

# Types and Hazards of Electrical Energy Storage Systems

## Project:

**Sicherheit und Zuverlässigkeit von PV-Anlagen mit Speichersystemen unter besonderer Berücksichtigung von Brandrisiken und Löschrstrategien (SPEISI)**

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# 1 Introduction

In this report the types of electrical energy storage EES systems and their features are listed. A brief classification is followed by a short description of the various EES types with their advantages, disadvantages and hazardousness concerning fire caused internally by the EES or externally by the surrounding area. The description of the EES based on the IEC White Paper „Electrical Energy Storage“ with a major contribution from the Fraunhofer ISE. [IEC11]

A widely-used approach for classifying EES systems employs a structure according to the type of energy used (see figure 1).

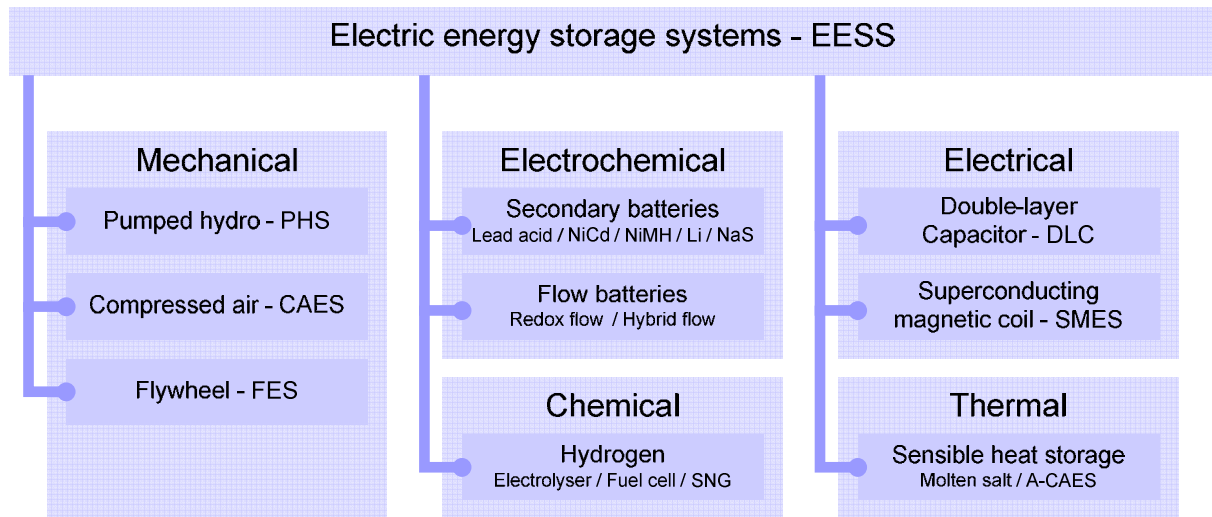


Figure 1: Classification of EES systems according to energy form

EES systems are classified into mechanical, electrochemical, chemical, electric and thermal energy storage systems:

- In **mechanical storage systems** the energy is stored with pumped hydro storage (PHS) systems in the difference in height of water masses, with compressed air energy storage (CAES) systems in compressed air and with flywheel energy storage (FES) systems in fast rotating masses. For energy transducers electromechanical engines and generators are used.
- In **electrochemical energy storage systems**, the electric power is converted by an electrochemical reaction in chemical energy and buffered. During discharging, the electric energy is delivered by reversing the electrochemical reaction again later. The energy conversion takes place by simultaneous partial reactions at the positive and negative electrodes, which are connected to one another via an electrolyte. If electrodes and electrolyte forming a strong bond in housing they are called secondary batteries. If the liquid electrolyte is pumped away after the reaction of the electrodes and stored separately they are called flow batteries.
- In **chemical energy storages systems** the energy in the form of hydrogen or synthetic methane is stored by the electrolysis of water and, for example reconverted via a fuel cell or a gas turbine back into electrical energy.
- In **electrical storage systems** the energy is stored with the double layer capacitor (DLC) in the electrical field and with the superconducting magnetic coil (SME) in the electrical field.
- In **thermal energy storage systems** in most cases electricity is not the direct input to such storage systems. But with the help of thermal energy storage the energy from renewable energy sources can be buffered and thus electricity can be produced on demand. Examples

are hot molten salts in concentrated solar power plants and the storage of heat in compressed air plants using an adiabatic process to gain efficiency.

The following comprehensive description of the various EES types with their advantages, disadvantages and hazards focuses on EES systems for residential houses. This means PHS, CAES, SMES, chemical and thermal storage systems are excluded because of their big size in power and energy and the high investment costs.

## 2 Description of the EES systems

### 2.1 Mechanical Storage

#### 2.1.1 Flywheel Energy Storage (FES)

In flywheel energy storage (FES) rotational energy is stored in an accelerated rotor, a massive rotating cylinder. The main components of a flywheel are the rotating body/cylinder (comprised of a rim attached to a shaft) in a compartment, the bearings and the transmission device (motor/generator mounted onto the stator). The energy is maintained in the flywheel by keeping the rotating body at a constant speed. An increase in the speed results in a higher amount of energy stored. To accelerate the flywheel electricity is supplied by a transmission device. If the flywheel's rotational speed is reduced electricity may be extracted from the system by the same transmission device. Flywheels of the first generation, which have been available since about 1970, use a large steel rotating body on mechanical bearings. Advanced FES systems have rotors made of high-strength carbon filaments, suspended by magnetic bearings, and spinning at speeds from 20,000 to over 50,000 rpm in a vacuum enclosure. The main features of flywheels are the excellent cycle stability and a long life, little maintenance, high power density and the use of environmentally inert material. However, flywheels have a high level of self-discharge due to air-resistance losses and bearings and suffer from low current efficiency.

Today flywheels are commercially deployed for power quality in industrial and UPS applications, mainly in a hybrid configuration. Efforts are being made to optimize flywheels for long-duration operation (up to several hours) as power storage devices for use in vehicles and power plants.

#### **Hazard potential:**

##### Electric:

In non-operation conditions there is no risk. Under operation conditions the electric hazard potential is similar to conventional electrical equipment with generator and motor function.

### Mechanical:

The energy is stored as kinetic energy of a rotating mass. In case of breaking parts or crash flung parts cause a risk. Friction in the system might cause heating and/or overheating. If the fly wheels are used in mobile systems, the gyrostatic effect has to be taken in consideration.

### Emissions:

The system is free of emissions. Emissions might be generated in case of overheating or fire by degrading or decomposing plastic material or isolation.

### Risk of fire/explosion:

The system is constructed mainly using non-flammable material. Risk of fire is similar to conventional electric installations with the special effect of heat generation by friction in the rotating parts.

## **2.2 Electrochemical Storage Systems**

In this part various types of batteries are described. Most of them are technologically mature for practical use. First, six secondary battery types are listed: lead acid, NiCd/NiMH, Li-ion, Na-ion, metal air, sodium sulphur and sodium nickel chloride; then follow two sorts of flow battery.

