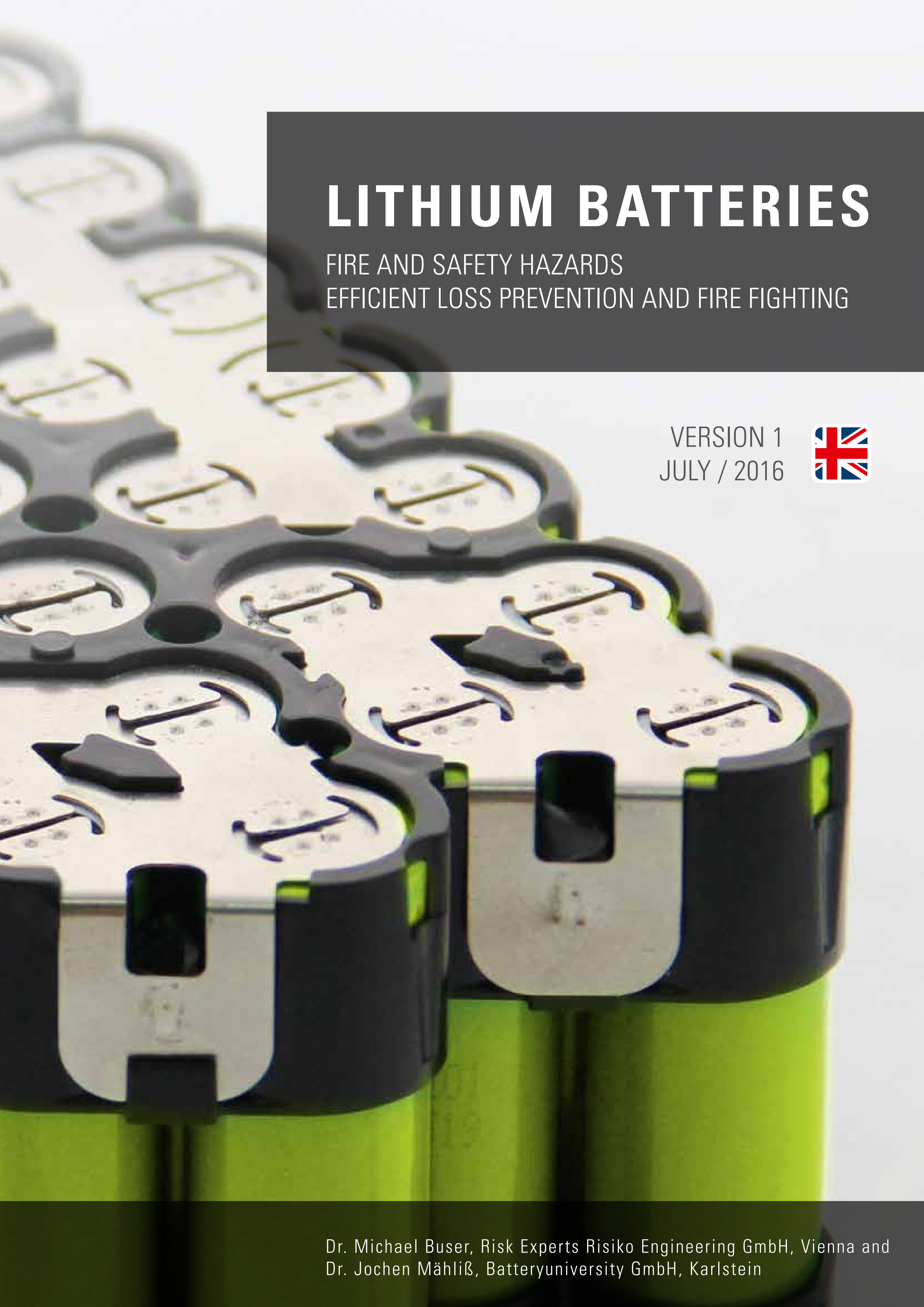

LITHIUM BATTERIES

FIRE AND SAFETY HAZARDS
EFFICIENT LOSS PREVENTION AND FIRE FIGHTING

VERSION 1
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RISK EXPERTS

CONTENT

1 LITHIUM BATTERIES: CONVERTING CHEMICAL ENERGY INTO ELECTRIC ENERGY

1.1 Basics

Batteries are means of storing chemical energy which are able to release the stored energy as electrical energy in electrochemical reactions. Mankind has been interested in the direct conversion of chemical energy into electric energy for more than 2,000 years. The first electrochemical power sources were already used some centuries BC for gilding metal objects.

Today there is a wide variety of battery types with different cathodes, anodes, and electrolytes, in different designs, sizes, and providing different powers, suited for various applications. The individual components can be combined in various ways; rapid technological progress makes it difficult to keep descriptions and lists of these individual components up to date.

The term “battery” originally referred to a group of several interconnected individual cells. The term’s meaning has changed so that “battery” may now also refer to a single cell (single-cell battery).

1.2 Why use lithium?

Compared to conventional battery systems, lithium batteries are a fairly recent technology. Although they have been introduced to the market only a relatively short time ago, they already have the most important market share in the field of portable batteries and have successfully replaced competing systems. According to different market analyses, the demand for lithium batteries will continue to increase.

Lithium is the lightest solid element in the periodic table of elements (atomic mass: 6.914 g/mol; density: 0.53 g/cm^3) and has the lowest electrochemical potential of all metals (-3.04 V vs standard hydrogen electrode). As a result, its capacity per weight and the cell voltage which can be reached in combination with different cathode materials are high, making it the ideal electrode material for chemical energy storage systems.

For these reasons, lithium batteries are becoming ever more widespread and used in all areas of everyday life. They are preferably used for off-line power supply or as backup batteries for electrical appliances. Lithium batteries have become particularly widespread in connection with the boom in mobile small appliances (smart phones, notebooks, cameras, etc.). They are, however, also becoming increasingly important for applications like small garden tools and so-called power tools, pedelecs, stationary energy storage systems for the independent power supply of individual households, forklifts, and electric cars. The use of lithium batteries in the automotive field is developing very fast (e.g. hybrid drive, high volt electric drive, etc.). To illustrate progress in the field of electromobility: Germany, for example, is planning to reach 1 million electric vehicles on its roads by 2020 (6 million by 2025).

The term “lithium battery” is an umbrella term referring to many different battery systems in which lithium is used in its pure form or in compounds as active material for the battery’s electrode.

Basically, there are two different battery types. While primary lithium batteries (lithium metal batteries) usually are non-rechargeable and thus intended for single use only, secondary lithium batteries (lithium ion batteries) are rechargeable and allow for the conversion of chemical energy into electrical energy to be reversed several times, making it possible to use these batteries several times.

System	**lithium metal**			**lithium ion**		
	lithium manganese dioxide	lithium sulfur dioxide	lithium thionyl chloride	lithium cobalt dioxide	lithium polymer	lithium polymer
Type	primary	primary	primary	secondary	secondary	secondary
Use	cell	cell	cell	battery	battery	battery
Components	Li/organic solvents, $LiClO_4$/ MnO_2	Li/organic solvents, $LiClO_4$/ SO_2	Li/LiAlCl4 in $SOCl_2$/ $SOCl_2$(C)	Li(C)/organic solvents, conducting salt $LiPF_6$/ $LiCoO_2$	Li(C)/polymeric electrolyte/ $LiMO_x$	Li(C)/organic solvents, conducting salt $LiPF_6$/ $LiFePO_4$
Voltage	3.0 V	3.0 V	3.7 V	3.7 V	3.6 V/3.7 V	3.2 V
Energy density	290 Wh/kg	220 Wh/kg	650 Wh/kg	180 Wh/kg	120-210 Wh/kg	120 Wh/kg
Applications	portable small appliances	almost exclusively in the military field	very high energy density, low self-discharge rate, and good low-temperature stability	mobile phones, notebooks	mobile phones, PDAs, and notebooks, model building	high-performance applications
Specific features	high energy density und good low-temperature stability, cost-efficient	high current-loads and good low-temperature stability	very high energy density, due to aggressive components largely only in the military field	high energy density	cell structure allows for manufacturing thin film cells and thus for cost-efficient design	high intrinsic safety

The advantages of lithium batteries compared to conventional chemical energy storage systems result from their electrochemical performance parameters:

- The high cell voltage of lithium cells allows for constructing batteries using one single cell only. Today’s modern mobile small electrical appliances (e.g. mobile phones) use only lithium ion batteries consisting of one single cell.
- Contrary to conventional rechargeable batteries, there is no memory effect (capacity loss caused by incomplete charging/discharging) in lithium ion batteries; they thus achieve efficiencies of up to 95% (ratio of amount of charge output to amount of charge input).
- The wide temperature range in which lithium batteries operate properly (-20 °C to + 70 °C), particularly good low-temperature stability, and their low self-discharging (storability) make lithium batteries indispensable for many applications.

