell voltage combined with higher energy density and better environmental properties are the driving forces that

With a longer track record, relatively high energy density, and good cyclic properties, NiMH batteries have also found applications in electric and hybrid vehicles.



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enabled NiMH batteries to capture market share from NiCd in consumer electronic products over the past decades. Today, Li-ion batteries have completely taken over the computer and mobile phone battery markets, though portable NiMH batteries are expected to remain on the market as a low-cost alternative to lithium batteries.

Energy-Dense Lithium-ion Batteries

Li-ion batteries were introduced onto the market in the mid 1990s, soon replacing the NiMH batteries in mobile phones, notebook computers, and other portable electronic devices. At the present time, the use of lithium batteries has been widely spread to a number of cheaper consumer products.

Li-ion batteries are still in a relatively early phase of development in relation to the energy storage industry, and have only been readily available for 15 years in the commercial market. This means that there is potential for both comprehensive technical development and price reductions.

It is important to remember that lithium-ion batteries are a generic name for a large number of different battery chemistries with varying properties and performance characteristics. Therefore, these are suited for a wide range of products.

At present, the development of lithium-ion batteries is mainly driven by the automotive industry and their need for an improved energy storage solution for electric and hybrid vehicles.

Selecting the Most Suitable Battery for Your Application

The choice of primary or secondary batteries depends on the technical requirements imposed by your product's intended use. Primary batteries are used for applications which either have low energy consumption and a relatively long storage time between uses, or in cases where it is difficult or inconvenient to charge the battery. Secondary batteries are primarily used when there is a need for high levels of energy or large load currents, and in cases where it is convenient to charge the batteries. Although rechargeable batteries have a greater initial investment cost, they are cost effective in high energy applications where one rechargeable battery can take the place of many primary battery replacements. It is interesting to note that on single use applications, primary batteries hold a 10% to 50% advantage in energy density over their rechargeable counterparts.

There is a wide variety of primary and secondary batteries. The most common primary systems are alkaline, lithium metal and zinc/air batteries. Common secondary batteries include lead acid, nickel/cadmium (NiCd), nickel/metal hybrid (NiMH) and Lithium-ion (Li-ion)/Lithium-polymer (Li-polymer) batteries dominate. Ongoing battery research strives to develop new systems that can match or exceed the performance and safety of existing systems, while reducing costs.

The expression "lithium batteries" is a generic name for battery technologies in which lithium-ions play a part in the primary electrochemical discharge and charge reactions. Lithium batteries

are available both as primary batteries (disposable batteries) and secondary batteries (rechargeable batteries).

The choice of the best battery for a specific purpose is determined by the power and energy requirements of the application, the operating environment, the electrical preconditions, and the cost aspects. The most important factors are:

- **Battery type**
Disposable or rechargeable
- **Electrochemical system**
Matching the benefits and disadvantages of the battery type to the requirements of the application
- **Voltage requirements**
Rated and operating voltage; minimum and maximum levels; voltage regulation; discharge profile, etc.
- **Load profile**
Resistive current or power discharge; single vs. variable load, etc.
- **Work cycle**
Continual or intermittent
- **Temperature specifications**
- **Lifetime**
- **Physical requirements**
Size, shape, connections, etc.
- **Storage requirements**
Shelf life, charge state when stored, environment, etc.
- **Charge and discharge states for rechargeable batteries**
Cycling batteries vs. energy storage batteries (flow charging); charge characteristics; efficiency and accessibility; discharge requirements
- **Environmental conditions**
Climate (temperature, humidity); pressure conditions; physical environment (impact, vibration, dust, acceleration), etc.
- **Safety and reliability**
Permitted variance; acceptable faults; sensitivity to gas leaks or leaks of electrolyte from the battery, etc.
- **Unusual or demanding operating conditions**
Extreme temperature conditions, standby times, high reliability, and rapid activation
- **Maintenance and replacement of unserviceable batteries**
- **Cost¹**
Initial and lifetime operating costs

¹ Although cost is at the bottom of this list, for many applications it is the number one consideration.

Lithium-based battery systems are characterised by high-energy density levels, relatively high voltages, and a low weight-to-volume ratio. However, they generally, tend to be more expensive than equivalent battery technologies with aqueous electrolytes, such as alkali disposable batteries and zinc/air batteries in the primary battery sector, and nickel metal hydride, nickel cadmium and lead batteries in the secondary battery sector. Because they are aqueous based, alkaline batteries are also viewed as being safer than flammable organic electrolyte-containing lithium batteries. This is not meant to imply that lithium batteries are unsafe.