### **2.2.1 Secondary Batteries**

#### **2.2.1.1 Lead Acid Batteries (LAB)**

Lead acid batteries are the world's most widely used battery type and have been commercially deployed since about 1890. Lead acid battery systems are used in both mobile and stationary applications. Their typical applications are emergency power supply systems, stand-alone systems with PV, battery systems for mitigation of output fluctuations from wind power and as starter batteries in vehicles. In the past, early in the "electrification age" (1910 to 1945), many lead acid batteries were used for storage in grids. Stationary lead acid batteries have to meet far higher product quality standards compared to starter batteries. Typical service life is 6 to 15 years with a cycle life of 1,500 cycles at 80 % depth of discharge, and they achieve cycle efficiency levels of around 80 % to 90 %. Lead acid batteries offer a mature and well-researched technology at low cost. There are many types of lead acid batteries available, e. g. vented and sealed housing versions (called valve-regulated lead acid batteries, VRLA). Costs for stationary batteries are currently far higher than for starter batteries. Mass production of lead acid batteries for stationary systems may lead to a price reduction.

One disadvantage of lead acid batteries is usable capacity decrease when high power is discharged. For example, if a battery is discharged in one hour, only about 50 % to 70 % of the rated capacity is available. Other drawbacks are lower energy density and use of lead, a hazardous material prohibited or restricted in various jurisdictions. Advantages are a favorable cost/performance ratio, easy recyclability and a simple charging technology. Current R&D on lead acid batteries tries to improve their behavior for micro/hybrid electric vehicles [etg08], [lai03].

## **Hazard potential:**

### Electric:

The series connection of single cells will lead to high voltages which requires the corresponding protection against high voltages and touching if the voltage is  $> 50$  V.

Battery cells are usually not protected against high currents, e.g. short circuit might cause extremely high currents. Usually only the complete battery installation is protected by fuses, there is no protection of intersections (risk during installation and maintenance).

Overload by high currents will lead to battery heating and installation parts (e. g. cell connectors with insufficiently tightened bolts) and might cause fire in the cables in case of short circuit.

Deep discharge/reverse polarization: Deep discharge results in a damage of the battery and a fast ageing. In case of reverse polarization gas formation and emission ( $H_2$ ,  $O_2$ ) will occur.

Overcharge: During overcharge an enhanced heating of the battery will be observed and gases ( $H_2$ ,  $O_2$ ) are produced and emitted. In case of heavy overcharge the emission of acid aerosols can take place. The limited gas generation is a permitted side reaction in lead acid batteries and leads to an internal mixing of the acid avoiding acid stratification. At the other hand excessive gassing leads to a damage of the battery by water loss, elevated temperatures, enhanced corrosion and shedding of active mass.

If VRLA batteries are used a thermal runaway of individual cells can be caused by insufficient cooling caused by strong packaging of the individual cells and/or insufficient ventilation at high charging rates (higher 5 hours current rate).

### Mechanical:

The large weight of the lead acid batteries causes a certain risk during transport. For the installation the allowed floor loading or the allowed max load of racks has to be taken into consideration. It has to be ensured that tilting or movement of the battery is excluded.

Mechanical damages of the battery cases might cause leakage of electrolyte (sulfuric acid). Sulfuric acid is strong caustic and corrosive. Contact with skin and incorporation has to be avoided. By acid leakage the isolation resistance of the battery installation might be impacted and no longer meet the required minimum value. The corrosive attack of the acid to metallic construction parts has to be taken into consideration as well as the damage of mineral construction materials (e.g. concrete).

### Emissions:

During charge and in particular during overcharge the development and emission of gases ( $H_2$ ,  $O_2$ ) is observed. If the overcharge current is too large, acidic aerosols can be emitted. For valve regulated lead acid batteries (VRLA) the emissions are significantly reduced but not completely suppressed.

The gas mixture ( $H_2$ ,  $O_2$ ) is highly explosive if the content of hydrogen in air exceeds 4 % and can be ignited inside the battery and in the near environment. To avoid this a minimum ventilation of the battery room or housing by aperture or a ventilation system is necessary. The requirements concerning the battery room, housing, aperture, ventilation system and electric safety are regulated by the DIN EN 50272-2:2001 = VDE 0510-2:2001 = IEC 62485-2:2010 "Safety requirements for secondary batteries and battery installations - Part 2: Stationary batteries".

The contact with acid aerosols (eyes, inhalation) has to be avoided ( by wearing personal protection equipment e.g. during refilling of water).

### Risk of fire/explosion:

For lead acid batteries the risk for fire and explosion is caused by the emission of H<sub>2</sub> und O<sub>2</sub>.

Furthermore parts of battery case and isolation are flammable. Sometimes cases are manufactured from self-extinguishing plastic materials. Beside the fire the burning plastic materials lead to a strong smoke generation and poised gases might be generated.

#### **2.2.1.2 Nickel Cadmium and Nickel Metal Hydride Batteries (NiCd, NiMH)**

Before the commercial introduction of nickel-metal hydride (NiMH) batteries about 1995, nickel cadmium (NiCd) batteries had been in commercial use since about 1915. Compared to lead acid batteries, nickel-based batteries have a higher power density, a slightly greater energy density and the number of cycles is higher; many sealed construction types are available.

From a technical point of view, NiCd batteries are a very successful battery product; in particular, these are the only batteries capable of performing well even at low temperatures in the range from -20°C to -40°C. Large battery systems using vented NiCd batteries operate on a scale similar to lead acid batteries. However, because of the toxicity of cadmium, these batteries are presently used only for stationary applications in Europe. Since 2006 they have been prohibited for consumer use.

NiMH batteries were developed initially to replace NiCd. Indeed, NiMH batteries have all the positive properties of NiCd batteries, with the exception of the maximal nominal capacity which is still ten times less when compared to NiCd and lead acid. Furthermore, NiMH batteries have 3 -5 times higher energy densities (energy per volume and weight). In portable and mobile applications sealed NiMH batteries have been extensively replaced by lithium ion batteries. On the other hand, hybrid vehicles available from Japan operate in many cases with sealed NiMH batteries, as these are robust and far safer than lithium ion batteries. NiMH batteries currently cost about the same as lithium ion batteries [etg08], [smo09], [dah03].

Concerning potential of hazards, NiCd and NiMH have the same features like lead acid.

### **Hazard potential:**

#### Electric:

See chapter on lead acid batteries.

Deep discharge/reverse polarization: NiCd und NiMH are relatively robust against deep discharge. Frequent deep discharge of NiCd batteries leads to the formation of dendrites causing internal short circuits and leave the battery unusable.

Overcharge: During overcharge an enhanced heating of the battery will be observed and gases (H<sub>2</sub>, O<sub>2</sub>) are evolved and emitted. In case of heavy overcharge the emission of alkaline aerosols can take place. The limited gas generation is a permitted side reaction in NiCd und NiMH batteries. For not valve regulated NiCd batteries the gassing leads to water loss, elevated temperatures and enhanced corrosion.