1.3 Lithium metal batteries

Non-rechargeable lithium metal cells are available in the customary sizes of conventional cells: button cells (CR2032), AAA (Micro), AA (Mignon), C (Baby), D (Mono), 9V. Their cell voltage is relatively high; they have high specific energies even at low temperatures and low self-discharge (shelf life of up to > 10 years).

- private: watches, small electrical appliances
- industry: measuring points
- safety technology: long-time smoke detectors
- motor vehicles: safety systems, communication systems, motor control, telematics, tire pressure monitoring system, etc.

Metallic lithium is used as anode material. The common commercial types are chiefly distinguished from one another by cathode materials and electrolytes used.

Various organic and inorganic materials (such as sulfur dioxide, thionyl chloride, iron sulfide, copper sulfide, manganese dioxide, silver chloride, etc.) are suitable cathode materials. The commercially most widespread lithium metal system is the lithium manganese dioxide cell (Li-MnO2); it is often used in a flat and round shape as button cell or in a cylindrical shape as round cell. Its rated voltage is 3.0 V and it is mainly used in small appliances (e.g. watches, calculators, etc.).

Organic solvents (such as propylene carbonate, ethylene carbonate, acetonitrile, γ-butyrolactone) or inorganic compounds (such as thionyl chloride) or solid electrolytes, polymer electrolytes or molten salts are usually used as electrolytes. To achieve a higher conductivity, conducting salts containing fluorine, such as $LiBF_4$, $LiCF_3SO_3$, or $LiN(SO_2CF_3)_2$, are added to the electrolyte.

Already more than 40 years ago, the first lines of rechargeable cells with lithium metal electrodes were tested in addition to single-use lithium metal cells. A significant disadvantage of these first rechargeable lithium metal cells consisted in the insufficient controllability of the electrochemical reactions, resulting in local short circuits and giving rise to safety hazards.

The demand for reversibility (discharging/charging) continued to constitute a huge challenge. As lithium is practically consumed in the course of the discharging process and a lithium metal electrode practically dissolves, it becomes impossible to reconstruct the electrode's geometry in the charging process. As this compromises their applicability, lithium metal electrodes are hardly suitable for being used in rechargeable secondary batteries – in spite of theoretic electrochemical advantages. New developments in the field of lithium polymer batteries seem to provide solutions for the problem of insufficient electrode integrity, so that secondary batteries with electrodes made of lithium metal have also been in use for some time.

1.4 Lithium ion batteries

There are different types of rechargeable lithium ion cells:

Round cell: The cell's individual layers are stacked and then wound around a rod. The resulting cylindrical jelly roll is then packed into a solid housing, which usually is connected with the anode tap (e negative electrode). The positive electrode is formed by the cell's top cover which is insulated from the housing.

Prismatic cell: Like round cells, prismatic cells are mostly rolled cells. Contrary to the round cells, the jelly rolls are not wound around a rod, but form a flat shape. The flat roll is then packed into a prismatic housing. The electrodes are typically insulated from the housing and contacted via the housing's top cover.

Pouch cell: As pouch cells look similar to sealed packages of ground coffee, they are also referred to as "coffee bag cells". Contrary to the other two cell types, this cell type does not have a solid housing, but is wrapped in plastic-coated aluminum foil. A stack of cells is formed to guarantee a certain degree of stability and uniform shape. This is achieved using layered cell stacks instead of the rolls otherwise used.

Rechargeable lithium ion batteries have a high specific power and energy density and do not show a memory effect (or hardly any memory effect, as in the case of lithium iron phosphate).

- private: mobile phones, notebooks, cameras, toys
- industry: portable electrical tools, safety power supply, emergency systems
- electromobility: cars, utility vehicles, electric bicycles, etc.
- backup storage: photovoltaics

The commercial success of rechargeable lithium batteries started with the introduction of a cell which used in graphite intercalated lithium instead of metallic lithium – the lithium ion battery. In this system, the active material of both the cathode and the anode is capable of reversibly intercalating lithium or lithium ions. Instead of metallic lithium, the negative electrode often comprises modified carbon with a layered structure (e.g. graphite) as active material.

In view of the requirements regarding energy density, cell voltage, and life cycles as well as sufficient dimensional stability of the electrodes, it has been primarily battery systems using electrodes made of a lithium-doted transition metal oxide of the $LiXO_z$ type (X = Co, Ni, Mn) which have proved themselves in practice; lithium-doted cobalt oxide ($LiCoO_2$, LCO) has become particularly widespread.

Anhydrous organic solvents (e.g. ethylene carbonate, diethylene carbonate, etc.) and polyvinylidene fluoride (PVDF) or polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) poly-mers in which conducting salts containing fluorine, such as $LiPF_6$ or $LiBF_4$, are dissolved are used as electrolytes for secondary lithium cells.

1.5 Applications

The advantages of rechargeable lithium batteries compared to other conventional rechargeable chemical energy storage systems (lead acid batteries, nickel cadmium batteries, nickel-metal hydride batteries) result from their electrochemical performance parameters: The high cell voltage of lithium ion cells of typically 3.6/3.7 V allows for constructing batteries using one single cell only. Modern mobile phones today work exclusively with lithium ion batteries and are usually equipped with a single-cell battery only. For the same application, a battery based on traditional nickel electrodes would require three serially connected 1.2 V cells. Contrary to conventional rechargeable batteries, lithium ion batteries show hardly any or only a very slight memory effect (capacity loss caused by incomplete discharging/charging), thus achieving efficiencies of up to 95% (ratio of amount of charge output to amount of charge input).

The wide temperature range in which lithium batteries can be used (-20 °C to + +70 °C), particularly good low-temperature stability, and the low self-discharge (shelf life of more than ten years) make lithium batteries indispensable for many applications.

Based on their power, lithium batteries can be divided into three categories:

Low-power batteries for mobile small electrical appliances (weight of ≤ 1 kg)

The first lithium batteries which were produced in significant numbers were mainly used in mobile small electric appliances. Lithium batteries have become particularly widespread in connection with the booming sector of mobile phones, digital cameras, and notebooks. They offer outstanding operating times at low weights. In processing and manufacturing facilities, modern lithium batteries are used for various applications – in particular for portable machine tools (cordless screwdrivers, cordless drills, etc.), but also for mobile lighting installations, mobile control devices, and mobile communication technology.

Medium-power batteries for applications in the medium-power spectrum (weight of > 1 kg but voltage of ≤ 60 V)

Lithium ion batteries are becoming increasingly important for use in light electric vehicles (LEV) and as energy storage systems for bicycles, scooters, lawn mowers, forklifts, etc.

High-power batteries (high-energy batteries) for electrically driven motor vehicles (voltage of > 60 V)

The use of lithium ion batteries in the automotive field (e.g. hybrid drives, high-volt electric drives, etc.) has increased rapidly. In 2009, the German government has adopted a "National Electromobility Development Plan" aiming at a substantial increase of the number of electrically driven vehicles. Germany wants to become the global leader in the electromobility field, and, by 2020, there shall be one million electric vehicles on German roads.

Modern lithium ion batteries for vehicles achieve an energy density of more than 120 Wh/kg (by comparison: conventional lead acid car batteries achieve approx. 30 Wh/kg). As applications are growing larger in size, they, of course, also need even larger storage systems which, on the one hand, provide a significantly higher energy content and, on the other hand, are capable of a high energy output. To achieve high voltages of several hundred Volt in high-performance high-energy battery systems, cells are connected in parallel or in series to form battery modules according to the respective current and voltage requirements; usually these battery modules are then again interconnected to form battery assemblies.

2 SAFETY TECHNOLOGY ASPECTS: RISKS AND HAZARDS

Due to the use of certain chemical compounds in combination with high energy densities and the use of control electronics (potential of technical defect) required for secondary batteries, lithium batteries are associated with specific potential hazards which need to be taken into special consideration with regard to safety.

Spectacular incidents have raised public awareness of potential problems associated with lithium ion and lithium metal batteries. Among other things this has led to several large-scale recalls of notebooks and smart phones in recent years.

- On 3 September 2010, UPS Airlines flight 6, a Boeing 747-400, crashed close to Dubai International Airport on its way to Cologne Bonn Airport, leaving two crew members dead. The crash had been caused by fire in the cargo area which contained lithium ion and lithium metal batteries.
- After a Boeing 787 (Dreamliner) coming from Narita/Japan had landed in Boston/US on 7 January 2013, fire broke out, caused by the thermal runaway of a lithium ion battery.
- On 12 July 2013, a non-rechargeable lithium metal battery in an ELT (emergency locator transmitter) of a Boeing 787 at London Heathrow Airport caught fire.
- On 6 November 2013, the third electric vehicle of the type Tesla Model S burned down.