Primary Lithium Batteries

Primary lithium batteries have existed since the 1970s. They are easy to use and provide a convenient source of energy for portable applications as they usually require no or very little maintenance. Modern lithium batteries have a long shelf life and can usually be stored for up to 10 years, while some with solid state electrolyte that can be stored for more than 20 years. The storage tolerance at elevated temperatures is generally good (in some cases up to 70°C).

There are 3 classes of primary lithium batteries:

- **Solid state batteries** – Characterized by low power but superior shelf lives, these batteries are used in products such as pacemakers and computer memory backup. The expression ‘solid state’ is used because the electrolyte is solid and the ion transmission between the electrodes takes place in a solid, non-electrically conductive material (usually a polymer).
- **Batteries with a solid cathode** – Found in coin cells or small cylindrical batteries, these batteries are used across a wide range number of applications, including clocks, memory circuits, photo and communication equipment, toys, flashlights, and more.
- **Batteries with soluble cathodes** – These industrial and military batteries are manufactured in large cell sizes up to 35-40 Ah, but are also available in smaller sizes that are commonly used, in medical and civilian applications.

The two most common primary lithium batteries² on the market are lithium disulphide (LiFeS₂) and lithium manganese dioxide (LiMnO₂) batteries. Both of these are of the solid cathode type and are sold as consumer batteries from electrical goods stores and supermarkets. Other primary lithium batteries are mainly intended for the professional market.

Over the last few years, battery types in which the cathode consists of a mixture of different electrode materials have been in development. The purpose of these batteries is to provide a system that can accommodate both high and low loads. One example is the battery that is used for implanted defibrillators that consist of silver-vanadium oxide (SVO) cathodes to absorb the peak load of a defibrillation, and carbon monofluoride ((CF)_x) for the baseline load between the defibrillation pulses.

² Table 1 (p. 20) lists the most common primary lithium battery chemistries and their properties.



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Secondary Lithium Batteries

Today, nearly all rechargeable lithium batteries are of the lithium-ion type, having a negative electrode that consists of a carbon-based material, usually graphite, or another type of alloy or material that permits intercalation.

Lithium-ion batteries were introduced by SONY in 1991, and were first used in advanced consumer electronics products, mobile phones, digital still and video cameras, as well as laptop computers. Today, lithium-ion batteries are used across a range of portable applications within consumer electronics, medical technology, and military systems. These batteries are characterized by a high energy density paired with a small volume and weight, which contrasts with other rechargeable batteries. Other properties include low self-discharge and relatively long recharge lifetimes (1,000 full depth cycles is routine). However, barriers include high costs, safety aspects, functional limitations at low temperatures, and high temperature limitations (Li-ion degrades rapidly at temperatures exceeding 55°C).

Carbon materials are used in lithium-ion batteries because carbon has the ability to reversibly absorb and release large quantities of lithium (Li:C=1:6) without altering the mechanical and electrical properties of the material. On the first charge of the battery (i.e. transport of lithium into the carbon), a protective outer layer called the Solid Electrolyte Interface (SEI) is formed. The SEI layer is important because it prevents the carbon anode from reacting with the electrolyte. In the absence of this layer at elevated temperatures, lithium-ion batteries would pose a safety risk.

There are a number of different chemistries within the lithium-ion family that are based on the choice of chemistry in the cathode material. Traditional lithium-ion batteries use cathodes made from cobalt dioxide (LiCoO_2). By adding nickel ($\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$), a layered material is obtained that is more stable and less expensive than pure CoO_2 . Manganese oxide spinel (LiMn_2O_4) is another common cathode material for lithium-ion batteries. Compared to cobalt, manganese oxide is cheaper but has a lower energy density and is less stable in terms of calendar and cycle life.³

In the last few years, lithium-ion batteries with cathodes made from lithium iron phosphate (LiFePO_4) have been marketed on a large scale, based on their higher safety levels and low cost. The benefits of LiFePO_4 have been achieved at the expense of their energy density and voltage. New electrode materials are being developed and tested constantly in order to produce lithium-ion batteries with properties that are suitable for different applications and areas of use.⁴

³ From a thermal/safety perspective, cobalt is generally considered the least stable cathode chemistry, but among the highest in terms of energy density.