In valve regulated or closed NiCd or NiMH batteries the overcharge current can be carried permanently up to a certain value. In case of too large overcharge currents the battery can be damaged (thermal runaway), fire and explosion can occur.

Overdischarge/reverse polarization: Reverse polarization in NiMH batteries leads to an oxidation of the hydride alloy and damages the alloy to become unusable for the storage of hydrogen (capacity loss, battery damaged).



### Mechanical:

See chapter lead acid batteries.

Damage of the battery case might lead to a leakage of the alkaline electrolyte (caustic and corrosive). The contact with the skin and the incorporation has to be avoided. By the leakage of electrolyte the isolation resistance of the battery installation might be lost and does not meet anymore the required standards. The reaction of the alkaline electrolyte with the CO<sub>2</sub> in the air will form carbonates (white crusts)

In case of NiMH batteries, the damage of the battery case will lead to an emission of hydrogen.

### Emissions:

During charging and in particular during overcharging the development and emission of gases (H<sub>2</sub>, O<sub>2</sub>) is observed. If the overcharge current is too large, alkaline aerosols can be emitted. For valve regulated NiCd batteries the emissions are significant reduced. NiMH batteries are generally closed batteries without emissions in regular operation mode. In case of overheating of NiMH batteries a high internal pressure can be caused, leading to a damage of the battery case and the emission of hydrogen.

The gas mixture (H<sub>2</sub>, O<sub>2</sub>) is highly explosive if the content of hydrogen in air exceeds 4 % and can be ignited inside the battery and in the near environment. To avoid this a minimum ventilation of the battery room or housing by aperture or a ventilation system is necessary. The requirements concerning the battery room, housing, aperture, ventilation system and electric safety are regulated by the DIN EN 50272-2:2001 = VDE 0510-2:2001 = IEC 62485-2:2010 Safety requirements for secondary batteries and battery installations - Part 2: Stationary batteries.

The contact with alkaline aerosols (eyes, inhalation) has to be avoided (by wearing personal protection e.g. during refilling water).

### Risk of fire/explosion:

See chapter lead acid batteries.

## **2.2.1.3 Lithium Ion Batteries (Li-Ion)**

Lithium ion batteries have become the most important storage technology in the areas of portable and mobile applications (e.g. laptop, cell phone, electric bicycle, electric car) since around year 2000. High cell voltage levels of up to 3.7 Volt mean that the number of cells in series with the associated connections and electronics can be reduced to obtain the target voltage. For example, one lithium ion cell can replace three NiCd or NiMH cells which have a cell voltage of only 1.2 Volt. Another advantage of Li-Ion batteries is their high gravimetric energy density, and the prospect of large cost reductions through mass production. Although Li-Ion batteries have a share of over 50 % in the small portable devices market, there are still some challenges for developing larger-scale Li-ion batteries. The main obstacle is the high cost of more than 600 USD/kWh due to special packaging and internal overcharge protection circuits.

Lithium ion batteries generally have a very high Ah efficiency, typically in the range of 95 % - 98 %. Nearly any discharge time from seconds to weeks can be realized, which makes them a very flexible and universal storage technology. Standard cells with 5,000 full cycles can be obtained on the market at short notice, but even higher cycle rates are possible after further development, mainly depending on the materials used for the electrodes. The main features of cells with different electrodes are summarized in table 1 [jos06], [wey14], [dah11].

**Table 1: Main features of cells with different electrodes**

Short name	LCO	LNO	LMO	NMC	NCA	LFP	LTO
Positive electrode	LiCoO <sub>2</sub>	LiNiO <sub>2</sub>	LiMn <sub>2</sub> O <sub>4</sub>	LiCo <sub>1/3</sub> Ni <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>	LiCo <sub>x</sub> Ni <sub>y</sub> Al <sub>z</sub> O <sub>4</sub>	LiFePO <sub>4</sub>	LFP / LCO, NMC, LMO
Negative electrode	Graphite						Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>
Energy density [Wh/kg]	110-190	~ 170	110-120	150-220	130-260	80-140	60-70
Nominal cell voltage	3.6 V	3.6 V	3.7 V	3.7 V	3.7 V	3.2 – 3.3 V	1.8 / 2.2-2.3 V
Cycle lifetime	500-1000	500-1000	500-1000	500-8000	300-2000	1000-6000	3000-15000
Characteristics	Energy	Power	Power	Power	Energy	Power	(Power), chargeable at low temperatures -20°C

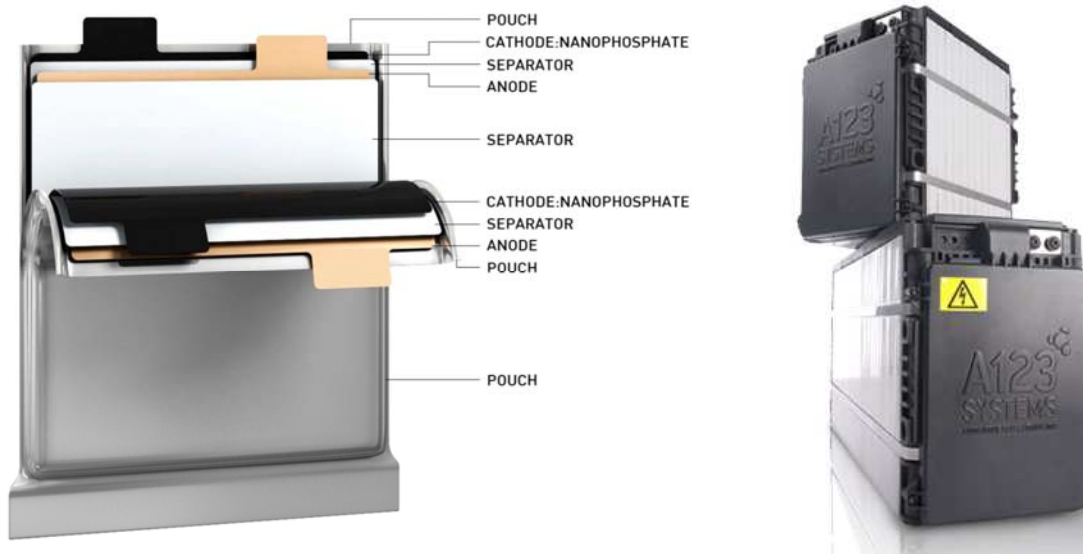
Since currently lithium ion batteries are still expensive, they can compete with lead acid and NiCd batteries in those applications which require short discharge times (e.g. as primary control backup), light weight (e.g. for transportable devices), high energy density (e. g. for electric vehicles).

Because of increasing mass production for electric vehicles and further technology improvement the specific price (€ / kWh) is decreasing continuously.

Lithium Ion battery technology is still developing, and there is considerable potential for further progress. Research is focused on the development of cathode materials.

Three typical cell constructions are known.