It is characteristic of a battery that it releases chemically stored energy in the form of electric energy in the course of the discharging process. In case of a “thermal runaway”, the entire energy is not released as electrical energy in a controlled manner, but uncontrollably in the form of thermal energy. In case of such a failure, the thermal energy released by a lithium ion battery may be 7 to 11 times higher than the energy stored electrically. The produced heat accelerates the reaction, resulting in a critical overheating of the battery.

In addition, it is possible that cathode materials disintegrate at high temperatures. This reaction also produces heat (exothermic reaction) and releases bound oxygen; when fire breaks out, the thus released oxygen makes it difficult to control the fire. It is even impossible to extinguish such a fire using conventional fire extinguishing methods.

2.1 Temperature stability

The ideal operating temperature of lithium batteries ranges from 20 °C to 40 °C. In this temperature range, lithium ion batteries are most efficient, while their aging behavior is still acceptable.

At temperatures below zero, cells may be irreversibly damaged if charged, for example when lithium is deposited on the anode ("lithium plating"). In the worst case, this may result in an internal short circuit.

Most lithium ion cells are not conceived for operating and storage at temperatures above 60 °C.
At higher temperatures, the pressure within lithium ion cells may increase, inflammable gases are released, cells may ignite, right up to self-accelerating "explosive" burning of the battery (thermal runaway). This makes it dangerous to leave fully charged mobile phones or laptops on the hot dash board in the car on sunny summer days, as temperatures inside the car may reach up to 80 °C. If devices are immediately used at such high temperatures, this results in further heating and damage or failure.

- 70 °C: Self-heating of graphite anode and electrolyte. Low-boiling electrolyte components start to evaporate, resulting in a pressure increase which may make the cell burst.
- 130 °C: PE, PP or PE/PP separator closes its pores ("shut-down"). Separator melts, direct contact between anode and cathode, further heating as a result of short circuit. Autocatalytic temperature increase.
- 150-250 °C: Some cathode materials start disintegrating already at these temperatures, releasing heat and oxygen in an exothermic reaction, which may result in a thermal runaway. Cathode material reacts exothermally with the electrolyte (degradation). Pressure increase within the cell due to evaporation and gases released by degradation. Cell housing swells and may even burst (emerging degradation gases are ignitable).
- 660 °C: Aluminum current collector (cathode) melts. Graphite is released, potential risk of dust explosion. Temperatures increase further, aluminum foil of the positive electrode ignites (metal fire).

2.2 Thermal runaway

Thermal runaway is a self-accelerating, exothermic chemical reaction which reaches very high temperatures very fast, resulting in the ignition of chemically intercalated lithium (metal fire).

2.3 Components and degradation products in case of fire

Normally, lithium cells are hermetically, i.e. gas-tightly, sealed, so that components are not released in the course of regular operation. If the housing is mechanically damaged or subjected to thermal stress in case of fire, various corrosive, toxic, and carcinogenic substances, but also inflammable components (powdery, gaseous, or liquid) may be released.

Lithium metal: The hazard potential of primary lithium batteries is basically due to the use of lithium metal. Lithium is highly reactive and is prone to brisk autocatalytic reactions. Lithium has a comparably low melting point (181 °C); molten lithium within a battery cell may result in uncontrollable conditions. If, due to a technical defect, for example, local temperatures exceed the melting point of lithium, this may result in “explosive” reactions between the metal and the electrolyte.

Hydrogen (hazard: detonating gas): If lithium metal is contacted with water (e.g. fire extinguishing water), this may give rise to further hazards. Due to the high reactivity of the alkali metal, water molecules (H_2O) are immediately broken down into their components, which may result in the formation of hydrogen gas (H_2). As hydrogen/air mixtures are ignitable in a wide range of mixing ratios (4 to 75 vol.% H_2 in air), very low electrostatic discharges or electrical ignition sparks (e.g. light switch) are sufficient as ignition sources to trigger a so-called detonating gas explosion.

Although lithium is not used in its pure form but in the form of chemical compounds (in the charged state as compound with intercalated lithium, for example; in the discharged state as lithium cobalt oxide, $LiCoO_2$) in secondary batteries, these lithium modifications may also form hydrogen gas when contacted with water.

Another danger in connection with water is associated with the electrode potential and the DC voltage between the two battery poles. Although it is hardly probable that the inner electrode body (lithium) of a fully enclosed cell gets into contact with water, the mere electrode tension between the two cell poles may be sufficient to break down water into its components (Hofmann degradation). Everyone will remember chemistry lessons at school, where in a simple experiment commercially available cells were immersed in a vessel containing salt water and the formation of hydrogen gas was demonstrated by the so-called oxyhydrogen test. Translating the knowledge gained in the experiment into practice, it becomes clear that, if charged cells or batteries are fully covered by fire extinguishing water or get carried away by fire extinguishing water and are flushed into reservoirs, there is a risk that hydrogen gas may develop due to the DC voltage between the battery poles, potentially resulting in a detonating gas explosion.

Graphite: A thermal runaway of large cell types may lead to the release of significant amounts of graphite. In rooms, this may result in a graphite dust explosion, on the one hand, and may, on the other hand, lead to the room’s contamination with conductive graphite dust, causing short circuits and thus the damage of electric and electronic devices.

Heavy metals: As secondary batteries often use oxides from so-called transition metals (cobalt, nickel, manganese), ashes and smoke in case of fire can be expected to contain powdery reaction products or residues, some of which are hazardous to health (cobalt) or toxic (nickel). An exposition to 25 mg of cobalt compounds may cause skin, lung and stomach diseases, damage to liver, heart, and kidneys as well as cancer in human beings. Inhaling nickel compounds increases the risk of developing carcinoma in the lungs and the upper respiratory tract.

Inflammable components: Some of the materials used in lithium batteries and of the individual battery components are combustible and highly inflammable. Parameters which are important for fire protection, such as flash point, ignition temperature, and combustion heat, point to a high fire load of the electrolyte materials used in lithium ion batteries. In most cases, the liquid electrolyte consists of inflammable organic solvents and a conducting salt. Organic solvents used in lithium batteries are usually highly inflammable and capable of forming explosive mixtures with air.

The conducting salt lithium hexafluorophosphate ($LiPF_6$): As compounds containing fluorine and/or phosphorus (e.g. the conducting salt used in most cases: lithium hexafluorophosphate ($LiPF_6$)) are used in lithium batteries, unspecific gaseous substances may be released in case of fire; these toxic substances which are then contained in the smoke may constitute a serious hazard to people and the environment. These compounds are highly hygroscopic, so that the tiniest amount of water (if atmospheric moisture enters into a burst cell body, for example) may trigger chemical reactions which may result in the formation of hydrofluoric acid (HF) and phosphoric acid (H_3PO_4).

Phosphoric acid (H_3PO_4) is strongly hygroscopic and has an irritant or corrosive effect on the eyes, the respiratory tract, and the skin; if ingested, it causes damage to the gastro-intestinal tract.

Hydrogen fluoride/hydrofluoric acid (HF) is a colorless gas (pungent odor, highly toxic, corrosive, and strongly hygroscopic) and causes adverse health effects already at the slightest concentrations (1.4 ppm) and serious or permanent damage (IDLH value: 30 ppm). In a reaction with water (e.g. fire extinguishing water), hydrofluoric acid (corrosive and irritant effect on mucous membranes and skin, risk of severe damage to eyes and lungs, disorders of metabolism, cardiovascular and nervous system, bone damage) is formed. Hydrofluoric acid is a strong contact poison which is particularly dangerous as it is immediately absorbed by the skin. This may cause burns of deep tissue layers and even bones without visible skin injuries.

When lithium ion batteries of common sizes (e.g. laptop batteries) catch fire, this may already result in the development of sufficient HF to constitute a critical hazard. Only an on-site measurement of HF may then provide information about the specific hazard situation. After a fire affecting lithium batteries there may be high HF concentrations in the smoke, making it impossible to exclude a contamination of building parts and installations with HF, even though they may not have been directly affected by the fire.

Other toxic compounds: Hydrogen phosphides (e.g. phosphine), which are classified as toxic and hazardous to water, may develop out of phosphorus-containing components. Phosphine may be inhaled and cause severe irritations of the respiratory tract, toxic pulmonary edema being the severest consequence of its inhalation.

Exposure to special risks in spite of fire detectors: Damaged lithium batteries may release toxic substances which are heavier than air (e.g. electrolyte and solvent vapors, hydrogen chloride from PVC conduits, carbon dioxide) as well as smoke and degradation components before and during a fire. The heavy components may gather on the floor and are not detected by optical smoke detectors installed on the ceiling.

