

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Electrochemical Energy Storage

Petr Krivik and Petr Baca

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/52222>

1. Introduction

Electrochemical energy storage covers all types of secondary batteries. Batteries convert the chemical energy contained in its active materials into electric energy by an electrochemical oxidation-reduction reverse reaction.

At present batteries are produced in many sizes for wide spectrum of applications. Supplied powers move from W to the hundreds of kW (compare battery for power supply of pace makers and battery for heavy motor vehicle or for power station).

Common commercially accessible secondary batteries according to used electrochemical system can be divided to the following basic groups:

Standard batteries (lead acid, Ni-Cd) modern batteries (Ni-MH, Li-ion, Li-pol), special batteries (Ag-Zn, Ni-H₂), flow batteries (Br₂-Zn, vanadium redox) and high temperature batteries (Na-S, Na-metalchloride).

2. Standard batteries

2.1. Lead acid battery

Lead acid battery when compared to another electrochemical source has many advantages. It is low price and availability of lead, good reliability, high voltage of cell (2 V), high electrochemical effectivity, cycle life is from several hundreds to thousands of cycles. Thanks to these characteristics is now the most widely used secondary electrochemical source of electric energy and represent about 60% of installed power from all types of secondary batteries. Its disadvantage is especially weight of lead and consequently lower specific energy in the range 30-50 Wh/kg.

Lead-acid batteries are suitable for medium and large energy storage applications because they offer a good combination of power parameters and a low price.

2.1.1. Battery composition and construction

Construction of lead acid (LA) battery depends on usage. It is usually composed of some series connected cells. Main parts of lead acid battery are electrodes, separators, electrolyte, vessel with lid, ventilation and some other elements.



Figure 1. Scheme of prismatic and spiral wound construction of LA battery

Electrode consists of grid and of active mass. Grid as bearing structure of electrode must be mechanically proof and positive electrode grid must be corrosion proof. Corrosion converts lead alloy to lead oxides with lower mechanical strength and electric conductivity. Grids are

made from lead alloys (pure lead would be too soft); it is used Pb-Ca or Pb-Sb alloys, with mixture of additives as Sn, Cd and Se, that improve corrosion resistance and make higher mechanical strength.

Active material is made from lead oxide PbO pasted onto a grid and then electrochemically converted into reddish brown lead dioxide PbO₂ on positive electrode and on grey spongy lead Pb on negative electrode.

Separators electrically separate positive electrode from negative. They have four functions:

1. to provide electrical insulation between positive and negative plate and to prevent short circuits,
2. to act as a mechanical spacer which holds the plates in the prescribed position,
3. to help retain the active materials in close contact with the grid,
4. to permit both the free diffusion of electrolyte and the migration of ions.

The materials used for separators can be wood veneers, cellulose (paper), usually stiffened with a phenol-formaldehyde resin binder, and those made from synthetic materials, e.g., rubber, polyvinyl chloride (PVC), polyethylene (PE), and glass-microfibre.

Electrolyte is aqueous solution of H₂SO₄ with density of 1.22-1.28 g/cm³. Mostly it is liquid, covered battery plates. Sometimes it is transformed to the form of gel, or completely absorbed in separators.

Vessel must to withstand straining caused by weight of inner parts of battery and inner pressure from gas rising during cycling. The most used material is polypropylene, but also, PVC, rubber etc. If overpressure rises inside classical battery during charging, problem is solved by valve placed mostly in lid.

There are some major types of battery construction: prismatic construction with grid or tubular plates, cylindrical construction (spiral wound or disc plates) or bipolar construction.

2.1.2. Principle of operation

Overall chemical reaction during discharge is:



Reaction proceeds in opposite direction during charge.

2.1.3. Types of LA batteries

According to the usage and construction, lead acid batteries split into stationary, traction and automotive batteries.

Stationary battery ensures uninterrupted electric power supply in case of failure in distributing network. During its service life battery undergo only few cycles. Battery life is as many as 20 years.

Traction battery is used for power supply of industrial trucks, delivery vehicles, electromobiles, etc. It works in cyclic regime of deep charge–discharge. Cycle life of the battery is about 5 years (1000 of charge–discharge cycles).

Automotive battery is used for cranking automobile internal combustion engines and also for supporting devices which require electrical energy when the engine is not running. It must be able of supplying short but intense discharge current. It is charged during running of engine.

According to the maintenance operation lead acid batteries could be branched into conventional batteries (i.e., those with free electrolyte, so-called 'flooded' designs), requiring regular maintenance and valve-regulated lead-acid (VRLA) maintenance free batteries.

