

Recommendations for fire brigade response when at risk through lithium cells, batteries and accumulators

Short title: Lithium batteries
Created by: Referat 10



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- Editorial changes

Note

A spelling that does equal justice to all genders is desirable. However, since corresponding newer spelling generally lead to major restrictions in readability, this has been dispensed with. Thus, for the entire document, the masculine form includes all genders unless explicitly stated otherwise.

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1. Aim of the Instruction Sheet

Fire brigade operations involving lithium batteries always include aspects of chemical operations in accordance with FwDV 500, which is why this Instruction Sheet presents the deployment instructions from the perspective of FwDV 500 with a focus on the C hazardous substances that occur. This Instruction Sheet also serves as a basic Instruction Sheet for other vfdb Instruction Sheets with other focal points or approaches.

For this reason, reference is made here both to the Instruction Sheet "Vehicles with Li-ion batteries" of Referat 6 and to the literature on industrial buildings and the fire protection infrastructure required for preventive fire protection - Referat 1 and Referat 14 or GdV - referred to here in the Instruction Sheet.

2. General information

The term "lithium battery" is used here as a collective term for the many different battery systems in which lithium is used in pure or bound form.

Like other batteries, lithium batteries can be divided into primary (non-rechargeable; e.g. in cameras) and secondary (rechargeable) batteries.

Compared to conventional batteries, they are characterised by high charge densities.

This Instruction Sheet focuses on lithium-ion batteries. These are also referred to as lithium-ion accumulators or secondary cells, but in the following the term "lithium battery" is used synonymously for the sake of understanding and for ease of use. Other types of lithium batteries are less common and have a different hazard potential with regard to fire. The principles of use that can be derived from the consideration of lithium-ion batteries can also be used for all other types.

Secondary lithium-ion cells and batteries are used in cylindrical, prismatic form and also in the form of soft packs of different sizes. The cells can also be used in large formats and in combination with other cells in modules, which then represent an increased risk compared to primary batteries at points of use.

The advantages of lithium batteries compared to conventional chemical energy storage devices (e.g. nickel-metal hydride batteries) result from the electrochemical performance parameters (see Table 1): high voltage, high energy density, low cell weight and wide temperature range. The hazards associated with this in use, depending on the energy density, i.e. the strength of the battery, are discussed here.

Table 1: Comparison of energy densities [Unit: Wh/kg]

	PB	NiCd	NiMH	Li-ion	Li-ion-polymer
Faktor	1 (Reference value)	2,5	4,3	5	3,9

The high performance parameters are achieved through a differentiated design compared to conventional batteries.

Chemical hazardous substances in the cathode and anode, in the electrolyte (solvent and conductive salt) and in the decomposition products are of particular importance for extinguishing/Chemical operations.

3. Structure and function of a Li-ion battery

A power storage module - known as a battery - consists of several cells. A common cell structure is shown in Figure 1 and described below:

Cathode:

This is an aluminium electrode coated with an active material (usually a lithium-metal mixed oxide, e.g. cobalt, nickel, manganese, iron). At elevated temperatures, these tend to self-decompose to varying degrees and release oxygen, which may have a fire-promoting effect. Therefore, suffocation or displacement of oxygen is not expected to have a lasting extinguishing effect.

Anode:

Usually, a copper foil coated with graphite. Positively charged lithium ions are embedded in the layered structure of the graphite.

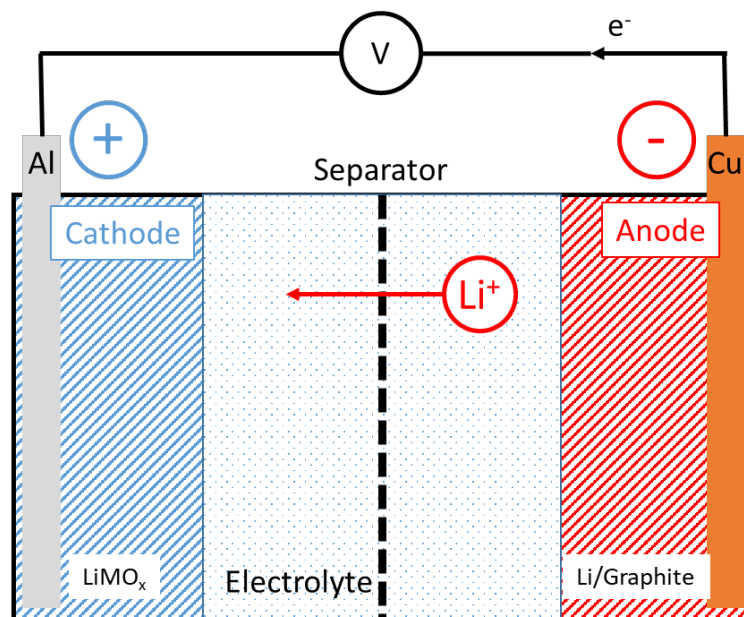


Figure 1: Schematic representation of the structure of a secondary lithium-ion battery during the discharging process [Source: vfdb Ref. 10]