2.4 Electrical hazards

Voltage: Between the poles of a battery there is a DC voltage. High-voltage batteries may thus constitute a hazard to people. High rated voltages of up to 800 Volt required for electric vehicles may cause electric shocks when the batteries are touched (note: DC voltages of 120 V are already life-threatening!).

When an electric vehicle is involved in an accident, rescue forces often do not know how to turn off the electrical system and where the cables run. As high-voltage battery storage systems cannot simply be turned off by an emergency switch, the high voltage is particularly dangerous for maintenance staff and rescue forces.

Electric current: For electric vehicle applications, battery systems have to temporarily provide currents of the order of several hundred Ampere. Electric current may cause dangers in connection with the formation of electric arcs (e.g. when lines break down) as well as overloads and short circuits. Short-circuits in the HV system of current lithium ion batteries may give rise to currents of 6,000 A and more within a few milliseconds (note: currents of 50 mA are already life-threatening!).

Such currents immediately result in local temperature increases, resulting in fire risks. High electrical powers cause overheating which may result in an uncontrollable thermal runaway. Heating results in a further increase of the transition resistance, which is a particularly critical development making temperatures increase even further, leading to a further increase of the transition resistance and so on. High temperatures resulting from this vicious circle may cause individual cell components (e.g. separators, electrodes) to melt, which may lead to short circuits and the development of fire.

2.5 Causes of battery fires

Improper handling: Dangerous situations often arise due to improper handling and use. Mechanical damage (e.g. caused by shock, impact, crushing, etc.), electrical failures (e.g. short circuits, overload, etc.), or thermal influences (e.g. heat from the outside, etc.) may result in the leaking of electrolytes, in overpressure reactions producing gaseous reaction products, fire incidents, or the violent bursting of batteries.

Overcharging a lithium ion battery may, for example, cause the cathode to disintegrate, releasing strong oxidants and giving rise to a strong exothermic reaction of the electrolyte. Consequently, a thermal runaway of the lithium ion cell may happen, developing hot gases which may lead to the cell bursting open and possibly to the ejection of burning cell components.

Mechanical damage: The mechanical damage of batteries may result in internal short circuits and fires. The housing may be damaged by manufacturing defects (e.g. improper assembly of individual battery components), mechanical stress, or overpressure within the cell. Overpressure usually develops when a cell is overheated as a result of an overload, a short circuit, or an overcharge.

Secondary thermal stress: Exterior thermal stress (caused by thermal radiation in case of fires, for example) may make components (e.g. separators) of lithium batteries melt, resulting in a short circuit, which, in turn, may easily cause a fire.

External short circuit: When the two poles of a battery are connected to one another (e.g. by a metal object), this results in an external short circuit.

Internal short circuit caused by a cell failure or crash: Among the main reasons for internal short circuits are manufacturing defects arising in the course of the production of lithium cells. If metal particles or other conductive impurities are enclosed between the separator and the electrode in the course of the manufacturing process, for example, this may result in a local defect of the separator film during operation and, thus, in an internal short circuit. The so-called "run effect" may result in microscopic separator defects developing into extensive cracks in the film material within days or weeks; the increase in temperature caused by the short circuit, which may seem insignificant at first (because it is just local), may then develop exponentially, resulting in a thermal runaway. In everyday usage, internal short circuits often remain unnoticed until they suddenly cause fires after longer operation times.

Overcharge: A cell or battery is charged to a level exceeding the end-of-charge voltage specified by the manufacturer. The fully charged cell is not able to store the energy supplied from the socket; consequently, the overcharged cell or battery heats up. Inside the cell, the organic electrolyte fluid may start evaporating and the crystalline layered structure may start disintegrating; in combination with a strongly exothermic reaction, this may lead to the release of elemental oxygen (oxidizing!).

The strong local temperature increase in the course of this process may start a fire and, under certain circumstances, may cause an "explosive" discharge reaction. In addition, a disposition of metallic lithium on the anode may occur (so-called "lithium plating"). Consequently, very small and fine lithium needles, so-called "dendrites", may form; they may then pierce the plastic separator and thus cause an internal short circuit.

Over discharge and exhaustive discharge: In case of over or exhaustive discharge, a cell or battery is further discharged even though the end-of-discharge voltage specified by the manufacturer has been reached. This results in an irreversible decomposition of the liquid electrolyte. When a lithium ion cell is exhaustively discharged and then charged again, the supplied energy can no longer be stored in the form of chemical energy, due to the lack of electrolyte fluid, so that the charging energy is converted into heat.

Cooling system defect (in large-scale batteries): If the internal cooling of the battery uses a cooling agent based on a glycol/water mixture (as is customary in large-scale batteries and car batteries), a defect of the cooling system and leaking cooling agent may give rise to the risk that capillary action makes the cooling agent rise between the cells, possibly resulting in a short circuit and the ultimate thermal runaway of the battery even several days later.

Counterfeit lithium ion batteries and chargers: Some companies (particularly in the field of consumer electronics) have posted warnings concerning counterfeit lithium ion batteries and chargers on their websites. They expressly point out that these products are not equipped with appropriate safety elements, which may give rise to different problems during use and charging processes: excessive heating, bursting and leaking of electrolyte, fire, injuries to users, e.g. burns. It is also stated that no liability will be assumed for malfunctioning or accidents caused by the use of non-original lithium ion batteries and chargers (including counterfeit products).

3 FIRST AID ON THE SPOT: FIRE AND EMERGENCY MEDICAL SERVICES

In case of fire, firefighters need to protect themselves against the fire and, in case of lithium batteries, against chemical substances. When accident victims are saved from electric and hybrid vehicles firefighters are exposed to great hazards due to the high voltages, making special requirements for personal protection equipment particularly important.

3.1 Hazards caused by HV energy storage systems after an accident

In principle, batteries in electric and hybrid vehicles are installed so that they are insulated from the car's body parts. When the insulation is damaged (e.g. in a crash), it may burst, causing parts of the car to become live. When the battery or live cables and components are damaged, electric arcs may develop. This may cause the battery or the vehicle to catch fire.

Although usually all poles of the battery are disconnected in case of a car crash, for example, so that the vehicle and its cables are no longer live, rescue forces can never know for sure whether the all-pole disconnection of the battery electronics of a crashed electric vehicle has really been successful. This means that the cables and electronic components could still be live. Live cables are orange, but rescue forces do not know where exactly they run through the vehicle. HV systems including lithium ion batteries are thus associated with additional hazards of electrical shocks, short circuits, and arc flash. For this reason, additional personal protection equipment is required, e.g. electrician safety gloves, insulating protective helmets, and arc flash visors, insulating tools, a cloth for covering live parts.

- High-volt cables often run through spars and supports on the vehicle's underbody. Special care needs to be taken when hydraulic rescue equipment is used.
- It is not possible to electrically discharge the HV energy storage systems at the accident site.
- The state of the HV energy storage system has to be continuously monitored (smoke development).
- The HV energy storage unit must not be touched.
- It is recommended to request a skilled person qualified for high-volt systems from the respective headquarters; such a professional is able to assess specific dangers and decide on the steps to be taken.

3.2 Fire hazards

Fire scenarios:

Under thermal stress, lithium cells tend to ignite "explosively" and are prone to producing the so-called "rocketing effect" (similar to aerosol cans). To prevent secondary fires and collateral damage, appropriate measures to protect adjacent areas need to be taken.

Just like in conventional vehicles, burning materials, e.g. plastics, in electric/hybrid vehicles produce hazardous smoke HV energy storage systems and their individual cells comprise mechanical safety installations which may, for example, open when temperature and pressure increase in case of fire, allowing for the release of gases and pressure relief.

Just like in case of accidents involving conventional cars, it cannot be excluded that a fire breaks out some time after an accident, particularly if HV energy storage systems are damaged.

Fire extinguishing agents

When fighting lithium battery fires, metal powder extinguishing agents, oxygen-displacing agents, or surfactant mixtures are, amongst others, recommended in addition to the conventional extinguishing agent water.

Water: In case of lithium battery fires, extremely high amounts of heat are released due to the high energy content. Taking into account the high fire load of lithium batteries and the thermal energy released in case of fire, the excellent heat binding property of water is efficient for fighting the fire. For this reason, firefighters normally use water as the conventional extinguishing agent.

If great amounts of water are used as early as possible, the water's cooling effect significantly decelerates the reaction and thus fire development. In addition, toxic smoke gases are precipitated. When water is used as an extinguishing agent, all damaged cells with open housings are slowly discharged as a consequence of their contact with water.