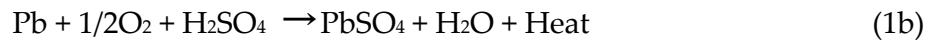
2.1.4. VRLA batteries

Originally, the battery worked with its plates immersed in a liquid electrolyte and the hydrogen and the oxygen produced during overcharge were released into the atmosphere. The lost gases reflect a loss of water from the electrolyte and it had to be filled in during maintenance operation. Problems with water replenishing were overcome by invention of VRLA (valve regulated lead acid) batteries.

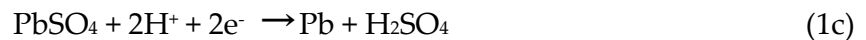
The VRLA battery is designed to operate with help of an internal oxygen cycle, see Fig. 2. Oxygen liberated during the latter stages of charging, and during overcharging, on the positive electrode, i.e.



travels through a gas space in separator to the negative electrode where is reduced to the water:



The oxygen cycle, defined by reactions (1a) and (1b), moves the potential of the negative electrode to a less negative value and, consequently, the rate of hydrogen evolution decreases. The small amount of hydrogen that could be produced during charging is released by pressure valve. The produced lead sulphate is immediately reduced to lead via the reaction (1c), because the plate is simultaneously on charge reaction:



The sum of reactions (1a), (1b) and (1c) is zero. Part of the electrical energy delivered to the cell is consumed by the internal oxygen recombination cycle and it is converted into heat.

There are two designs of VRLA cells which provide the internal oxygen cycle. One has the electrolyte immobilized as a gel (gel batteries), the other has the electrolyte held in an AGM separator (AGM batteries). Gas can pass through crack in the gel, or through channels in the AGM separator.

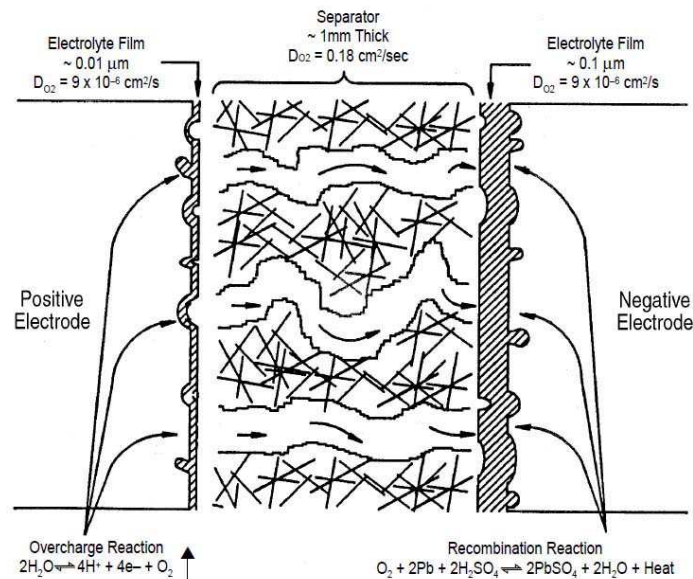


Figure 2. Internal oxygen cycle in a valve regulated lead acid cell (Nelson, 2001).

When the cell is filled with electrolyte, the oxygen cycle is impossible because oxygen diffuses through the electrolyte very slow. On the end of charge, first oxygen (from the positive), and then both oxygen (from the positive) and hydrogen (from the negative), are liberated and they are released through the pressure valve. Gassing causes loss of water and opens gas spaces due to drying out of the gel electrolyte or a liquid electrolyte volume decrease in the AGM separators). It allows the transfer of oxygen from the positive to the negative electrode. Gas release from the cell then falls rapidly (Rand et al., 2004).

2.1.5. Failure mechanisms of LA batteries

Lead acid batteries can be affected by one or more of the following failure mechanisms:

1. positive plate expansion and positive active mass fractioning,
2. water loss brought about by gassing or by a high temperature,
3. acid stratification,
4. incomplete charging causing active mass sulphation,
5. positive grid corrosion,
6. negative active mass sulphation (batteries in partial state of charge (PSoC) cycling - batteries in hybrid electric vehicles (HEV) and batteries for remote area power supply (RAPS) applications).

Repetitive discharge and charge of the LA battery causes expansion of the positive active mass because product of the discharge reaction PbSO_4 occupies a greater volume than the positive active material PbO_2 . Charging of the cell restores most of the lead dioxide, but not within the original volume. The negative active mass does not show the same tendency to expand. Reason could be that lead is softer than lead dioxide and that is why the negative active material is more compressed during discharge as the conversion from lead to the more voluminous lead sulphate proceeds. Another reason could be that spongy lead

contains bigger pores than pores in lead dioxide and therefore is more easily able to absorb a lead sulphate without expansion of a negative active mass. Progressive expansion of the positive electrode causes an increasing fraction of the positive active material. This material becomes to be electrically disconnected from the current collection process and it causes decreasing of the cell capacity. (Calabek et al., 2001).