⁴ Table 2 (p. 23) shows a comparison of the main types of lithium-ion batteries that are currently on the market.

Present research into rechargeable lithium-ions is driven mainly by the automotive industry, which requires high-performing batteries with long calendar and charge lifetimes, high discharge currents, and rapid charging capabilities to allow manufacturers to meet their cost targets.

R&D Trends in Lithium-ion Batteries

A transition to cheaper and less toxic electrode materials (cathodes)
(including phosphates, silicates, etc.)

A transition to materials that have higher, reversible lithium reception.
(greater absorption of lithium atoms leads to higher battery capacity)

The development of materials that can withstand rapid charges
(from 0 to 90% SOC in ten minutes)

Batteries for the automotive industry and stationary installations
(power supplies and energy supplies)

Increased cell size in the form of stored energy capacity

Battery systems with high voltage levels
(including electrolytes that can withstand higher electrode potential without degrading or reacting with the environment)

Battery systems with enhanced safety
(compared to current battery types)

Recently, titanate and anodes composed of tin, carbon and silicon have entered the commercial battery market. The main advantage of titanate is in its highly stable structure and its lack of increase in volume during battery charging. Lithium's mobility within the material is very rapid, which permits the battery to be charged and discharged at high currents. Limitations include low cell voltage due to the high electrode potential of titanate (compared to that of lithium intercalation into carbon), and higher costs compared to carbon-based electrodes.

Silicon and tin are both limited by very large electrode expansion during charging – approximately 300% and 250%, respectively. However, both of these material groups are attractive because of their high energy density and relatively low electrode potential. Silicon is especially interesting in the way that it permits very large quantities of lithium to be stored in the anode structure. Moreover, the material is neither expensive nor toxic.

Development on the cathode side is more multi-faceted. Materials being discussed are metal phosphates, layered metal oxides, and silicates. The metal phosphates are being promoted thanks to their chemical stability, leading to increased safety compared to traditional cobalt-based cathode materials. Magnesium and manganese phosphates, as well as iron silicate, are also all relatively cheap and non-toxic materials. The layered metal oxide structures are expected to offer rapid lithium mobility, thereby permitting high charge and discharge currents, but the material is still relatively expensive and associated with safety problems.

Over the next 20 years, lithium batteries are expected to dominate the market for rechargeable batteries, while NiCd and NiMH batteries will continue to be used in some niche applications.

Risks and Safety Factors for Lithium Batteries

While high energy density is noted as a benefit of lithium batteries, high energy content, is responsible for safety risks associated with lithium-based chemistry, in comparison to other battery systems. 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 flammable 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. Both lithium metal and charged Li-ion anodes react violently with water, generating highly flammable hydrogen gas. The cells also contain compounds that are toxic and may form harmful combustion products.

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 possibly fire/explosion. Elevated temperatures accelerate the normal chemical processes taking place in the battery cell, leading to cell aging and loss of capacity. Heat can either be generated by the cell itself (decomposition, internal short circuits and also during normal usage) or come from an external source. Uneven heat across the cells in a battery pack will cause the cells to age at different rates, which can lead to problems in cell balancing. Cell balancing relates to how cells perform together inside a battery pack. The greater the spread in max/min cell capacities, the quicker a battery pack will lose capacity and fail. This is why, during battery pack assembly, much care is taken to choose cells whose capacity and impedance are well matched.

A battery stack is never stronger than the weakest cell.

Low temperatures can also pose a problem. 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 (i.e. lithium plating). Lithium is known to form dendrites when plated, and these can result in internal cell short circuits if the dendrites pierce the separator barrier membrane.

External Causes of Battery Failure

Oftentimes battery failures are the result of conditions which generate heat within the battery cell, and lead 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 short circuit current can generate heat in the cell. The most efficient way of preventing this from happening is to employ smart battery design to ensure the positive and negative poles are physically isolated from each. This can be achieved 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 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 PTC components in their cells. These components are commonly integrated into the caps of cylindrical sized cells, such as the 18650.

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 energy supplied is partially consumed by side reactions in the cell, such as gassing and decomposition, which lead to increases in temperature. If the temperature is too high, it may lead 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 that the lithium-ions will not properly diffuse into the anode structure during charge, but rather precipitate as lithium metal on the anode surface. This not only results in loss of cell capacity but increases the risk of internal short circuits during subsequent use.