Fighting lithium battery fires requires significantly more fire extinguishing water than fighting conventional fires. It has to be taken into account that, due to the solid encasings of batteries, it is not possible to directly cool the cells. As a consequence, more water is needed.

Attention needs to be paid to the development of hydrogen. Under certain circumstances, hydrogen may form ignitable mixtures with ambient air and start burning very abruptly. Hydrogen/air mixtures are ignitable in a wide range of mixing ratios (4 to 77 vol.% H_2 in air) and only require very low ignition power, i.e. very low electrostatic discharges are sufficient as ignition sources.

Metal powder extinguishing agents/sand: The extinguishing effect of metal powder extinguishers or sand is mainly based on the principle of cutting off oxygen supply by covering burning materials. These extinguishing agents, however, do not have any cooling effect so that thermal energy released in case of fire cannot be efficiently reduced. When removing the extinguishing agent covering the burning materials, there is also a risk of strong deflagration reactions caused by the then available oxygen.

Because of the high thermal energies released by lithium battery fires and the problems associated with the use of metal powder extinguishing agents in advanced fire scenarios (How can the extinguishing agent be distributed to cover the entire area affected by the fire?), metal powder extinguishing agents and sand are only used at the incipient stage of smaller fires. For larger damage scenarios, metal powder extinguishing agents or sand are hardly the agents of choice. This also holds true for ABC dry powders.

Oxygen-displacing extinguishing agents: Gaseous oxygen-displacing extinguishing agents (e.g. CO_2 extinguishing agents) suppress fire and reduce the energy released, but they do not have a cooling effect, either, which, in case of lithium battery fires, has a significant influence on the success (or failure) of extinguishing operations. The oxygen-displacing effect is not very efficient in case of lithium battery fires, either. The oxygen released from the cells after the decomposition of the cathode's active material allows for a partial oxidation (=continued burning) even without the supply of external oxygen from the air. This means that the use of gaseous extinguishing agents is hardly efficient from the point of view of fire protection.

Extinguishing agent additives: Some extinguishing agent producers try to meet the challenges associated with an efficient extinction of lithium battery fires by adding different additives (e.g. calcium salts, gelling agents, swelling agent, surfactants, etc.) to the extinguishing water. It is a fact that extinguishing agent additives may increase heat transfer to the extinguishing agent, so that the use of appropriate additives may help to reduce the required amount of water and accelerate successful fire extinction.

Recent studies on special additives have shown good results in individual experiments. The individual comparing experiments were, however, carried out using different steel pipe types and flow rates, which makes it difficult to compare them. Moreover, it is possible to achieve similar results using conventional multi-application foams. They were, however, not used in the comparing extinguishing experiments.

This means that it is entirely possible to successfully extinguish fires using certain additives (i.e. they are suitable, in principle, and not harmful); an objective evaluation of these extinguishing agent additives compared to conventional multi-application foams is, however, hardly possible for the above reasons. Thus, the product presentations of these "novel" extinguishing agents do not show any objective advantages (which could be legitimately advocated).

3.3 Chemical hazards

- When vehicles, in particular modern vehicles, catch fire, there is always the problem that, due to the materials used, greater amounts of smoke and energy are released.
- Acids and heavy metals, which may be generated in the course of vehicle fires, are diluted by the extinguishing water, but still may be contained in high concentrations in the smoke. Electrolytes leaking from the HV energy storage system are usually irritant or corrosive. Skin contact with and an inhalation of the fumes has to be absolutely avoided.
- Firefighters should thus always wear self-contained breathing apparatus. Protective clothing according to the EN 469 standard provides protection against heat and, to a certain degree, against acids to avoid any contamination of the skin.
- To bind any leakage, conventional binders should be used.

3.4 Course of action at the site of an accident

- Make sure that the vehicle is voltfree: All live lines need to be disconnected. Turn off the ignition (disconnect 12 V battery).
- Disconnect interlock and service disconnector socket from the HV battery.
- Protect against automatic restoring of power: Keep ignition key, interlock and service disconnector socket in a safe place.
- Make sure that the vehicle is voltfree using an approved voltage tester.
- Ground and short-circuit.
- Cover adjacent live parts.

3.5 Additional advice

- Electric and hybrid vehicles do not make any sound when they are turned on. Electric vehicles may thus move quietly and "unnoticed" any time: vehicles need to be secured against rolling away.
- Damaged cells (and cells under thermal stress) are prone to delayed self-ignition (even after a successful extinguishing operation). For this reason, electric and hybrid vehicles must NEVER be left unattended or parked indoors.
- Damaged high-volt batteries or their components are to be treated as hazardous materials when transported and thus have to be loaded and unloaded by professionals, transported on open vehicles and stored in the open air.
- Recovering vehicles from water: The risk of electric shocks caused by the HV system is principally not higher in water. The recovering procedure is the same as for conventional vehicles. There are no greater hazards for the drinking water than in case of conventional vehicles.
- Caution: voltages of up to 1,000 V! Due to the electric hazards, rescue workers have to adhere to the principles of fighting fires in electric installations and comply with steel pipe distances according to VDE 0132.

4 CONVENTIONAL LOSS PREVENTION: GENERAL SAFETY RULES AND PROTECTION MEASURES

Basic principles of handling and storing of lithium batteries in companies: The Occupational Health and Safety Act and the Work Safety Regulation oblige the operator to evaluate potential hazards caused by technical installations and devices in a hazard assessment and to implement consequential protective measures. This basically also applies to lithium batteries.

For efficient damage prevention in connection with lithium batteries, conventional protection concepts providing for conventional measures which have proved efficient for producing, handling, and storing inflammable substances are entirely suitable.

4.1 Structural fire protection measures

Spatial and structural separation which avoids the exposition of production facilities and storage areas to inflammable substances has proved efficient to prevent damage. It is thus basically recommended to allow lithium batteries to be stored and handled only in specific areas separated by fire-resistant means or when an appropriate safety distance is maintained. Based on international damage experience, a standard of 90 minutes fire-resistance (firewall) and a safety distance of at least 20 meters have been established.

If a spatial or structural separation of individual areas is not possible for operational reasons, the minimum fire prevention requirements provide for sufficiently dimensioned corridors and safety distances of at least 2.5 m within one fire compartment combined with additional organizational and technical protection measures.

In addition to the separation of areas in which lithium batteries are manufactured or stored according to fire prevention principles, potential hazards can be further reduced by encapsulating individual batteries or lots (cassettes or containers made of non-inflammable materials). In most cases, it is, however, difficult to put this solution into practice.

4.2 Organizational fire prevention measures:

As fire risks are mostly related to improper handling or operating errors and hardly ever to technical errors, organizational loss prevention plays a particularly important role. An adequate training of employees so that they can handle batteries correctly (as in the case of hazardous materials) and the provision of specific operating instructions are basic prerequisites.

Simple preventive measures, such as the efficient prevention of short circuits at the battery poles by using pole caps, avoiding thermal radiation by heating facilities and the sun by choosing adequate storage areas, keeping safety vents unblocked, and mounting signs explaining the correct storage of battery cells in the warehouse, can be easily implemented and are at the same time very efficient.

To prevent an internal short circuit caused by damaged electrode surfaces or separator materials, mechanical damage of cell components by impact, shock, or crushing needs to be excluded. Damaged products (even in case of very small damage) have to be immediately disposed of in a professional way.

To minimize high-risk areas, lithium batteries should be stored separately, i.e. not together with other products and substances.

Hand-held fire extinguishers with special extinguishing powder (class D) have proved efficient for quickly fighting small fires at the incipient stage. They are, however, only efficient in the first phase of small incipient fires affecting only a small number of cells. Hand-held fire extinguishers with carbon dioxide (CO_2) or conventional chemical dry powder are only efficient to a certain extent and thus less suitable.

If lithium batteries have to be provided at production sites, the number of batteries should be kept as low as possible (“daily need”). In the area of pick-up and processing positions, additional fire extinguishers have to be provided (pay attention to choose the right extinguishing agent). Corridors of 2.5 m around pick-up areas efficiently prevent fire from spreading. It is ideal to use fire-resistant storage cabinets/containers. If there are fire extinguishing systems in the areas concerned, it has to be verified that these systems (incl. the extinguishing agent they use) are suitable for the potential hazard of lithium batteries and capable of efficiently fighting a lithium battery fire.

4.3 Safety systems

Currently, there is hardly any well-founded knowledge concerning the efficiency of technical protection concepts and solutions using safety systems (fire extinguishing systems) used in areas where lithium batteries are handled and stored, and there are no standardized concepts for these systems. In spite of the apparent risk potential, no extinguishing system concept has been established as standard. It is thus not possible for professionals to exclusively recommend a certain fire extinguishing system concept.