Figure 3. Positive active mass fractioning

Gas evolving during overcharge leads to reduction of the volume of the electrolyte. Some of the active material consequently loses contact with the electrodes. Drying out increases the internal resistance of the battery which causes excessive rise of temperature during charging and this process accelerates water loss through evaporation.

During charge, sulphuric acid is produced between the electrodes and there is a tendency for acid of higher concentration, which has a greater relative density, to fall to the bottom of the lead acid cell. Acid stratification can be caused also by preferential discharge of upper parts of the cell, because of lower ohmic resistance of these parts. Concentration of electrolyte in the upper part of the cell is temporarily lower than on the bottom of the cell. It leads to discharge of the bottom parts and charge of the upper parts of the cell. The vertical concentration gradient of sulphuric acid can give rise to non uniform utilization of active mass and, consequently, shortened service life through the irreversible formation of PbSO_4 (Ruetschi, 2004).

When the electrodes are repeatedly not fully charged, either because of a wrong charging procedure or as a result of physical changes that keep the electrode from reaching an adequate potential (antimony poisoning of negative electrode), then a rapid decreasing in battery capacity may occur because of progressive accumulation of lead sulphate in active mass. Sulphation is creation of insulation layer of lead sulphate on the electrode surface. It leads to inhibition of electrolyte contact with active mass. Sulphation grows during the long term standing of the battery in discharge state, in case of electrolyte stratification, or incomplete charging. In the course of sulphation originally small crystals of lead sulphate

grow to big ones. Big crystals of lead sulphate increase internal resistance of the cell and during charging it is hardly possible to convert them back to the active mass.

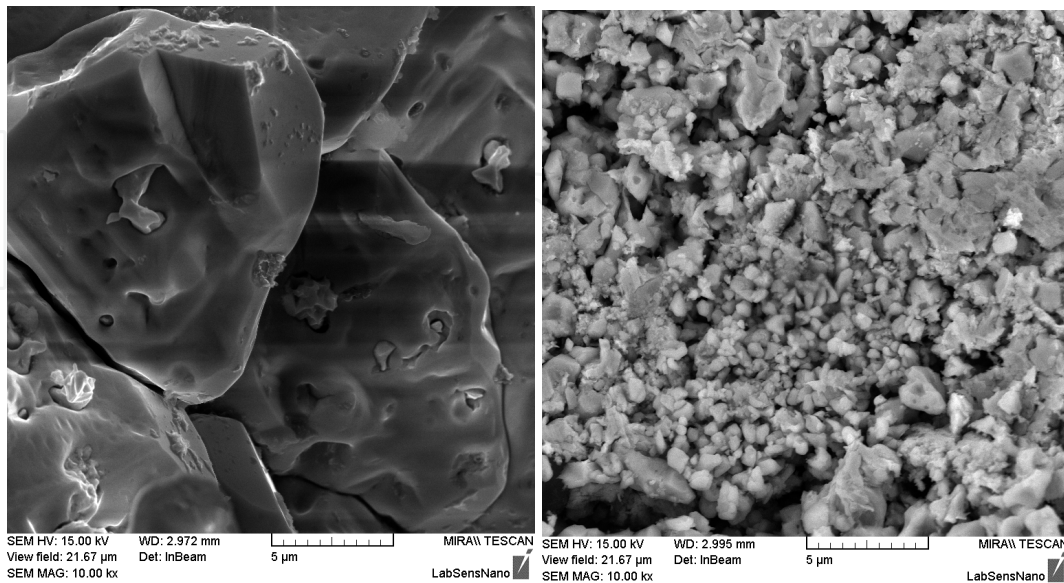


Figure 4. SEM images of negative active mass. Sulphation on the left, healthy state on the right

During charge the positive grid is subject to corrosion. Lead collector turns on lead dioxide or lead sulphate. The rate of this process depends on the grid composition and microstructure, also on plate potential, electrolyte composition and temperature of the cell. The corrosion products have usually a bigger electric resistance than positive grid. In extreme cases, corrosion could result to disintegration of the positive grid and consequently to collapse of the positive electrode.