The separator is both the most complex and most sensitive component of a secondary Li-ion battery. On the one hand, the separator's task is to separate the cathode and anode or to isolate the two half cells from each other. On the other hand, it must be permeable to lithium ions in order to enable ion exchange. The separator therefore consists of a semi-permeable membrane (plastic film). Poor quality, destruction due to mechanical impact or external heat exposure lead to failure of the separator and an internal short circuit.

The electrolyte is necessary for the mobility flow of the ions. It consists of an organic solvent (e.g. ethylene carbonate), a conducting salt dissolved in it and other additives. The organic solvents (i.e. hydrocarbons) are flammable. Lithium hexafluorophosphate (LiPF₆), which is very sensitive to moisture, is used almost exclusively as the conductive salt.

Lithium compound - Basics

Lithium hexafluorophosphate is a highly reactive compound. In addition, the other components of a lithium battery are highly flammable.

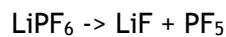
Equalising reactions during overcharging, for example through the decomposition of water as with other batteries, are not possible.

Internal protective circuits are designed to prevent deflagration by preventing overcharging or deep discharge, whereby triggering destroys the functionality of the battery.

Mechanical damage can lead to internal short circuits. The resulting high current can melt the housing and cause the components to ignite. The defect may not be immediately recognisable. The effect can also occur after a longer period of time, for example after 30 minutes. Further time sequences must be determined on site and depend on the individual case .

4. Properties and behaviour of the chemical hazardous substances in the components

As described above, lithium hexafluorophosphate can be used as the conductive salt in the batteries. This decomposes from approx. 150 °C, releasing gaseous phosphorus pentafluoride:



If water is present, this conducting salt reacts to release hydrogen fluoride according to the following reaction equation:



Humidity in the air or water produced during a fire (e.g. of the electrolyte or the plastic housing) may be sufficient for this purpose.

Notes:

Caution - Chemical hazardous substances in the event of damage

Lithium compounds decompose when exposed to heat

Explosion hazard due to outgassing electrolytes

Formation of hydrofluoric acid in a humid atmosphere

THEREFORE

Respiratory protection when working near a vehicle

Body protection form 1 as PPE is sufficient (e.g. car fire)



5. Special hazards during firefighting operations in the presence of lithium batteries

The following hazards must be observed at the site of operation:

- Spread
- Respiratory toxins
- Chemical hazardous substances
- Explosion
- Electricity

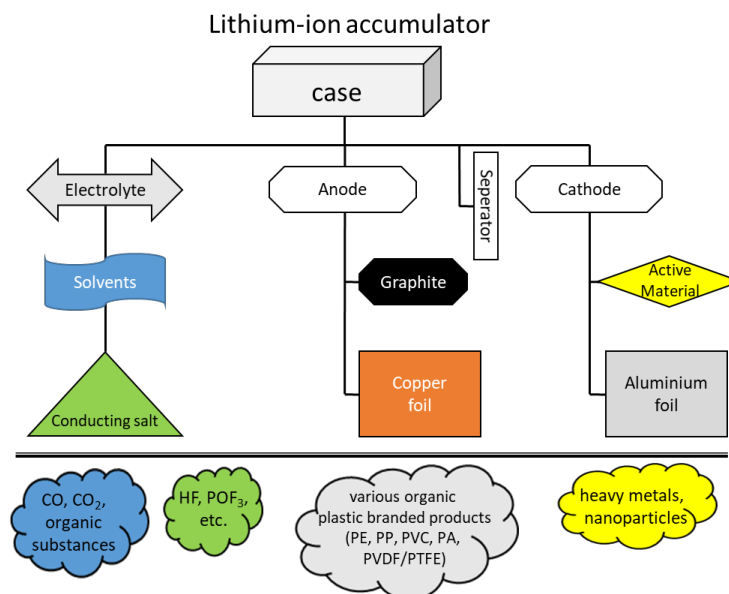


Figure 2: Composition and hazardous substances in lithium battery fires [Source: vfdb Ref. 10]

In addition to the hazards mentioned so far, heavy metals and nanoparticles can also be released when using Li batteries.

5.1. Danger from leaking chemical hazardous substances

Lithium cells are sealed gas-tight so that no substances can escape during normal operation. If the housing is mechanically damaged, the contents can escape in gaseous or liquid form.