- Pouch or Coffee-bag (stacked, zig-zag folded, flat pack winding),  
*(sometimes these cells are called prismatic cells as well)*
- cylindrical cells (spiraled wound electrodes in metal cylinder)
- Prismatic, hard case (prismatic case made from Al, stainless steel or plastic, stacked electrodes, flat wided jelly, sometimes more than one jelly role in one case)



**Figure 2: Li-Ion pouch (prismatic) cell design and battery module (A123)**



**Figure 3: Li-Ion type 26650 cylindrically wound cell design (SONY)**



**Figure 4: Li-Ion prismatic hard case cell design (ZSW-manufacturing, 2015)**

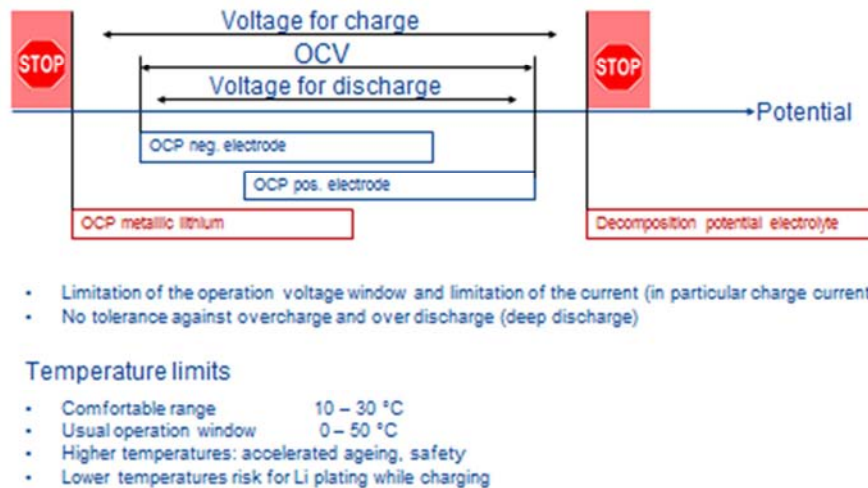
**Hazard potential:**

General:

Li-Ion batteries do not have allowed side reactions such as water electrolysis in classical water based batteries. Therefore Li batteries have a strongly limited voltage operation window (see the following figure). Operating the battery outside this window leads to a damage of the battery in worst case with a catastrophic event like fire or explosion. Some materials used for the

positive electrode show an exothermic reaction if the temperature exceeds a critical value. The critical temperature can be caused by overcharging, internal or external short circuits or external heating.

### Operation limits for Li-Ion- batteries



**Figure 5: Operation limits for Li-ion batteries [dan15]**

#### Electric:

High voltages: see chapter lead acid batteries

Because of the high potential risk almost all Li-battery applications (even small ones) use without exception a fuse in the cell string for protection against short circuit.

Furthermore, there are several cell designs using an internal protection mechanism against high currents. As there are usually no detailed information on this given in the data sheet, in every case it has to be considered that related to the low internal resistance of Li cells a short circuit might cause extremely high currents. Correlating to the low heat capacity of Li cells, the temperature rises strongly and ignition of the cells might be caused.

Deep discharge/reverse polarization: During deep discharge/reverse polarization the negative electrode reaches potentials where the current collector of the negative electrode made from Cu starts to corrode. This Cu might be deposited at the cathode during the continuous over discharge or will be deposited at the negative electrode during the following charge. The deposited Cu might cause an internal short circuit of the cell and might result in a catastrophic event. Therefore, deep discharge/reverse polarization has to be avoided for Li cells in every case and once a cell has suffered from deep discharge the cell has to be taken out of operation and must not be recharged.

Overcharge: During overcharge decomposition reactions take place at the electrodes. These decomposition reactions frequently lead to a catastrophic event. Therefore, some cell designs have a protection mechanism against overcharge. Usually a Li battery has to be protected against overcharge by different independent mechanisms including BMS control.

Because of the importance to keep within the voltage operation window usually every single cell voltage is monitored and a balancing system will keep the individual cell voltages close together in a small voltage band.

### Mechanical:

Even if the Li batteries are more lightweight compared to LAB, they have still a potential risk during transport. In every case, Li batteries are dangerous goods for transport.

Mechanical damages at the battery case must be avoided, as these damages might lead to catastrophic events by internal short circuits, emission of evaporated electrolyte and in worst case to fire.

### Emissions:

Li-batteries do not have any emissions during regular operation; therefore no requirements related to ventilation are given.

Emissions for Li-batteries are caused in case of damages. In a simple event the overpressure vent might get opened, which allows the evaporation of the electrolyte in the environment. In this case the rooms have to be ventilated and the opened cell has to be removed (no further use possible) and transferred to the final disposal. The direct contact with spilled electrolyte has to be avoided as well as the inhalation of the fume. Spilled electrolyte has to be collected by suitable absorber material.

Emissions in result of severe events (e.g. crash, short circuit, overcharge, fire or for similar reasons) are poisonous and they might form explosive mixtures with air. The emissions are usually a mixture of evaporated electrolyte, degradation products of the electrolyte (CO, CO<sub>2</sub>, H<sub>2</sub>, aldehydes, etc.) and conductive salt. The emissions might contain HF and carrier parts of the active mass (e.g. metal oxides). The locations of such an event may only be entered by trained personal with breathing protection and protection clothes.

### Risk of fire/explosion:

Li-batteries have to be protected against high temperatures. At elevated temperatures the ageing effects are accelerated. At temperatures at around 80°C first reactions can be activated resulting in a self-heating. At around 90°C the internal vapor pressure of the electrolyte might exceed the value of the opening pressure of the safety vent and evaporated electrolyte will be emitted. Emitted electrolyte, vapor of electrolyte and there degradation products are flammable and in certain concentration levels with air explosive.

Above 130°C the separator could melt and might cause a serious internal short circuit accompanied with the emission of gaseous flammable electrolyte and decomposition products. Furthermore solid parts of the cell can be emitted which have high temperatures (glowing) and might act as source of ignition for the emitted gases.