Apart from current limiters, it is important to maintain 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. The dissolved copper may also serve as starting point for creating an internal short. Rechargeable batteries also need to be fitted with an over-voltage protection to prevent early aging. Depending on the application and the complexity of the battery, over-voltage and low-voltage protection at the stack level is not always sufficient, 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 and exposed primarily to the same loads and other conditions – this will allow for the capacity to be evenly distributed. Otherwise, the weakest cell is at risk of being discharged and forced to reverse its poles, meaning that the cell could 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. The pole reversal will lead to a number of unwanted reactions within the battery such as heat generation, which has consequences both on aging and safety.

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. In worst case, lithium dendrites can form, creating internal short circuits. Consequently, charging primary lithium may result in venting or 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

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.

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. Contaminants 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 (i.e. coin cells) often lack the integrated safety components at cell level, but are considered safe simply because of their small energy content. Larger cylinder batteries and prismatic cells often have safety valves which act as a pressure vent, fuse, or PTC.

Greater safety risks are involved when a battery consists of several cells. In such cases, the cells should be permanently connected 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 prevent pole reversal of an individual cell in a series, or a combination of serial and parallel connected cells.

Rechargeable lithium-ion batteries

If a laptop, for example, catches fire, this field failure can be attributed to overcharging or an internal short circuit arising from debris during manufacture. 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 $> 200^{\circ}\text{C}$ 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. The overpressure leads to the cell venting, which liberates electrolyte aerosol into the surrounding area and poses the threat of igniting. In extreme cases, the cell splits or explodes unless the overpressure can be ventilated out 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 cause a cascade effect. This is particularly true for a series stack of cylindrical cells whose venting electrolyte ignites and behaves like a torch, with focused, directional burning of pressurized flammable organic electrolyte solvents.

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. Already at temperatures below 90°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.

However, not all cells that develop an internal short circuit will suffer thermal runaway. This outcome is influenced by several factors:

- Size and location of the short circuit
- Size and design of the cell
- Active material in the cell – cobalt oxide, for example, is more reactive than manganese dioxide and iron phosphate
- Thermal properties of the cell materials, and the cells' abilities to disseminate heat
- Age, history, and state of charge for the cell

Internal short circuits caused by production factors may occur in all types of Li-ion cells and it is nearly impossible to completely eliminate this type of fault. There are various types of integrated protection at cell level that attempt to prevent and counteract risks.

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Figure 1 shows a cut-through of a cylinder cell. At the top of the cell there is a safety valve and two mechanical protectors in the form of a CID (current interrupt device) which trigger at a pressure of around 10 bar. Both of these are irreversible and do not allow the cell to function if either of these protectors are 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 typically consists of three 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 aluminum 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.