- The electrolyte can escape in liquid form.
- The solvents are flammable and highly irritant. Depending on the mixture used, the flash point is over 100°C, but this can be lowered by fine dispersion (spray mist) or wicking.
- The conductive salt forms hydrofluoric acid or gaseous hydrogen fluoride when exposed to moisture and temperature. These compounds have a corrosive effect, are highly toxic (acutely toxic) and irritate the respiratory tract.
- In gaseous form, mainly vaporised electrolyte (explosion hazard) and decomposition products of the electrolyte are released, which can also be flammable and toxic. Some heavy metal particles with small diameters as well as various toxic and irritating fire gases are present.
- Contaminated extinguishing water (corrosive, partially contaminated with heavy metal salts) can enter the sewage system. Ensure that extinguishing water is retained!






Classification according to GHS: Lithium hexafluorophosphate [LiPF₆]	
	
	<p>H301: Toxic if swallowed. H314: Causes severe skin burns and eye damage. H372: Causes damage to organs (or state all organs affected, if known) through prolonged or repeated exposure Contact with water produces hydrogen fluoride.</p>
Classification according to GHS: Hydrogen fluoride [HF]	
	
	<p>H300: Fatal if swallowed. H310: Fatal in contact with skin. H330: Fatal if inhaled. H314: Causes severe skin burns and eye damage. EUH 071: Corrosive to the respiratory tract. AEGL-2 (4h): 12 ppm!</p>

Figure 3: Hazard due to conductive salt, labelling according to GHS [Source: vfdb ref. 10]

5.2. Danger due to fire and/or explosion

- Some of the materials used in lithium batteries are flammable and easily ignited.
- Some of the cathode materials used decompose spontaneously at high temperatures, releasing heat and oxygen.
- As this reaction is exothermic and also releases oxygen, this can lead to a very rapid thermal runaway of the cell.
- Thermal runaway is triggered by excessively high cell temperatures, which can be attributed to the following causes, among others:
 - Excessive external heating (fire, defective climate chamber)
 - External short circuit
 - Internal short circuit due to cell fault or mechanical damage
 - Overcharging of the cell
 - Overdischarge of the cell
- Storing a large number of lithium batteries in closed rooms can lead to explosive fires.

As soon as respiratory toxins are released during a mission involving lithium batteries due to damage and/or fire, it is strongly recommended that self-contained breathing apparatus be worn in accordance with the principles of use set out in FwDV 7. Special attention must be paid to the fire secondary products and C-hazardous substances described above.

5.3. Danger due to electricity

Depending on the type of vehicle (hybrid/sports electric car/truck/bus etc.), vehicle batteries today have nominal voltages ranging from around 100 V to 800 V. This means that system components can carry a current of several 100 A. Against this background, the principles of use must be observed in the event of an electrical hazard.

6. Recommendations for firefighting operations

Due to the involvement of chemical hazardous substances in fire brigade operations in the presence of lithium batteries, the principles of Fire Service Regulation 500 "Units in NBC Operations" (FwDV 500) must be observed.

General deployment principles according to FwDV 500:



- Observe wind direction (approach, course of operation)
- Keep your distance - hydrofluoric acid (hydrofluoric acid)
- Observe personal protection (respiratory poisons, explosion hazard, chemical hazards)
- Cordon off the danger zone immediately
- Self-contained breathing apparatus (SCBA), body protection form 1(SCBA)
- Avoid ignition sources
- It is essential to observe further spread

General tactical instructions for carrying out operations

- Position the vehicle outside the danger zone, note the change in wind direction.
- Rescue people and fight fires using respiratory protection and body protection form 1.
- Only deploy essential personnel in the danger zone, keep your distance if possible.
- Always use suitable self-contained breathing apparatus.
- Clear the immediate danger zone outdoors.
- If it is necessary to work on the battery itself or in the immediate vicinity, the personal protective equipment may need to be extended.
- If skin contact with hydrofluoric acid is suspected, consult a doctor.
- If possible, monitor the temperature using a thermal imaging camera; if a rapid rise in temperature is observed, a decomposition reaction is to be expected (above 100°C). A follow-up check using a thermal imaging camera is also recommended.
- The primary extinguishing agent is water, as this not only extinguishes the fire but also cools the battery to counteract further decomposition. Some of the decomposition products are also dissolved and diluted. It should be borne in mind that the structural arrangement of the Li batteries in modules means that extinguishing water often cannot penetrate them completely. This means that complete cooling cannot usually be achieved. The use of foam and extinguishing additives is generally possible.
- If necessary, bind pools with chemical binders

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