Experience with battery fires and the use of conventional fire extinguishing technology (sprinkler systems, gas extinguishing systems, etc.) has shown that it is particularly because of the enormous energy content of lithium batteries that huge amounts of heat are released in the event of fire. Fire protection system concepts are faced with significant challenges, particularly where conventional water extinguishing technology (e.g. sprinkler systems) is applied. The focus lies in particular on warehouses with mixed stock (e.g. freight warehouses, central warehouses, etc.) where, when the stock is stored in a chaotic way, lithium batteries may be stored next to conventional goods. Conventional extinguishing systems are often not able to efficiently fight battery fires. Re-ignition hazards also constitute a considerable challenge for fire extinguishing system concepts.

Each area of application of lithium batteries has specific requirements. For the time being, when looking for appropriate protection concepts, hazards will have to be analyzed specifically for each individual case. Handling and storing lithium batteries requires solutions tailored to the respective requirements of specific applications.

In addition to automatic fire extinguishing systems, structural and organizational measures also have to be taken into account. Efficient protection concepts using sprinkler systems need to be reviewed individually.

Fire detection

In areas where lithium batteries are stored or used extensive early fire detection systems are indispensable. At least it has to be made sure that all areas where lithium batteries are handled are monitored by a fire detection system which is capable of automatically alarming a permanently manned station.

Targeted fire-fighting on site, e.g. by firefighters, requires the precise detection of the fire’s location in the warehouse. Pinpoint fire detection is, however, complicated by ventilation conditions in the warehouse, e.g. caused by the movement of storage and retrieval vehicles.

To evaluate fire detection, degradation products of different loss scenarios have to be analyzed and detection mechanisms have to be adapted to the ventilation conditions in the warehouse. In the event of damage, two cases have to be distinguished:

- If the assumed progress of the damage scenario is slow, cold smoke and degradation gases which are heavier than air develop (e.g. electrolyte and solvent vapors, hydrogen chloride from PVC conduits, carbon dioxide).
- There is smoke containing components which are lighter than air (e.g. carbon monoxide, hydrogen fluoride).

As a result, there are special technical fire detection requirements. There need to be sensors in the upper and lower areas of the warehouse. Reliable fire detection has to cover the warehouse's entire height and surface area. If necessary, smoke aspiration systems or alarms in ventilation ducts for exhaust air also have to be provided.

Ventilation technology is faced with special challenges by the different specific gravities of components in relation to air: specifically heavy gases have to be sucked off from the warehouse's floor area, using fresh air from above, while specifically light gases have to be sucked off from the roof area, using fresh air from below. The supply of exhaust air/fresh air has to be switchable. It is a problem that the gases cannot be sucked off directly where they develop, but only from the floor or roof area. In the worst case, harmful substances may thus be sucked through the entire warehouse, resulting in the deposition of substances and contamination. The construction of appropriate fire compartments can reduce this risk.

Water extinguishing systems

Water helps to contain the consequences of lithium battery fires and to make the fire controllable. The use of water has a cooling effect, which prevents the fire from spreading and reduces its intensity. An early triggered extinguishing system, complete wetting and cooling of the burning materials significantly decelerate the reaction of the lithium battery and thus the development of fire.

Early triggered sprinkler or spray extinguishing systems using high amounts of water offer efficient protection. When conventional water extinguishing systems (e.g. sprinkler systems) do not respond fast enough and their performance is insufficient, water mist technology offers a possible solution. Water mist reliably achieves extinguishing and cooling effects and prevents re-ignition.

Gas extinguishing systems

Gas extinguishing systems use liquefied gas (N_2, CO_2) having a positive inerting effect. The amounts of gas usually employed only allow for removing a small amount of thermal energy, however.

As huge amounts of heat are released by lithium battery fires, this concept seems hardly suitable for extinguishing systems in this case, as it is only capable of binding limited amounts of heat.

Permanent inerting

If the installation of an extinguishing system is not possible for economic reasons or if there are other reasons against installing a water extinguishing system, loss prevention concepts need to focus on preventing fires from breaking out in the first place. In this connection, oxygen reducing technologies offer promising solutions.

Basically, the concept of permanent inerting by flushing an area with nitrogen allows for containing fire risks. Nitrogen is introduced into an area to be protected in a controlled way, reducing the oxygen content and thus the risk of fire breaking out due to external causes in the batteries' environment.

It has to be taken into account, however, that the cathodes of secondary batteries are usually made of metal oxides which, in case of fire, may release the chemically bound oxygen. This formation of additional oxygen presents a huge challenge which needs to be taken into account for permanent inerting concepts. When using protective concepts based on permanent inerting, stricter requirements concerning the building structure's integrity also need to be taken into account. For these reasons, the suitability of the permanent inerting concept needs to be evaluated for each individual case to find out whether it is possible to achieve the protection targets applying this technology.

5 APPLICATION-SPECIFIC LOSS PREVENTION: PRODUCT-SPECIFIC SAFETY RULES AND PROTECTION MEASURES

The potential hazards of lithium batteries are determined by the product itself and the power it provides. Accordingly, protection measures and safety rules also have to be based on these parameters.

5.1 Protection and monitoring systems on batteries

An application of protection and monitoring systems and a monitoring of the battery state using sensors constitute important safety criteria:

- use of PTC resistors or PTC thermistors (PTC – positive temperature coefficient): components whose electrical resistance increases when the temperature increases so as to limit charge and discharge currents.
- use of CID (circuit interrupt device or current interrupt device): if gas pressure is detected inside the cell (caused by a beginning overcharge and increasing temperatures), the electrical contact to one of the poles is interrupted.
- use of shut-down separators: three-layer separators which lose their porosity in case of a temperature increase due to the partial melting of one layer, so that the current flow is interrupted
- use of a safety vent: predetermined breaking point activated at a certain internal gas pressure allowing for venting gases in a controlled way This prevents the batteries from bursting violently.

If cell states and charging and discharging processes are monitored by measuring cell voltage, temperature, battery current, state of charge, it is possible to turn off the battery system or disconnect individual cells if any safety-relevant malfunctions caused by user errors occur. The battery management system guarantees that the storage will always be optimally used, even in case of aging cells and diverging cell capacities and internal resistances (“cell balancing”). When a great number of cells are charged together, the risk of an overcharge of individual cells has to be prevented, for example. Due to the batteries’ working principle, the individual cells show a certain variance and may contain different amounts of residual charge. For this reason, some cells may reach the maximum voltage sooner than others in the course of the charging process, so that there may be overvoltage in some cells or the charging process may be interrupted prematurely. The weakest cells determine the behavior of the entire battery system. It may thus be necessary to monitor individual cells:

The prevention of electric and electronic errors is linked to the function of “intelligent” systems for monitoring and controlling battery parameters.

5.2 E-bikes and pedelecs: special requirements and safety measures

Contrary to charging stations for electric vehicles, charging devices for e-bikes and pedelecs are not suitable for being used under all ambient conditions. The use of these charging devices under extreme temperatures or in humid environments may result in hazardous operating conditions and fire. The use of chargers which are not approved by the manufacturer may also result in hazardous operating conditions. If inflammable materials are then stored close to batteries or chargers, it does not take a lot of time until larger fires develop when these batteries or chargers ignite or heat up strongly.

Damage events caused by e-bikes or pedelecs show that some e-bikes of the lower price range, in particular, do not have battery management systems (BMS) to monitor the batteries.

- The device must never be close to inflammable materials (parking, charging, etc.). The charging process should be carried out in an environment without fire loads.
- Never leave batteries unattended during charging, e.g. in the night (they should preferably be monitored by a fire detector).
- Batteries need to be protected from frost.
- Charging devices must only be used under dry conditions, e.g. in cellars or garages; they may only be used in the open when protected against humidity by waterproof boxes, pockets, or the like, or if they have been expressly approved for outdoor use by the manufacturer (heat accumulation caused by charging batteries in too small boxes and pockets or the covering of batteries or chargers have to be avoided).
- When batteries are charged indoors, it has to be taken in mind for immediate charging processes that the battery needs at least ten minutes to adapt to the room's temperature after having been used at low temperatures outside. A temperature shock during the charging process may give rise to fire risks.
- To enlarge the cycle-life of the battery, cyclists should never charge the battery over 90% or discharge it below 10% state of charge (SOC). If pedelecs are not used over a longer period of time, e.g. in winter, exhaustive discharge has to be prevented by recharging.
- Always look for the GS (Geprüfte Sicherheit meaning "tested safety") sign when buying batteries. This label guarantees that the manufacturer has complied with all safety requirements.
- Do only charge e-bikes with the original charger and use high-quality batteries and chargers.
- Never carry out any technical changes and, in particular, never manipulate the safety equipment.
- After a fall or accident, have the battery checked. Internal damage may trigger a fire – even at a later point in time.