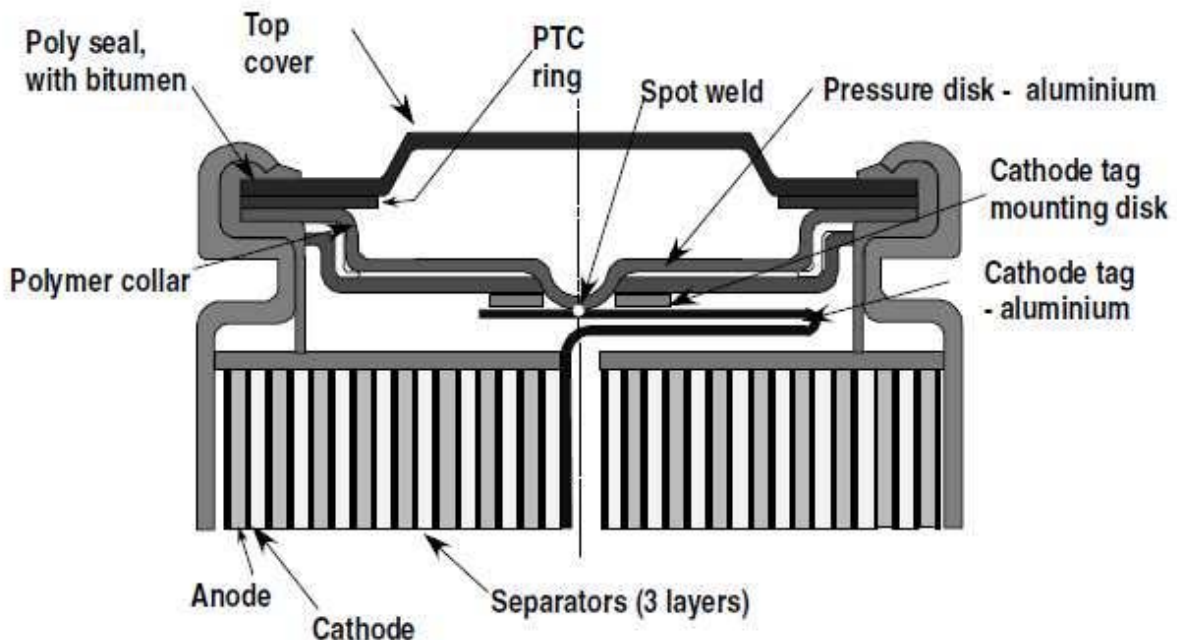


Figure 1 Cut-through of a Li-Ion cylinder cell

Testing and Evaluating Lithium Batteries

There are a variety of methods used to evaluate and qualify a battery's function and safety. The following four categories can be used to qualify a battery and thereby ensure a battery-driven product functions properly.

- **Electrical Performance Testing** – An evaluation of a battery's electrical functioning: available capacity at different loads and surrounding temperatures, cycle lifetime, calendar lifetime in storage, charging receptivity, impedance as a function of charging state, etc.
- **Environmental Safety Testing** – Simulating environmental conditions to which the battery could be exposed: vibrations, falls, knocks and blows, damp, high temperatures, quick temperature changes, etc.
- **Failure Analysis Testing** – Evaluating the battery's ability to withstand different types of stress that can arise intentionally or unintentionally during use: overcharging, short circuiting, incorrect installation, etc.
- **Effect on the environment** – Chemical analysis of heavy metal content

Many of these tests are mandated by legal requirements. For example, transportation testing in accordance with UN requirements for transporting dangerous goods (UN Manual of Tests and Criteria section 38.3) is required in order to transport lithium batteries and cells, as well as products that contain lithium batteries.

Several countries apply limits for certain heavy metals in batteries. The chemical elements that are most commonly regulated are mercury, cadmium and lead (the EU Battery Directive regulates all three of these elements).

It is 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 accidental short circuits.

Electrical Performance Testing

A battery's technical specifications say a lot about the charge behind the apparatus it is powering. Available battery capacity and the number of discharge cycles are strongly affected by actual conditions of use. Similar battery cells from different manufacturers or even different models from the same manufacturer do not need to have the same properties.

The functioning of the battery is governed by the chemical reactions that are possible in each individual case. The balance between different components, additives, pollutant contents, etc. is very important to cell chemistry. Cell design and the manufacturers' recipes for electrode and electrolyte composition are carefully guarded secrets and are competitive tools among manufacturers. The extent of the testing which is carried out by cell and battery manufacturers can also vary from case to case.

Testing represents a cost, and one can therefore assume that low-budget products in many cases have undergone less extensive testing than advanced products from more renowned and experienced manufacturers.



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Minimum Requirements in Standards

The type tests found in IEC standards provide tools for evaluating the electrical properties of lithium cells and batteries. IEC 60086-1 and IEC 60086-2 describe dimensional requirements for primary batteries of different cell types and sizes. The corresponding standard for rechargeable cells and batteries is IEC 61960. It is generally the case that all batteries must comply with standard requirements. Most modern, battery-driven products available on the market impose higher or more extensive requirements on their batteries and so standard tests should be supplemented with application-specific discharge and lifetime tests. Cell and battery suppliers should be able to provide reports from tests carried out and be able to account for the extent and frequency of tests.

Safety Testing for External Influences

The UN's transport testing is a prime example of safety testing designed to establish the battery's safety properties in the event of external influences. The test program includes a total of eight tests designed to simulate conditions that could occur in a transport situation.

- T1 Simulation of High Height (test to recreate low pressure when flying)
- T2 Thermal Shock (exposing the battery to alternating high and low temperatures)
- T3 Vibration Test
- T4 Fall Impact Test
- T5 External Short-Circuiting
- T6 Blow Test
- T7 Overcharging Test
- T8 Forced Discharging

It is not enough to test the individual cells that are included in a battery pack. The whole battery pack must be tested if it consists of several cells. Re-testing is also required if the product is modified in a way that could affect the results of testing, or if the product's weight (primary lithium batteries), Wh-content, or voltage (rechargeable lithium cells and batteries) are changed. Transportation rules require that lithium batteries and products containing lithium batteries are packed, marked, and accompanied by safety documentation in accordance with given requirements. Some countries/transport authorities set higher requirements than those described in UN 38.3. Today, transports in the U.S. are subject to more extensive requirements.