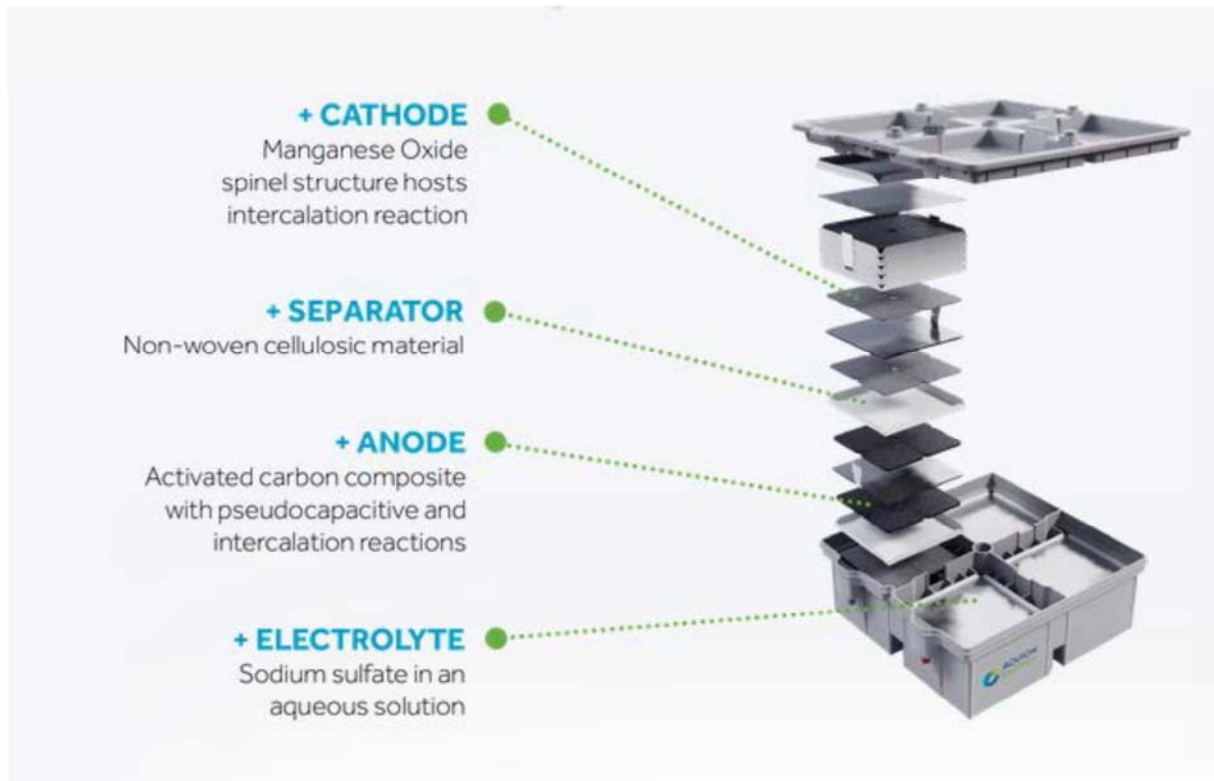
At very high temperatures a decomposition of metal oxides with formation of oxygen takes place. Therefore, the fire of a burning battery might not be stopped or extinguished just by excluding the oxygen of the air. The internally formed oxygen will promote the fire.

If a cell in a battery catches fire or is encountering a thermal runaway, the probability is high that the fire/thermal runaway propagates through the complete battery by heat transfer. To reduce this risk the cell/battery can be cooled down by water.

In case of fire construction parts made of plastic and isolation material might generate a lot of soot and might form poisonous gases as well.

#### 2.2.1.4 Sodium Ion Batteries (Na-Ion)

The sodium-ion battery is a relatively new technology, It is since 2014 available from the company Aquion in the US. The development has been done in recent years, driven mainly in the US by the Carnegie Mellon University in Pittsburgh and the company Aquion Energy [whi12].



**Figure 3: Typical Na-ion stacked cell and battery module (Aquion Energy)**

The sodium-ion battery is made of relatively inexpensive materials such as manganese oxide in a spinel structure (cathode) which host the intercalation reaction of sodium, activated carbon (anode) and an electrolyte consisting of sodium sulfate (Glauber's salt) dissolved in water. The electrodes are, as in lead acid batteries 3-6 mm thick and can be stacked relatively easily or installed vertically in a housing. Further advantages result from the lack of toxicity and the fact that the electrolyte is non-flammable. In addition it has according to manufacturer a very high cycle resistance > 3000 and requires no active battery management.

A disadvantage of the system is the relatively low energy density of 20 -30 Wh / kg comparable with lead batteries, therefore it is particularly suitable for stationary use. Furthermore, the energy efficiency is lower as of lithium-ion batteries, it is in the range of about 90 % at a discharge duration of 10-20 hours. This is comparable with the value of lead-acid batteries.

#### **Hazard potential:**

In general the hazard potential of the aqueous Na-ion battery is comparable to lead acid batteries, with the general difference that materials are used, which are known as not sensitive.

Active material as manganese oxide and activated carbon are no critical materials. Under dry conditions carbon material is flammable and manganese oxide promote fire by the release of oxygen during thermal decomposition. However, as these materials are under flooded condition in aqueous electrolyte there is almost no risk.

The electrolyte is sodium sulfate dissolved in water. This salt solution is not poisonous and not caustic. Contact with skin is no problem. In medicine low concentration in water are used as aperient.

Because of the lower voltage of the system water electrolysis takes place to a very limited extent in within the allowed voltage operation band, the reason for a very high coulomb efficiency (almost 1). However, under strong overcharge condition, formation and emission of hydrogen and oxygen takes place and requires a ventilation if the overcharge cannot be avoided.

### **2.2.1.5 Metal Air Batteries (Me-Air)**

A metal air electrochemical cell consists of the anode made from pure metal and the cathode connected to an inexhaustible supply of air. For the electrochemical reaction only the oxygen in the air is used. Among the various metal air battery chemical couples, the lithium air battery is most attractive since its theoretical specific energy excluding oxygen (oxygen is not stored in the battery) is 11.14 kWh/kg, corresponding to about 100 times more than other battery types and even greater than petrol (10.15 kWh/kg). However, the high reactivity of lithium with air and humidity can cause fire, which is a high safety risk.

Currently only a zinc air battery with a theoretical specific energy excluding oxygen of 1.35 kWh/kg is technically feasible. Zinc air batteries have some properties of fuel cells and conventional batteries: the zinc is the fuel, the reaction rate can be controlled by varying air flow, and oxidized zinc/electrolyte paste can be replaced with fresh paste. In the 1970s, the development of thin electrodes based on fuel-cell research made small button prismatic primary cells possible for hearing aids, pagers and medical devices, especially cardiac telemetry. Rechargeable zinc air cells have a difficulty in design since zinc precipitation from the water-based electrolyte must be closely controlled. A satisfactory, electrically rechargeable metal air system potentially offers low materials cost and high specific energy, but none has reached marketability yet [wor02][atw11].

#### **Hazard potential:**

Metal air batteries might have a risk concerning the high reactivity of metals like Li.

Other materials like Zn, Al, and Mg are almost stable because of their primary oxide layer at the surface. Powders of these materials are risky, because of the large surface area and the reactivity with oxygen.