5.3 Storage: batteries and battery-operated products

Low-power lithium batteries

This category includes all single-cell batteries and small batteries which are primarily used for the following fields: computers, multimedia, small electronic devices, small tools, etc.

- There are no special safety provisions for this category, as long as all provisions by the manufacturer and institutions issuing safety certificates are complied with.
- For greater amounts which are stored contiguously (volumes of more than 7 m^3 or more than 6 Europallets), the advice for medium-power lithium batteries applies.

Medium-power lithium batteries

Batteries of this category are, for example, used for bicycles with an accessory electric drive (pedelec, e-bike), e-scooters, light electric vehicles (LEV), larger gardening tools, different small vehicles, and the like, but also as modules for manufacturing high-power batteries.

- Medium-power batteries have to be stored in areas separated by fire-resistant means or in separate areas with sufficient clearance (e.g. in storing areas or containers for hazardous material).
- It is not permitted to store them in the same storing area with other goods.
- The storing area needs to be monitored by an appropriate fire detection system which is connected to a permanently manned station.
- In case of larger stocks (covered area of > 60 m^2 and/or stored to heights of > 3 m) the advice for high-power lithium batteries applies.

High-power lithium batteries

Batteries of this category are characterized by providing particularly high power. Currently, they are mainly used for electromobility applications (automotive) and large off-line equipment.

- The minimum requirements for high-power batteries correspond to the measures to be taken for medium-power lithium batteries
- Additionally, a hazard analysis should be carried out individually for every application.
- Protection measures and fire protection concepts are established individually for each case, providing individual solutions specifically tailored to the respective application scenario.

A fire in a warehouse where lithium ion batteries are stored can be assumed to be only smoldering at first, releasing small amounts of energy and heat.

When lithium ion batteries start burning (due to a short circuit, for example), carcinogenic polycyclic aromatic hydrocarbons, hydrogen fluoride, and heavy metal deposits are developed among others. This has to be kept in mind to make sure that the use of a warehouse contaminated in the course of a fire event is not hazardous to health at a later stage.

Large fire experiments carried out in the insurance sector (FM Global and VdS Schadenverhütung) have shown that the use of water as a fire extinguishing agent (possibly using additives) is basically efficient (although the framework for its efficient use is quite restricted).

It is hardly possible to protect a warehouse using spray nozzles or sprinklers on the ceiling, if batteries are intended to be stored there relatively close to one another, as these systems cannot guarantee that a sufficient amount of water reaches the covered areas of the warehouse. Fire extinguishing systems require extinguishing sections which are as small as possible to allow for targeted fire-fighting, while keeping damage caused by water to a minimum.

Classification Power	Lithium metal battery (UN 3090)	Lithium ion battery (UN 3480)
Low	≤ 2 g total lithium content	≤ 100 Wh per battery
Medium	> 2 g lithium per battery and ≤ 12 kg gross per battery	> 100 Wh per battery and ≤ 12 kg gross per battery
High	> 2 g lithium per battery and > 12 kg gross per battery	> 100 Wh nominal energy and/or > 12 kg gross per battery

5.4 Transport: road, rail, water, air

For every mode of transport, there are specific provisions concerning the transport of hazardous material. Hazardous goods regulations are based on the UN Model Regulations which are compiled and defined by an international commission (United Nations Economic Commission for Europe (UNECE)). These regulations are then translated into international law and adapted to the specific requirements of the individual modes of transport (road, rail, water, air). In Germany, the Federal Institute for Materials Research and Testing is the competent authority.

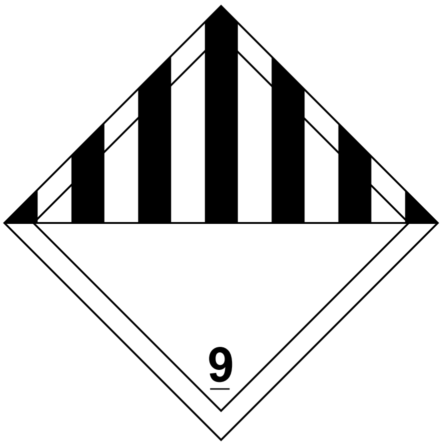
Mode of transport	Organization / Agreement	Rules
Road transport	UN Economic Commission for Europe (UNECE)	Accord européen relatif au transport international des marchandises Dangereuses par Route (ADR)
Rail transport	Intergovernmental Organization for International Carriage by Rail (OTIF)	Regulations concerning the International Carriage of Dangerous Goods by Rail (RID)
Air transport	International Civil Aviation Organisation (ICAO)	ICAO Technical Instructions (TI)
	International Air Transport Organisation (IATA)	IATA Dangerous Good Regulations (DGR)
Sea transport	International Maritime Organization (IMO)	International Maritime Dangerous Goods (IMDG)
Inland navigation	UN Economic Commission for Europe (UNECE)	Accord européen relative transport international des marchandises Dangereuses par voices de Navigation interieures (ADN)

According to the UN Regulations on the Transport of Dangerous Goods, all lithium metal batteries and lithium ion batteries are classified in Class 9 (miscellaneous hazardous substances and articles).

The transport of lithium batteries is subject to hazardous goods legislation. Lithium metal and lithium ion cells and batteries are classified as follows:

UN number	Designation and description
3480	LITHIUM ION BATTERIES (including lithium ion polymer batteries)
3481	LITHIUM ION BATTERIES CONTAINED IN EQUIPMENT or LITHIUM ION BATTERIES, PACKED WITH EQUIPMENT (including lithium ion polymer batteries)
3090	LITHIUM METAL BATTERIES (including batteries of lithium alloys)
3091	LITHIUM METAL BATTERIES CONTAINED IN EQUIPMENT or LITHIUM METAL BATTERIES PACKED WITH EQUIPMENT (including batteries of lithium alloys)

If lithium metal cells contain more than 1 g lithium or if lithium metal batteries contain more than 2 g lithium or if lithium ion cells have a rated energy content of more than 20 Wh or if lithium ion batteries have a rated energy content of more than 100 Wh, a label showing the symbol of Hazardous Goods Class 9 (10 x 10 cm, seven black stripes on a contrasting background) needs to be applied to the packaging:



If threshold values are not exceeded, batteries can be transported according to ADR Special Provision 188 and IATA DGR Packing Instruction 965, Section II; the lithium battery handling label needs to be applied to the packaging, however.

A certification according to UN Manual Tests and Criteria, Part III, Section 38.3. is required for the admission of lithium batteries to transport:

- Test 1: simulation of altitude (simulates pressure drop during air transport)
- Test 2: thermal test (rapid and extreme temperature changes
- Test 3: vibration (vibrations in the course of transport)
- Test 4: shock (simulation of possible impacts during transport)
- Test 5: external short circuit
- Test 6: impact / crushing (mechanical damage)
- Test 7: overcharge
- Test 8: forced discharge (exhaustive discharge)

For air transport, the packaging provisions laid down in the IATA Dangerous Goods Regulations apply. Contrary to the ADR guidelines for road transport, for example, there are complicated supplementary provisions and variations not only for individual states, but also for individual airline companies.

The following provisions for the transport of lithium metal or lithium ion batteries as cargo can be found in the IATA DGR, for example:

	Permitted in or as carry-on baggage	**Permitted in or as checked baggage**	**Permitted on one´s person**	**The approval of the operator(s) is required**	**The pilot-in-command must be informed of the location**
Battery-powered wheelchairs or other similar mobility devices with non-spillable wet batteries or with batteries which comply with Special Provision A123 or A199 (for details, see 2.3.2.3 and 2.3.2.4).	NO	YES	NO	YES	NO
Battery-powered mobility aids with lithium ion batteries (collapsible), lithium-ion battery must be removes and carried in the cabin (for details, see 2.3.2.4(d)).	YES	NO	NO	YES	YES
Lithium battery-powered electronic devices. Lithium ion batteries for portable (including medical) electronic devices, a Wh rating exceeding 100 Wh but not exceeding 160 Wh. For portable medical electronic devices only, lithium metal batteries with a lithium content exceeding 2g but not exceeding 8g.	YES	YES	YES	YES	NO
Spare lithium batteries. Lithium ion batteries for portable electronic devices (including medical devices) with a Wh rating exceeding 100 Wh but not exceeding 160 Wh. For portable electronic devices only, lithium batteries with a lithium content exceeding 2g but not exceeding 8g. Maximum of two spare batteries in carry-on baggage only. These batteries must be individually protected to prevent short circuits.	YES	NO	YES	YES	NO
All spar batteries, including lithium metal or lithium ion cells or batteries, for such portable, electronics devices must be carried in carry-on baggage only. These batteries must be individually protected to prevent short circuits.	YES	NO	YES	NO	NO

Transporting damaged lithium batteries: Special precautions need to be taken for transporting lithium ion batteries which are suspected to be defective or damaged. If one of the following questions is answered with yes, the packaging and transport provisions for defective batteries apply:

- Is the housing of battery cells damaged or severely deformed?
- Is liquid leaking from the housing?
- Is there a special gas smell?
- Is there a measurable increase in temperature even in the turned-off state?
- Are there any molten or deformed plastic parts?
- Can you see any molten power cords?
- Does the battery management system (if in place) identify any defective cells?