ANSI/UL and IEC standards consist of a combination of environmental influence and simulated tests which focus on evaluating fire safety. The requirement for approval is generally that the cell or battery does not explode or burn during the course of a test. Despite minor differences in the degree of strictness between ANSI/UL and IEC standards, the tests are similar.

Not meeting UN transport requirements can affect the timetable for product launch and may involve considerable costs for the equipment manufacturer, who must then take responsibility for carrying out the testing. Cell and battery suppliers should be able to provide test reports from

completed testing in accordance with ANSI/UL 1642 (cells) and 2054 (battery packs) or IEC 60086-4 (primary lithium cells and batteries) or IEC 62133 (rechargeable cells and batteries), and should be able to account for the extent and frequency of tests carried out, both as part of ongoing production checks and as final checks on the finished cells and batteries. If, as a buyer, you are unsure whether the battery has been tested or whether the testing has been carried out in the right way, then you should carry out your own verification in accordance with relevant standard methods.

Battery Testing Standards

Most national and regional standards, such as EN, are based on the corresponding IEC standard and are therefore referred to in the current version of IEC. In some cases, national standards are not updated at the same time as IEC. For that reason, it is important to fully understand which tests have been carried out in accordance with the current guidelines and, where necessary, be able to supplement the tests carried out with further tests.

For transport rules, the method of transport governs the applicable guidelines: ADR/RID for land transport; IMDG-code for sea transport; and ICAO-TI or IATA-DGR for air transport. Refer to the UN Manual of Test and Criteria.

UN's transport testing for all batteries that contain lithium

- ST/SG/AC.10/11/Rev.5; UN Manual of Tests and Criteria, Rev.5 (2009)

Primary Batteries

- IEC 60086-1: Primary batteries - Part 1: General, Ed 10.0 (2006)
- IEC 60086-2: Primary batteries - Part 2: Physical and electrical specifications, Ed. 11.0 (2006)
- IEC 60086-4: Primary batteries - Part 4: Safety of lithium batteries, Ed. 3.0 (2007)
- ANSI/UL 1642: Lithium Batteries, Ed. 4, (2005, with revisions 11/2009)
- ANSI/UL 2054: Household and Commercial batteries (2004, with revisions 11/2009)

Rechargeable Batteries

- IEC 62133: Secondary cells and batteries containing alkaline or other non-acid electrolytes - Safety requirements for portable sealed secondary cells, and for batteries made from them, for use in portable applications, Ed. 1.0 (2002)
- IEC 61960: Secondary cells and batteries containing alkaline or other non-acid electrolytes - Secondary lithium cells and batteries for portable applications, Ed.1.0, (2003)
- ANSI/UL 1642: Lithium Batteries, Ed. 4, (2005, with revisions 11/2009)
- ANSI/UL 2054: Household and Commercial batteries (2004, with revisions 11/2009)



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Construction Requirements for Battery-Powered Equipment

When securing product certification for your equipment, product or device, all cells and/or batteries must be approved individually.

If you are seeking CB Certification for a product containing rechargeable Li-ion batteries, you must complete testing in accordance with IEC 62133 (effective May 1, 2012). Lithium cells and batteries certified to ANSI/UL 1642 and ANSI/UL 2054 must undergo and fulfill additional testing in order to conform to IEC 62133.

CB Certification for primary lithium batteries requires IEC 60086-4. Product certification ensures that compliant equipment will be safe if a component fails. To safe-guard against failure, a risk analysis assessment can be performed based on initial test results. While protection is only required against reverse current for a primary lithium battery or cell, it may also be appropriate to specify regular checks on the protective components. For batteries or cells that are tested and certified as short-circuit-proof, no further protection is needed. For other batteries, a current-limiting component is also required to limit the discharge current. The reverse and discharge currents to which the battery has been certified must not be exceeded in the case of a failure.

For secondary lithium batteries (i.e. rechargeable batteries and cells), the charging battery protection circuits are investigated. The battery must be protected against excessive discharge current, charging current, and charging voltage. Where appropriate, it may also be necessary to monitor the battery's temperature in order to shut down the device and mitigate the effects in case of over-temperature. If the battery protection is not certified, two independent protective measures are required for each of the three parameters. In addition, a risk analysis based on testing should be carried out to show that it is improbable that faults should occur in both protective circuits simultaneously.