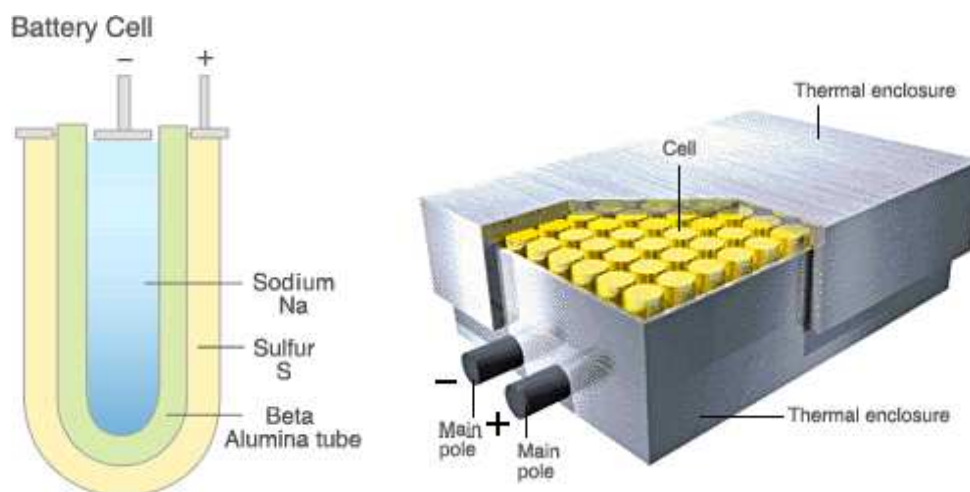
For rechargeable Zn batteries it has to be taken into consideration that during charge at the zinc electrode hydrogen can be generated usually suppressed by inhibitors and additives. At the other hand there is an oxygen releasing electrode during charge. The formed oxygen will promote fire reactions when the oxygen concentration is increased.

Usually Zn-air systems are working with alkaline electrolyte, therefore the comments given for risks with alkaline electrolytes in the chapter NiCd and NiMH has to be considered.

### **2.2.1.6 Sodium Sulphur Batteries (NaS)**

Sodium sulphur (NaS) batteries consist of liquid (molten) sulphur at the positive electrode and liquid (molten) sodium at the negative electrode; the active materials are separated by a solid beta alumina ceramic electrolyte. The battery temperature is kept between 300 °C and 350 °C to keep the electrodes molten. NaS batteries reach typical life cycles of around 4,500 cycles and have a discharge time of 6.0 to 7.2 hours. They are efficient (DC based energy round trip efficiency is 70 85 %) and have fast response.

These attributes enable NaS batteries to be economically used in combined power quality and time shift applications with high energy density. The NaS battery technology has been demonstrated at around 200 sites in Japan, mainly for peak shaving, and Germany, France, USA and UAE also have NaS batteries in operation. The main drawback is that to maintain operating temperatures a heat source is required, which uses the battery's own stored energy, partially reducing the battery performance. In daily use the temperature of the battery can almost be maintained by just its own reaction heat, with appropriately dimensioned insulation. Initial capital costs are approximately 2,000 USD/kW and 350 USD/kWh. Since around 1990 NaS batteries have been manufactured by one company in Japan, with a minimum module size of 50 kW and with typically 300 kWh to 360 kWh. It is not practical for the present to use only one isolated module. Because 20 modules are combined into one battery the minimal commercial power and energy range is on the order of 1 MW, and 6.0 MWh to 7.2 MWh. These batteries are suitable for applications with daily cycling. As the response time is in the range of milliseconds and NaS batteries meet the requirements for grid stabilization, this technology could be very interesting for utilities and large consumers [esp11], [kaw11].



**Figure 4: NaS Battery: Cell design and 50 kW module (NGK)**

### 2.2.1.7 Sodium Nickel Chloride Batteries (NaNiCl)

The sodium nickel chloride (NaNiCl) battery, better known as the ZEBRA (Zero Emission Battery Research) battery, is also a high temperature (HT) battery as NaS battery and has been commercially available since about 1995. It is also a high-temperature (around 270 °C) system that uses nickel chloride instead of sulphur for the positive electrode. NaNiCl batteries can withstand limited overcharge and discharge and have potentially better safety characteristics and a higher cell voltage. They tend to develop low resistance when faults occur and this is why cell faults in serial connections only result in the loss of the voltage from one cell, instead of premature failure of the complete system. These batteries have been successfully implemented in several electric vehicle designs (Think City, Smart EV) and are an interesting opportunity for fleet applications. The present science is developing advanced versions of the ZEBRA battery with higher power densities for hybrid electric vehicles, and also high-energy versions for storing renewable energy for load-leveiling and industrial applications [esp11].



## **Hazard potential of high temperature batteries: (NaNiCl<sub>2</sub> and NaS)**

### Electric:

As the battery is encapsulated in a thermal isolation battery case, it is almost impossible to get in contact with free battery parts. Only the external terminals can be contacted and these contacts are only under voltage after the BMS closed the internal switches.

### Overcharge:

Na-NiCl<sub>2</sub> batteries have some excess of Na for overcharge, reacting with the liquid electrolyte NaAlCl<sub>4</sub>. This allows the continuation of the current flow without raising the voltage.

Tests for NaS batteries have shown, that during overcharge the temperature did not increase above 400°C and all components were kept inside the battery, no emissions.

Internal short circuit by cracks in the solid electrolyte: In this case the molten salt electrolyte (NaAlCl<sub>4</sub>) reacts with the sodium and forms NaCl and Al. The cells fail and form a passive resistor in a similar range as a good cell.

### Mechanical:

In case of a mechanical crash the solid electrolyte might be heavily damaged and the sodium and the NiCl<sub>2</sub> will be mixed. In this case the system releases exothermic energy by the direct reaction of the energy storing components. However, the energy release is rather limited and is just 82 % of the stored electric energy. By this fast internal reaction the direct reaction of sodium with oxygen of the environment is avoided, a reaction which would release much more energy.

In NaS batteries an internal safety tube ensures, that the available amount of Na faced to the solid electrolyte is limited, so even if the solid electrolyte breaks, the amount of reacting Na is small enough to prevent a catastrophic event.

### Emissions:

The Zebra Battery as well as the NaS battery is a closed system and do not have any emissions.

### Risk of fire/explosion:

By the robust thermal isolation, the battery is not only protected against heat loss from inside the battery, it is protected as well from any fire attack from outside.

Cell and battery design including the thermal isolation cover for the battery and the robust construction guarantee a high safety level of the ZEBRA battery as well as for the NaS battery.

## **2.2.2 Flow Batteries**

In conventional secondary batteries, the energy is charged and discharged in active masses of the electrodes. A flow battery is as well a rechargeable battery but the energy is stored in one or more electroactive species which are dissolved in liquid electrolytes. The electrolytes are stored externally in tanks and pumped through the electrochemical cell(s) that converts chemical energy directly to electricity and vice versa. The power is defined by the size and design of the electrochemical cell whereas the energy is given by the size of the tanks. With this characteristic flow batteries can be fit to a wide range of stationary applications. Originally developed by NASA in the early 70's as EES for long term space flights, now flow batteries are in the focus to store energy for durations of hours or days with up to several MW power. Flow batteries are classified in redox flow batteries and hybrid flow batteries as described in the following.

### 2.2.2.1 Redox Flow Batteries (RFB)

In redox flow batteries (RFB) two liquid electrolyte dissolutions containing dissolved metal ions as active masses are pumped to the opposite sides of the electrochemical cell. The electrolyte at the negative and positive electrode is called anolyte and catholyte, respectively. During charging and discharging the metal ions stay dissolved in the fluid electrolyte as liquid; no phase change of these active masses takes place. Anolyte and catholyte flow through porous electrodes, separated by a membrane which allows protons to pass through it for the electron transfer process. During the exchange of charge a current flows over the electrodes, which can be used by a battery-powered device. During discharge the electrodes are continually supplied with the dissolved active masses from the tanks; once they are converted the resulting product is removed to the tank.