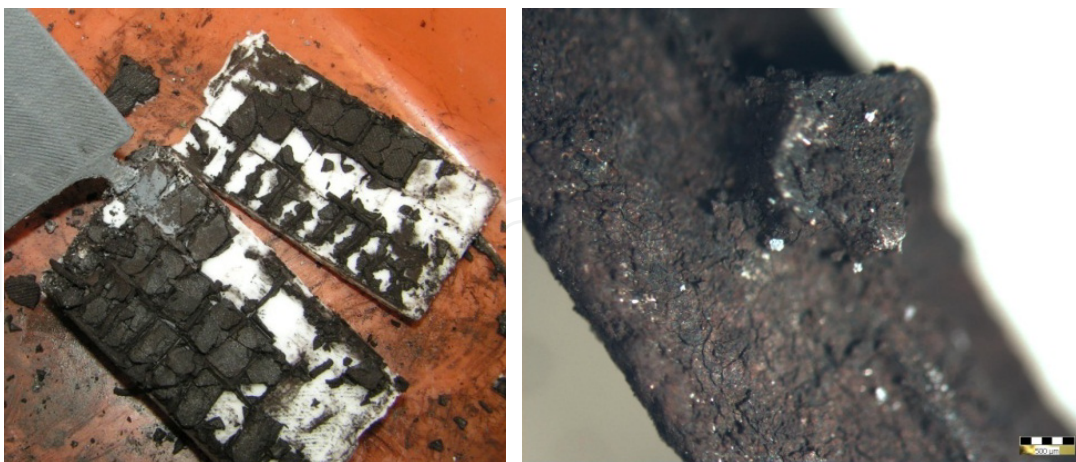


Figure 5. Positive grid corrosion

2.2. Ni-Cd battery

They are main representative of batteries with positive Nickel electrode; other possible systems could be system Ni-Fe and Ni-Zn, Ni-H₂ or Ni-MH.

2.2.1. Battery composition and construction

The nickel cadmium cell has positive electrode from nickel hydroxide and negative electrode from metallic cadmium, an electrolyte is potassium hydroxide. The nickel cadmium battery is produced in a wide range of commercially important battery systems from sealed maintenance free cells (capacities of 10 mAh - 20 Ah) to vented standby power units (capacities of 1000 Ah and more). Nickel cadmium battery has long cycle life, overcharge capability, high rates of discharge and charge, almost constant discharge voltage and possibility of operation at low temperature. But, the cost of cadmium is several times that of lead and the cost of nickel cadmium cell construction is more expensive than that of lead acid cell. And there is also problem with the manipulation of toxic cadmium. But also low maintenance and good reliability have made it an ideal for a number of applications such (emergency lighting, engine starting, portable television receivers, hedge trimmers, electric shavers, aircraft and space satellite power systems).

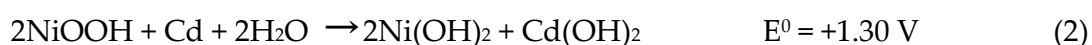
Depending on construction, nickel cadmium cells have energy densities in the range 40-60 Wh/kg (50-150 Wh/dm³). Cycle life is moving from several hundreds for sealed cells to several thousands for vented cells.

Cell construction is branched to two types. First using pocket plate electrodes (in vented cells). The active material is found in pockets of finely perforated nickel plated sheet steel. Positive and negative plates are then separated by plastic pins or ladders and plate edge insulators. Second using sintered, bonded or fibre plate electrodes (in both vented and sealed cells). In sintered plate electrodes, a porous sintered nickel electrode is sintered in belt furnace in reducing atmosphere at 800 to 1000°C. Active material is distributed within the pores. In sintered plate cells, a special woven or felted nylon separator is used. It permits oxygen diffusion (oxygen cycle) in sealed cells. In the most common version, a spiral or prismatic construction of cells is used.

The electrolyte is an aqueous solution KOH (concentration of 20-28% by weight and a density of 1.18-1.27 g/cm³ at 25°C). 1-2% of LiOH is usually added to electrolyte to minimize coagulation of the NiOOH electrode during charge/discharge cycling. For low temperature applications, the more concentrated KOH solution is used. When it is operating at high temperature it is sometimes used aqueous NaOH electrolyte.

2.2.2. Principle of operation

The overall cell reaction during discharge:



It is notable that amount of water in the electrolyte falls during discharge. Ni-Cd batteries are designed as positive limited utilizing oxygen cycle. The oxygen evolved at the positive electrode during charge diffuses to the negative electrode and reacts with cadmium to form Cd(OH)₂.

In addition, carbon dioxide in the air can react with KOH in the electrolyte to form K_2CO_3 , and $CdCO_3$ can be formed on the negative plates. Both of these compounds increase the internal resistance and lower the capacity of the Ni-Cd batteries.

Ni-Cd batteries suffer from the memory effect (see also chapter Ni-MH battery). Besides Ni-Cd batteries also suffer from high rate of self-discharge at high temperatures.