Environmental Considerations for Lithium Batteries

Although batteries are not yet covered by legislation on chemicals, the "Regulation on Batteries," which is based on the EU Battery Directive, governs the use of certain heavy metals in batteries. Unfortunately, this legislation has not kept pace with technological developments in the battery field. This is also the case when it comes to environmental labeling requirements on batteries, such as the Swan Label.

There are at least three key factors that can be used when determining how environment friendly a battery is:

- Battery lifespan and the number of cells required to achieve the desired battery function in the equipment or apparatus
- Recyclability
- Chemical content



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Upper Limits and Labeling Requirements

The EU Battery Directive is currently the most far-reaching Directive regulating hazardous elements used in batteries. The Directive includes fixed upper limits by weight for how much cadmium (20 ppm) and mercury (5 ppm) batteries can contain. This excludes military and certain industrial batteries, as well as batteries for emergency and alarm systems, cordless power tools, and a number of medical equipment products. The Battery Directive and all related national legislation within the EU also cover labeling requirements for batteries with mercury, cadmium, and lead (40 ppm) content, along with requirements on the collection and treatment of spent batteries.

Rechargeable Batteries are Preferable

When used in the same application, rechargeable batteries are more environmentally friendly than single-use batteries. This is because the total amount of battery waste will be lower as the same battery can be recharged numerous times. Within the group of primary batteries (single-use batteries), lithium cells offer an advantage in the form of higher energy density compared to alkaline batteries, which enable a longer operating time. Most primary lithium cells also have a higher cell voltage which also means they need fewer cells to achieve the desired operating voltage in the apparatus. With fewer cells required to achieve the same performance and lifespan, primary lithium cells appear more advantageous from an environmental perspective than other primary cells. These same arguments can be used in favor of lithium-ion cells, as these have a higher cell voltage than other rechargeable cell types.

Battery Recycling

Recyclability is dependent on 1) the availability of efficient collection systems that ensure batteries do not end up in landfill sites, and 2) financial incentives to recover the materials found in batteries. Here, traditional chemical batteries are actually an advantage compared to lithium-ion batteries, as traditional batteries have a high content of metals that have a second-hand value on commodities markets:

- Lead batteries can be used directly in the manufacturing of new lead batteries
- Nickel from recycled nickel cadmium and nickel metal hydride batteries is used by the steel industry to manufacture stainless steel

Cell Content Reused in Construction Industry

Lithium-ion batteries contain relatively small quantities of elements that are financially viable to recover, though the large variety of cell chemistries available on the market makes recycling more difficult. Recycling processes for lithium-ion batteries are able to recover cobalt, nickel and copper from battery waste. The residual cell content is combusted and the ash can be used in the construction industry.



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Unfortunately, with the trend in lithium-ion technology moving towards an increased use of materials that are not of interest to recover – such as manganese dioxide, iron phosphate and mixed oxide materials containing little or no cobalt – the cost of collection and recycling of lithium-ion batteries largely falls on consumers when the manufacturers attempt to recoup their product liabilities.

Product Life Cycle

The environmental impact of batteries is a very complex issue. In order to be able to evaluate and compare different batteries against each other, it is desirable to take the entire life cycle of the product into account: the extraction and refining of the raw materials, cell and battery manufacturing, product lifespan in operation, plus waste disposal and recycling processes. Both manufacturers and consumers of battery-powered products should do their utmost to minimize the total number of batteries required during the lifetime of the product in order to minimize its environmental impact.

How Can Intertek Help?

From hybrid electric vehicles to medical device batteries, personal electronics, and renewable energy, Intertek has a depth of experience in battery testing services. We help to ensure your energy storage technologies meet performance, reliability and safety criteria. From testing to consultation Intertek can help ensure you are on the right path to meeting the relevant Directives and Regulations. Far from being just a testing facility, Intertek be your point of contact when it comes to keeping pace with the ever-changing landscape of energy storage compliance.

About Intertek

Intertek is a leading provider of quality and safety solutions serving a wide range of industries around the world. From auditing and inspection, to testing, quality assurance and certification, Intertek people are dedicated to adding value to customers' products and processes, supporting their success in the global marketplace. Intertek has the expertise, resources and global reach to support its customers through its network of more than 1,000 laboratories and offices and over 30,000 people in more than 100 countries around the world. Intertek Group plc (ITRK) is listed on the London Stock Exchange in the FTSE 100 index.