Theoretically a RFB can be “recharged” within a few minutes by pumping out the discharged electrolyte and replacing it with recharged electrolyte. That’s why redox flow batteries are under discussion for mobile applications. However, up to now the energy density of the electrolytes is too low for electric vehicles (EV).

Today various redox couples have been investigated and tested in RFB. For example, the Fe-Ti system, the Fe-Cr system and the polyS-Br system (Regenesys installation in UK with 15 MW and 120 MWh, but never commissioned) [jos09]. The vanadium redox flow battery (VRFB) has been developed the furthest; it has been piloted since around 2000 by companies such as Prudent Energy (CN) and Cellstrom (AU). The VRFB uses a  $V^{2+}/V^{3+}$  redox couple as negative electrode agent and a  $V^{4+}/V^{5+}$  redox couple in mild sulphuric acid solution as positive electrode agent. The main advantage of this battery is the use of ions of the same metal on both sides. Although crossing of metal ions over the membrane cannot be prevented completely (as is the case for every redox flow battery), in VRFBs the only result is a loss in energy. In other RFBs, which use ions of different metals, the crossover causes an irreversible degradation of the electrolytes and a loss in capacity. The VRFB was pioneered at the University of New South Wales (UNSW), Australia, in the early 1980s. A VRFB storage system up to 500 kW and 10 hours has been installed in Japan by SEI. SEI has also used a VRFB in power quality applications (e.g. 3 MW, 1.5 sec.). In Europe VRFB storage systems are for example manufactured by Schmid (kilowatt class) for residential application and by Gildemeister (10 kilo- and several 100 kilowatt class).

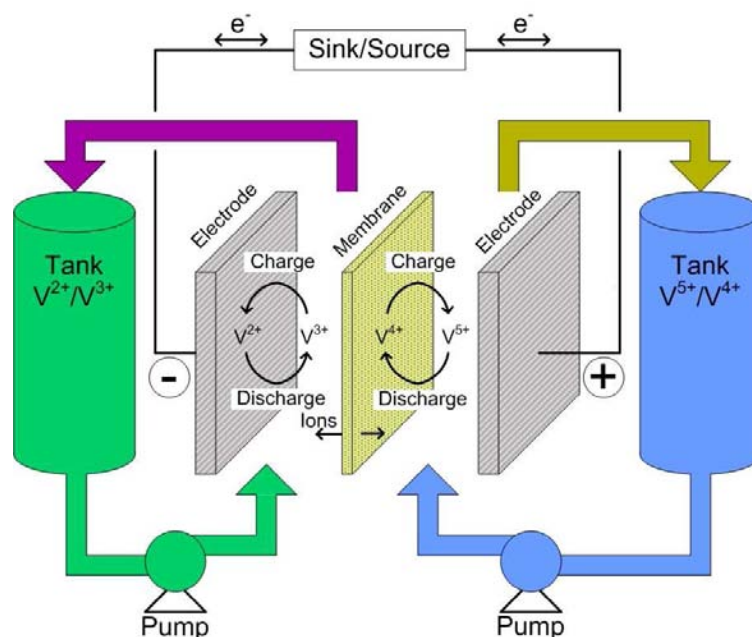


Figure 5: Schematic of a Vanadium Redox Flow Battery (Fraunhofer ISE)

## **Hazard potential:**

### Electric:

See chapter lead acid batteries.

Overdischarge/reverse polarization: Is usually not critical in Vanadium redox flow batteries. In this case, positive and negative electrodes are just changing. As long as the electrodes do not include very special catalyzer the electrodes are not damaged.

Overcharge: During overcharge all species are in the highest oxidized status at the positive side and the lowest reduced status at the negative side. Therefore the current flows into the alternative water electrolysis reaction and forms the gases  $H_2$  and  $O_2$ . As  $H_2$  is formed during charge and would be captured in the tank of the negative electrode, the tank is usually purged by  $N_2$  which at the other side prevents the oxidation of  $V^{2+}$  by the oxygen in air.

### Mechanical:

For the storage of the energy a large volume of liquid is required. Tanks have to be constructed in that way to withstand the hydrostatic pressure and to be robust enough to prevent easy damage of the tank by mechanical attack. Furthermore, the electrolyte is pumped through tubes and finally through manifolds, leading to an enhanced risk for leakage or spillage of electrolyte.

The electrolyte is vanadium salt solution in sulphuric acid. Skin- and eye contact has to be avoided. Safety barriers are necessary as the electrolyte is hazardous to water.

### Emissions:

During charge and in particular during overcharge the development and emission of gases ( $H_2$ ,  $O_2$ ) is observed.

In case of leakage the emission of electrolyte might occur. If there are small leaks the electrolyte might get sprayed out when the electrolyte is pumped through the tubes.

### Risk of fire/explosion:

Risk for explosion is existing, if the hydrogen is not removed permanently from the system. Tubes and tanks are usually made from plastics, which might get inflamed in particular if they are empty.

## **2.2.2.2 Hybrid Flow Batteries (HFB)**

In a hybrid flow battery (HFB) one of the active masses is internally stored within the electrochemical cell, whereas the other remains in the liquid electrolyte and is stored externally in a tank. Therefore hybrid flow cells combine features of conventional secondary batteries and redox flow batteries: the capacity of the battery depends on the size of the electrochemical cell. Typical examples of a HFB are the Zn-Ce and the Zn-Br systems. In both cases the anolyte consists of an acid solution of  $Zn^{2+}$  ions. During charging Zn is deposited at the electrode and at discharging  $Zn^{2+}$  goes back into solution. As membrane a microporous polyolefin material is used; most of the electrodes are carbon-plastic composites. Various companies are working on the commercialization of the Zn-Br hybrid flow battery, which was developed by Exxon in the early 1970s. In the United States, ZBB Energy (US) and Premium Power (US) sell trailer-transportable Zn-Br systems with unit capacities of up to 1 MW / 3 MWh for utility-scale

applications [jee10]. 5 kW / 20 kWh systems for community energy storage are in development as well.

### **Hazard potential:**

The risk potential is similar to the conventional redox flow system. Hydrogen might be formed during charging.

However, for  $\text{ZnBr}_2$  or  $\text{ZnCl}_2$  batteries the emission of  $\text{Cl}_2$  or  $\text{Br}_2$  is an additional risk. The elements are usually fixed in a chemical complex reducing the vapor pressure significantly. In case of high temperature exposition the stability of the complex is limited and the elements might be emitted to a certain extent. The halogen gases are caustic and corrosive. Even under normal temperature conditions over a long time the marks of corrosion will be visible in particular at metal surfaces in the close environment of the battery.

## **2.3 Electrical Storage Systems**

### **2.3.1 Double-Layer Capacitors (DLC)**

Electrochemical double-layer capacitors (DLC), also known as supercapacitors, are a technology which has been known for 60 years. They fill the gap between classical capacitors used in electronics and general batteries, because of their nearly unlimited cycle stability as well as extremely high power capability and their many orders of magnitude higher energy storage capability when compared to traditional capacitors. This technology still exhibits a large development potential that could lead to much greater capacitance and energy density than conventional capacitors, thus enabling compact designs.