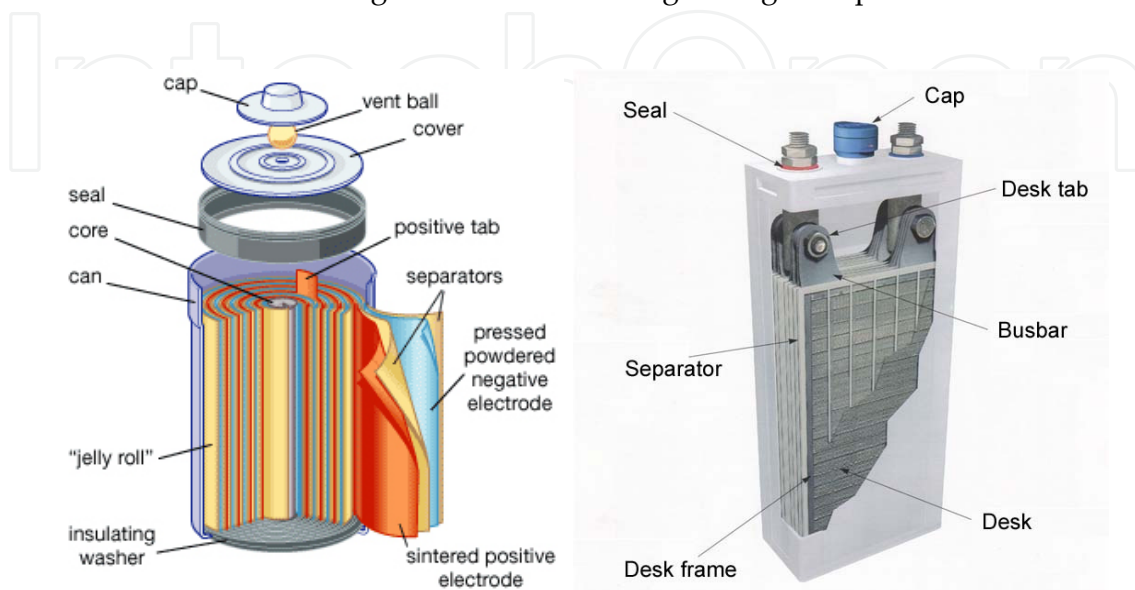


Figure 6. Scheme of spiral wound and prismatic construction of Ni-Cd battery

3. Modern batteries

3.1. Ni-MH battery

3.1.1. Battery composition and construction

The sealed nickel metal hydride cell has with hydrogen absorbed in a metal alloy as the active negative material. When compare with Ni-Cd cell it is not only increases the energy density, but also it is a more environmentally friendly power source. The nickel metal hydride cell, however, has high selfdischarge and is less tolerant to overcharge than the Ni-Cd cell.

Positive electrode is $NiOOH$, negative electrode contains hydrogen absorption alloys. They can absorb over a thousand times their own volume of hydrogen: Alloys usually consist of two metals. First absorbs hydrogen exothermically, a second endothermically. They serve as a catalyst for the dissociative adsorption of atomic hydrogen into the alloy lattice. Examples of used metals: Pd, V, Ti, Zr, Ni, Cr, Co, Sn, Fe, lanthanides and others. The AB_2 series ($ZrNi_2$) and the AB_5 series ($LaNi_5$) are usually used.

Design of the cylindrical and prismatic sealed Ni-MH cells are similar as with a nickel cadmium cells (see Fig. 7). Hydrophilic polypropylene separator is used in Ni-MH cell.