Some hazards, like the formation of gas within the battery housing, cannot be detected from the outside. If possible, damaged battery systems should be slowly discharged by a competent expert and left standing and monitored for several days. Ideally, the manufacturer of the battery system is contacted.

If a competent expert cannot exclude that accelerated disintegration, dangerous reactions, flame formation, or the hazardous release of toxic, corrosive, or inflammable gases or fumes could occur under normal transport conditions, cells or batteries can only be transported under the conditions defined by the competent authority (Federal Institute for Materials Research and Testing).

5.5 Disposal: recycling and waste management

Consumers are obliged to dispose of batteries at an appropriate collection point provided by dealers or communities. It is not allowed to dispose of batteries in the domestic waste. This provision applies to all batteries, independent of type, size, and application. The return rate of lead acid batteries amounts to more than 95% in Germany, while the return rate of lithium batteries is still insufficient.

Used, undamaged lithium ion batteries (UN 3480) and lithium metal batteries (UN 3090) are accepted in collection boxes (completely discharged, with taped poles). Used large lithium batteries (high-energy batteries: e.g. e-bikes, laptops, cordless screwdrivers) with a weight of more than 500 g per piece need to be packaged separately in specifically labelled yellow collection boxes. There are special transport provisions for damaged high-energy batteries.

Waste disposal companies are faced with various challenges in connection with the collection, return, and recycling of batteries. When batteries are delivered, a visual inspection is carried out to find lithium batteries (it is not always easy to identify them). Some batteries are also stored in the waste treatment companies. The rearrangement of bulk material is particularly difficult. There is a potential fire hazard when collecting, storing, and recycling used or damaged batteries:

- unprotected contacts, residual charge, insufficient packaging
- transfer using a wheeled loader and a clam, crushing in a shredder

It is comparably easy to implement collection and return systems for batteries which are not built-in parts of devices; broken electric devices with built-in batteries constitute a huge waste management challenge. Electric and electronic devices increasingly often comprise high-performance high-energy batteries containing lithium as primary energy sources or back-up batteries. The use of such batteries makes higher safety requirements necessary when broken devices are returned. In many cases, the batteries are built-in parts of the devices. Due to batteries which contain lithium in broken electric devices, there is a higher fire risk, particularly when the batteries are damaged.

There have already been numerous fire incidents caused by lithium batteries in disposal companies. The most serious incidents happen when batteries are transferred and stored. There are various causes of fire:

- "self-ignition" when unpacking new stacked components (with lithium batteries), cause: short circuit due to improper handling
- fire in the granular material, cause: "self-ignition" after damage (crushing) of electric components (incl. lithium batteries) by wheeled loader
- fire in the shredder, cause: "self-ignition" after mechanical crushing of electric components (incl. lithium batteries)
- fire in a collecting container, cause: "self-ignition", no outside influence

Consequently, there is a number of requirements addressed to different players:

- skills training: raising the awareness of everyone involved in battery disposal (consumers, transport, disposal, etc.) of the special hazard potential of lithium batteries and training them in handling it.
- approval authorities: in addition to personal and environmental protection, the protection of assets needs to be established as an equal target.
- collection logistics: reform of collection logistics to avoid transfers
- identification: clear and uniform labelling of devices containing high-energy batteries by the manufacturers
- consumer information: informing consumers of the hazards and the necessary care which needs to be taken when disposing of devices and batteries.
- disposal chain: the last owner should principally separate batteries from broken electric devices (if possible) and dispose of them separately.
- insurance companies: risk bearers increasingly focus on risk-adequate premiums (risk premiums) with individual coverage concepts for various company types and require disposal companies to assume a greater share of responsibility (higher deductibles).
- transport: Transports which should be hazardous material transports and constitute a risk to health and the environment must not be tolerated. Costs or additional efforts required are no valid arguments when lives and the environment are endangered.
- Adequate protection concepts and efficient measures

When looking for adequate solutions for collection points and recycling plants, risk-adequate protection concepts should comprise hazard-specific assessments in combination with efficient measures. Lithium batteries should ideally be identified and separated from other materials at delivery. Strict controls immediately after delivery and a continuous inspection on sorting lines before crushing should be organized. As lithium batteries are both fire loads and ignition sources, fire load should be limited, preferably by spatial separation, a modular assembly of facilities, and the provision of separate storage sites. Measures to spread burning bulk materials need to be in place.

Functional concepts for efficient fire prevention absolutely require extensive early fire detection systems and automatic extinguishing systems. It also has to be made sure that an adequate extinguishing water source (stored amount of water and pumping power) is available, taking into account the huge fire load at collection points.

6 Perspectives

The German government has adopted the National Electromobility Development Plan, which intends to make Germany a leading market for electromobility. According to this plan, 1 million electric vehicles should be moving on German roads by 2020 (6 million by 2025).

The required battery capacity will continue to increase in the long run; according to a study carried out by Roland Berger, from 6.5 million kWh today to approx. 130 million kWh by 2020. The demand production facilities have to satisfy will thus also increase. According to serious estimations, investments amounting to EUR 4.8 billion per year will be required to build new production facilities to be able to provide the required production capacities Prognoses show that enormous financial and technological efforts will be required to reach the optimistic targets in the field of electromobility.

New storage technologies require new charging technologies: The need for charging stations will increase analogously to the increasing need for modern energy storage systems. Thus, technological framework conditions and safety requirements for battery charging facilities have changed significantly. To limit risks (and prevent damage) the following questions will have to be answered:

- Where are charging stations going to be installed?
- Who will be responsible for installing (operating) these charging stations?
- Who will use these charging stations?

New battery charging technologies will present new challenges in terms of operating safety:

- **Wired (conductive):** In case of (wired) AC charging, the charging unit converting the AC available via the network into DC required for charging is built into the vehicle. The charging unit for (wired) DC charging is located outside the vehicle. The vehicle is supplied with DC requested by the vehicle directly by a DC charging station.
- **Wireless (inductive):** In an inductive charging process, energy is transferred wirelessly via an electromagnetic field, similar to an induction hob or an electric toothbrush.
- **Battery change:** When the battery needs to be changed, the entire battery system is removed from the car and replaced by a charged battery system. This energy supply method allows for replacing a discharged battery with a fully charged one in a few minutes' time.

Safe charging infrastructure significantly influences the safety of the charging process, as the charging unit for batteries is either directly connected to the supply network or to the electric facility of a power recipient in such a supply network. In both cases, it is the highest priority to guarantee utmost operating safety.

By installing charging stations in private and public areas and extending charging infrastructures, new user groups will have to deal with the safety of battery charging facilities:

- electricians
- home owners and real estate owners
- real estate managers and car park operators
- public administration employees
- architects and urban planners
- grid operators and energy suppliers

7 Conclusion

Basically we can assume that lithium batteries and the corresponding charging technologies are comparably safe when handled and operated properly. Sophisticated manufacturing technology and protection mechanisms built into the batteries allow users to handle these chemical energy storage systems safely.

It has to be taken into account, however, that due to the use of certain chemical compounds in combination with high energy densities and possible technical defects, lithium batteries are associated with special potential hazards which need to be taken into special consideration when safety is concerned.

Batteries are basically intended to store huge amounts of energy and release this chemically stored energy in the course of the discharging process in the form of electric energy. If technical defects or improper handling result in an uncontrolled and accelerated release of the chemically stored energy, the energy is usually not released in electric, but in thermal (!) form: fire (damage to property and the environment, personal injuries). The risks associated with handling and providing lithium batteries during production and their storage thus constitute a special challenge for fire prevention and personnel safety.

In view of the rapid growth and spreading of modern battery systems and the corresponding charging technologies, these challenges need to be solved quickly.

As a matter of principle, it is recommended to treat lithium batteries as hazardous material during production, manufacturing, storage, and transport. To efficiently prevent damage, efficient structural fire prevention and, in particular, the implementation of comprehensive organizational protection measures play an important role.

Each area of application dealing with lithium batteries has specific requirements. For the time being, when looking for appropriate protection concepts, hazards will have to be analyzed specifically for each individual case. Handling and storing lithium batteries requires solutions tailored to the respective requirements of individual applications.

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