The two main features are the extremely high capacitance values, of the order of many thousand farads, and the possibility of very fast charges and discharges due to extraordinarily low inner resistance which are features not available with conventional batteries.

Still other advantages are durability, high reliability, no maintenance, long lifetime and operation over a wide temperature range and in diverse environments (hot, cold and moist). The lifetime reaches one million cycles (or ten years of operation) without any degradation, but the solvent used in the capacitors remains a disadvantage, since it deteriorates in 5 or 6 years irrespective of the number of the cycles. They are eco-friendly and easily recycled or neutralized. The efficiency is typically around 90 % and discharge times are in the range of seconds to hours.

They can reach a specific power density which is about ten times higher than that of conventional batteries (only very-high-power lithium batteries can reach nearly the same specific power density), but their specific energy density is about ten times lower.

Because of their properties, DLCs are suited especially for applications with a large number of short charge/discharge cycles, where their high performance characteristics can be used. DLCs are not suited for the storage of energy over longer periods of time, because of their high self-discharge rate, their low energy density and high investment costs.

Since about 1980 they have been widely applied in consumer electronics and power electronics. A DLC is also ideally suited as a UPS to bridge short voltage failures. A new application could be the electric vehicle, where they could be used as a buffer system for the acceleration process and regenerative braking [esp11].

## **Hazard potential:**

### Electric:

See chapter lead acid batteries.

Overdischarge/reverse polarization: Is usually not critical for DLC. In this case, positive and negative electrodes are just changing. Surface groups at the activated carbon material might be oxidized or reduced without significant influence on the performance.

Overcharge: Charge at higher potentials as specified will lead to a decomposition of the electrolyte. Usually acetonitrile is used as the solvent in the electrolyte. The decomposition of the electrolyte will lead to an increase in internal pressure and if the pressure exceeds the opening pressure of the integrated rated break point, the electrolyte will get sprayed out. As acetonitrile is flammable and in a certain range explosive in mixture with air, excessive overcharge might result in fire or explosion.

### Mechanical:

Mechanical damages will lead to a leakage and evaporation of electrolyte, resulting in drying out of the capacitor and loss of functionality.

### Emissions:

DLC are closed systems. Emission takes place in case of overcharge, overheating or long time operation at high temperatures and high voltages. The emissions are flammable and explosive in a certain range.

### Risk of fire/explosion:

Risk for fire and explosion is given, if the cell case gets opened / ruptured. If the electrolyte burns/decomposes under oxygen limited conditions, poisonous HCN might be formed besides CO and CO<sub>2</sub>.

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## 4 Appendix: Overview of Electrical Energy Storage Systems (EESS) Technical Data

Table 4: Overview of electrical energy storage systems (EESS) technical data

Battery Technology	Nominal Voltage [V]	Capacity per Cell [Ah]	Response Time	Energy Density [Wh/kg]	Energy Density [Wh/l]	Power Density [W/l]	Typical Discharge Time	Energy-Efficiency $\eta_{wh}$ [%]	Lifetime [a]	Typ. Cycle Lifetime [cycles]	Typical applications
PHS	-	-	min	0.2 - 2	0.2 - 2	0.1 – 0.2	hours	70 - 80	> 50	> 15,000	Time shifting, Power quality, Emergency supply
CAES	-	-	min		2 - 6	0,2 – 0.6l	hours	41 - 75	> 25	> 10,000	Time shifting
Flywheel	-	0.7-1.7MW	< sec	5 - 30	20 - 80	~ 5000	seconds	80 - 90	15 - 20	$2 \cdot 10^4 - 10^7$	Power quality
Lead-acid	2.0	1 - 4000	< sec	30 – 45	50 – 80	90 - 700	hours	75 – 90	3 - 15	50 - 2000	Off-Grid, Residential, Emergency supply, Time shifting, Power quality
NiCd Vented sealed	1.2	2 – 1300 0.05 -25	< sec	15 – 40 30 - 45	15 – 80 80 -110	75 – 700	hours	60 – 80 60 - 70	5 - 20 5 - 10	1500 – 3000 500 - 800	Off-Grid, Residential, Emergency supply, Time shifting, Power quality
NiMH sealed	1.2	0.05 -110	< sec	40 – 80	80 – 200	500 - 3000	hours	65 – 75	5 - 10	600 - 1200	Electric vehicle
Li-Ion	3.7	0.05 -100	< sec	60 - 200	200 - 400	1300 - 10000	hours	85 - 98	5 - 15	$500 - 10^4$	Power Quality, Network efficiency, Off-Grid, Residential, Time shifting, Electric vehicle
Na-Ion	1.8	0.5 -100	< sec	20 – 30	25 - 40	3 - 10	hours	80 - 90	5 - 15	> 3000	Time shifting, Off-Grid, Residential
Battery Technology	Nominal Voltage [V]	Capacity per Cell [Ah]	Response Time	Energy Density [Wh/kg]	Energy Density [Wh/l]	Power Density [W/l]	Typical Discharge Time	Energy-Efficiency $\eta_{wh}$ [%]	Lifetime [a]	Typ. Cycle Lifetime [cycles]	Typical applications

Zinc Air	1.0	1 - 100	< sec	130 - 200	130 - 200	50 - 100	hours	50 - 70	> 1	> 1000	Off-Grid, Residential, Electric Vehicle
NaS	2.1	4 - 30	< sec	100 - 250	150 - 300	120 - 160	hours	70 - 85	10 - 15	2500 - 4500	Time shifting, Network efficiency, Off-Grid, Residential
NaNiCl	2.6	38	< sec	100 - 200	150 - 200	250 - 270	hours	80 - 90	10 - 15	~ 1000	Time shifting, Electric vehicles, Residential,
VRFB	1.6	-	sec	15 - 50	20 - 70	0.5 - 2	hours	60 - 75	5 - 20	> 10.000	Time shifting, Network efficiency, Off-Grid, Residential,
HFB	1.8	-	sec	75 - 85	65	1 - 25	hours	65 - 75	5 - 10	1000 - 3650	Time shifting, Network efficiency, Off-Grid
Hydrogen central decentral	-	-	min	33,330	600 (200 bar)	0.2 - 2 2.0 - 20	hours - weeks	40 - 50	10 - 30	$10^3 - 10^4$	Time Shifting
SNG	-	-	min	10,000	1,800 (200 bar)	0.2 - 2	hours - weeks	35 - 40	10 - 30	$10^3 - 10^4$	Time Shifting
DLC	2.5	0.1- 1500 F	< sec	1 - 15	10 - 20	$4 \cdot 10^4 - 10^5$	seconds	85 - 98	4 - 12	$10^4 - 10^5$	Power Quality, small appliances (watch)
SMES	-	-	< sec		6	2600	seconds	75 - 80			Time Shifting, Power Quality