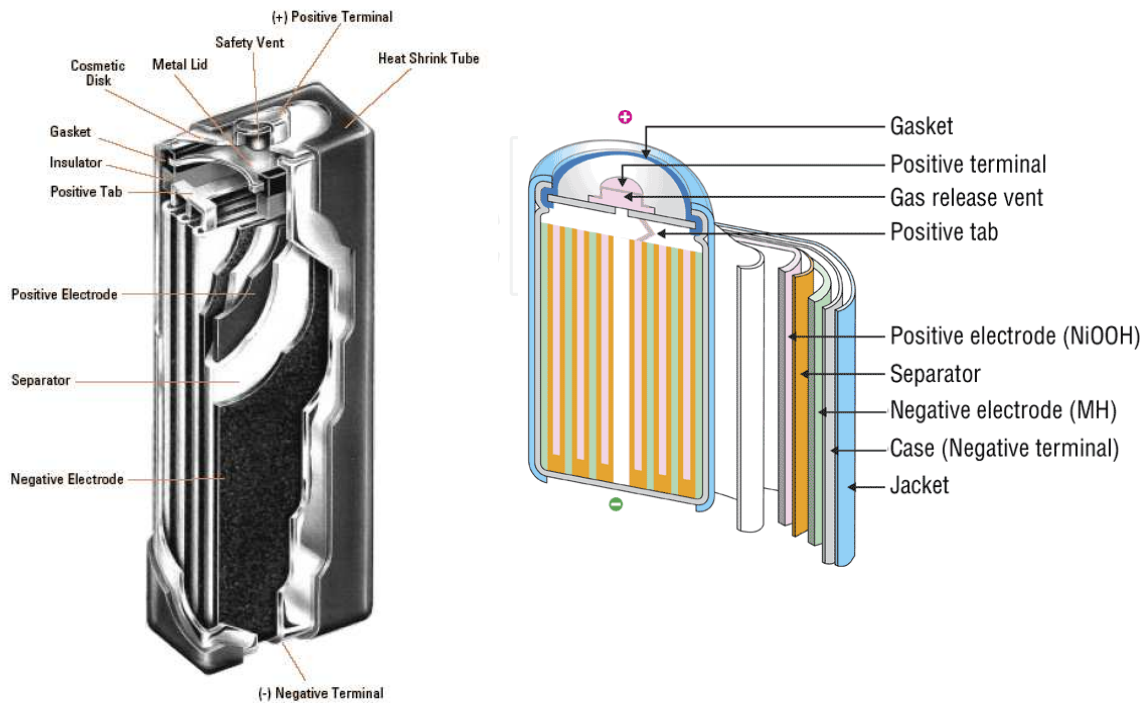


Figure 7. Scheme of prismatic and spiral wound Ni-MH battery

3.1.2. Principle of operation

The overall reaction during discharge:



The electrolyte is concentrated potassium hydroxide, voltage is in the range 1.32-1.35 V, depending on used alloy. Water is not involved in the cell reaction.

The energy density is 25% higher than a Ni-Cd cell (80 Wh/kg), power density around 200 W/kg, cycle life over 1000 cycles. Self-discharge is high - up to 4-5% per day. It is caused especially by the hydrogen dissolved in the electrolyte that reacts with the positive electrode.

Ni-MH batteries are used in hybrid electric vehicle batteries, electric razors, toothbrushes, cameras, camcorders, mobile phones, pagers, medical instruments, and numerous other high rate long cycle life applications.

3.1.3. Memory effect

Ni-MH batteries also suffer from the memory effect. It is a reversible process which results in the temporary reduction of the capacity of a Ni-Cd and Ni-MH cell. It is caused by shallow charge-discharge cycling.

After shallow cycling there is a voltage step during discharge, i.e. as if the cell remembers the depth of the shallow cycling. The size of the voltage reduction depends on the number of preceding shallow cycles and the value of the discharge current. But the capacity of the cell is not affected if the cell is now fully discharged (to 0.9 V) and then recharged. Deep discharge then shows a normal discharge curve. It seems that some morphological change occurs in the undischarged active material during the shallow cycling. It could cause a reduction of the cell voltage during following discharge. The effect is probably based on an increase in the resistance of the undischarged material (γ -NiOOH formation on overcharge during the shallow cycles) (Vincent & Scrosati, 2003).

Progressive irreversible capacity loss can be confused with the reversible memory effect. The former is caused different mechanisms. For example by a reduction in the electrolyte volume due to evaporation at high temperatures or prolonged overcharge. Irreversible capacity loss can also be caused by internal short circuits.

3.2. Li-ion battery

Lithium is attractive as a battery negative electrode material because it is light weight, high reduction potential and low resistance. Development of high energy density lithium-ion battery started in the 1970s. The lithium-ion cell contains no metallic lithium and is therefore much safer on recharge than the earlier, primary lithium-metal design of cell.

3.2.1. Battery composition and construction

The principle of the lithium-ion cell is illustrated schematically in Fig. 8. The lithium ions travel between one electrode and the other during charge and discharge.

The most of commercial lithium-ion cells have positive electrodes of cobalt oxide. Other possible positive electrodes are except LiCoO_2 and LiNiO_2 based on especially manganese oxide, namely, LiMnO_2 and LiMn_2O_4 .

Negative electrode is carbon, in the form of either graphite or an amorphous material with a high surface-area. Carbon is an available and cheap material of low weight and also it is able to absorb a good quantity of lithium. When paired with a metal oxide as the positive electrode it gives a cell with a relatively high voltage (from 4 V in the fully charged state to 3 V in discharged state) (Dell & Rand, 2001).

Electrolyte is composed from organic liquid (ether) and dissolved salt (LiPF_6 , LiBF_4 , LiClO_4). The positive and negative active mass is applied to both sides of thin metal foils (aluminium on positive and copper on negative). Microporous polymer sheet between the positive and negative electrode works as the separator.