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Table 1 – Primary Lithium Batteries

System	Construction	Cell voltage [V]		Specific energy [Wh/kg]	Energy density [Wh/l]	Power density	Discharge profile	Usage	Properties
		Rated	Operating voltage 20°C						
Category 1 – Solid state system									
Li/I ₂		2.8	2.6-2.8	220-280	820-1030	Very low	Relatively flat	Coin cells and special batteries for e.g. pacemakers	<ul style="list-style-type: none"> - High energy density - Withstands low current and power loads - High reliability - Cells constructed with cathode limitation - Long shelf life: 15-20 years in normal conditions; stored for up to one year at 100°C - Used in pacemakers, digital watches
Category 2 – Batteries with solid cathodes									
Li/(CF) _n or LiCF _x	Coin cell Spiral "jelly-roll" Rectangular plates	3.0	2.7-2.5	220-590	550-1050	Low-medium	Relatively flat	Coin cells Cylindrical batteries (commercial and military)	<ul style="list-style-type: none"> - Highest theoretical energy density - Withstands medium to low loads - Wide temperature range: 20-60 °C - Flat discharge curve
Li/FeS ₂	"Bobbin" and "jelly-roll" cylindrical cells	1.5	1.5-1.4	260	500	Medium-high	High initial drop in voltage, then flat		<ul style="list-style-type: none"> - Replacement batteries for type AA household batteries - Tolerates high power - Good temperature properties - Long charge retention
Li/MnO ₂	Coin cell	3.0	3.0-2.7	230-270	535-620	Low-high	Low-high	Cylindrical up to 22 Ah	<ul style="list-style-type: none"> - High specific energy and energy density - Wide temperature range - Withstands relatively high discharge currents - Relatively cheap
Li/AgV ₄ O ₁₁	Prismatic	3.2	3.2-1.5	270	780	Low-medium	Rel. complex discharge curve	Special batteries for medical implants	<ul style="list-style-type: none"> - Used in implants and other medical devices - High energy density - Multi-step discharge - Good load properties

For more information about Intertek's Testing and Certification capabilities, please contact Intertek at 1-800-WORLDFLAB, email icenter@intertek.com, or visit our website at www.intertek.com.



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Category 3 – Batteries with soluble cathodes									
Li/SO ₂	Spiral "jelly-roll"	3.0	2.9+-2.7	260	415	High	Very flat	Cylindrical cells up to 35 Ah	<ul style="list-style-type: none"> - Manages high current and power loads - Excellent low temperature properties - Long shelf life
Li/SOCl ₂	Bobbin; Spiral Prismatic cells with electrode plates	3.6	3.6-3.4	275-590	630-1100	Low-medium	Flat	Cylindrical cells 2-30 Ah	<ul style="list-style-type: none"> - One of the highest OCV voltages and energy densities of all of the commercial batteries - High specific energy - Withstands low discharge loads
Li/SO ₂ Cl ₂	Spiral	3.95	3.5-3.1	450	900	Medium-high	Flat	Cylindrical cells 7-30 Ah	<ul style="list-style-type: none"> - High energy density. - Manages high discharge loads - Good high temperature properties - Excellent storage properties

Table 2 – Rechargeable Lithium-ion Batteries

Cathode Material	Rated Voltage [V]	Charge Limit [V]	Energy Density [Wh/kg]	Power Density	Common Applications	Comments
LiCoO ₂	3.6	4.2	110 -190	Low-medium	Mobile phones, Cameras, Laptops	<ul style="list-style-type: none"> - Highest energy density - Most common battery type in portable appliances since the 1990s
LiMn ₂ O ₄	3.7-3.8	4.2	110 -130	Medium-high	Hand tools Medical equipment	<ul style="list-style-type: none"> - Low internal impedance - Withstands relatively rapid charging - Withstands relatively high discharge currents - Low energy density
LiNiMnC oO ₂	3.7	4.1-4.3	100 -160	High	Hand tools Medical equipment	<ul style="list-style-type: none"> - High energy density - Withstands rapid charge - Withstands high discharge currents
LiNiCoAl O ₂	3.7	4.3-4.5	100 -150	High	Vehicles	<ul style="list-style-type: none"> - High energy density - High cell voltage
LiFePO ₄	3.2-3.3	3.6	95 -120	Medium-high	Hand tools Medical equipment	<ul style="list-style-type: none"> - Long charge lifetime - Withstands rapid charge - Withstands high discharge currents

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