Lithium-ion cells are produced in coin format, as well as in cylindrical and prismatic (see Fig. 9) shapes.

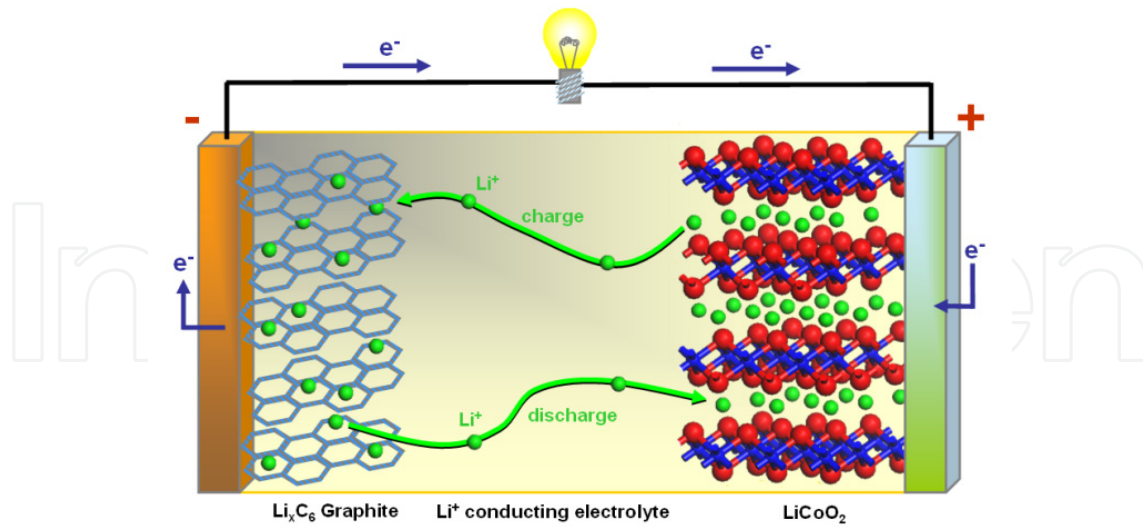


Figure 8. The principle of the lithium-ion cell

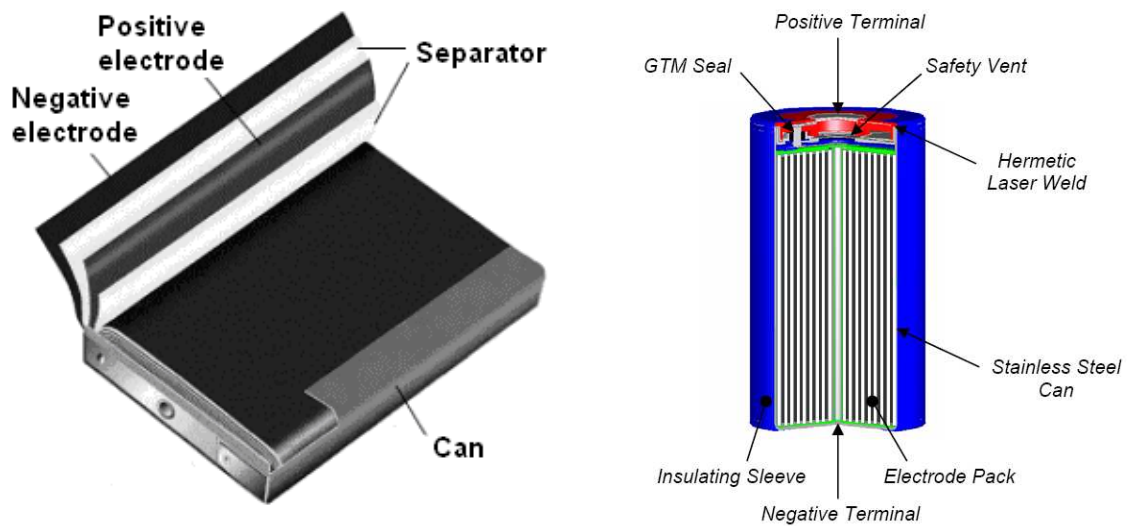


Figure 9. Prismatic and cylindrical Li-ion cell construction

3.2.2. Principle of operation

The positive electrode reaction is:

Positive electrode:



Negative electrode:



where x moves on negative electrode from 0 to 1, on positive electrode from 0 to 0.45.

The most important advantages of lithium-ion cell are high energy density from 150 to 200 Wh/kg (from 250 to 530 Wh/l), high voltage (3.6 V), good charge-discharge characteristics, with more than 500 cycles possible, acceptably low selfdischarge (< 10% per month), absence of a memory effect, much safer than equivalent cells which use lithium metal, possibility of rapid recharging (2h).

Main disadvantage is a high price of the lithium-ion battery. There also must be controlled charging process, especially close the top of charge voltage 4.2 V. Overcharging or heating above 100°C cause the decomposition of the positive electrode with liberation of oxygen gas (LiCoO_2 yields Co_3O_4).

3.2.3. Li-pol battery

Polymers contained a hetero-atom (i.e. oxygen or sulfur) is able to dissolve lithium salts in very high concentrations. Some experiments were made with polyethylene oxide (PEO), which dissolves salts lithium perchlorate LiClO_4 and lithium trifluoromethane sulfonate LiCF_3SO_3 very well. But there is disadvantage - the conductivity of the solid solution of lithium ions is too low (about 10^{-5} S/m) on room temperature. But when higher temperature is reached (more than 60°C), transformation of crystalline to amorphous phase proceeds. It leads to much better electrical conductivity (10^{-1} S/m at 100°C). This value allows the polymer to serve as an electrolyte for lithium batteries. But thickness of the polymer must be low (10 to 100 μm). Polymer electrolyte is safer then liquid electrolyte, because it is not flammable (Dell & Rand, 2001).

4. Special batteries

4.1. Ag-Zn battery

4.1.1. Battery composition and construction

The zinc-silver oxide battery has one of the highest energy of aqueous cells. The theoretical energy density is 300 Wh/kg (1400 Wh/dm³) and practical values are in the range 40-130 Wh/kg (110-320 Wh/dm³). Cells have poor cycle life. But they can reach a very low internal resistance and also their high energy density makes them very useful for aerospace and even military purposes.

The silver positive active mass is formed by sintering of silver powder at temperatures between 400 and 700°C and it is placed on silver or silver-plated copper grids or perforated sheets.

The zinc negative electrode prepares as mixtures of zinc, zinc oxide and organic binding agents. The aim is to produce electrodes of high porosity. Other additives include surface active agents to minimize dendritic growth and mercuric ions to increase the hydrogen overvoltage of the zinc electrode (reduce gassing during charge) and so reduce corrosion.

Electrolyte is water solution of KOH (1.40 to 1.42 g/cm³).

The separator is the most important component of zinc-silver oxide cell. It must prevent short circuit between electrodes, must prevent silver migration to the negative electrode, to control zincate migration, to preserve the integrity of the zinc electrode. The separator must have a low ion resistance with good thermal and chemical stability in KOH solution. Typical separators used in Ag-Zn battery, are of cellophane (regenerated cellulose), synthetic fiber mats of nylon, polypropylene, and nonwoven rayon fiber mats. Synthetic fiber mats are placed next to the positive electrode to protect the cellophane from oxidizing influence of that material. In most cells the separators are in form of envelopes completely enclosed the zinc electrodes (Vincent & Scrosati, 2003).

Commercial cells are generally prismatic – see Fig. 10 in shape and the case is usually plastic. Construction must be able to withstand the mechanical stress. The cells are usually sealed with safety valves. The volume of free electrolyte is very small. It is absorbed in the electrode pores and separator.

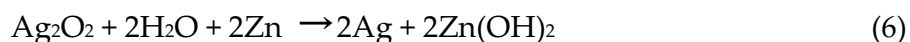
The energy density of practical zinc-silver oxide cells is some five to six times higher than that of their nickel-cadmium cells. The main disadvantage of the system is its high cost combined with a poor cycle life.



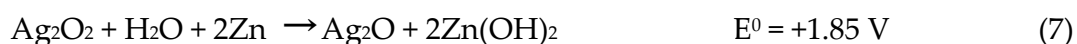
Figure 10. Ag-Zn prismatic and submarine torpedo battery

4.1.2. Principle of operation

The overall cell reaction during discharge:



The cell discharge reaction takes place in two stages:



During discharge there rises metal silver inside positive electrode and that is why inner electrical resistance drops in discharged state. Maximum temperature range is from -40 to 50 °C. Self discharge of Ag-Zn battery at 25 °C is about 4% of capacity per month.

Zinc-silver oxide secondary cells with capacities of 0.5-100 Ah are manufactured for use in space satellites, military aircraft, submarines and for supplying power to portable military equipment. In space applications the batteries are used to increase the power from solar cells during period of high demand, e.g. during radio transmission or when the sun is eclipsed. At other times the batteries are charged by the solar cells.

4.2. Ni-H₂ battery

4.2.1. Battery composition and construction

The Ni-H₂ battery is an alkaline battery developed especially for use in satellites (see Fig. 11). It is a hybrid battery combining battery and fuel cell technology.

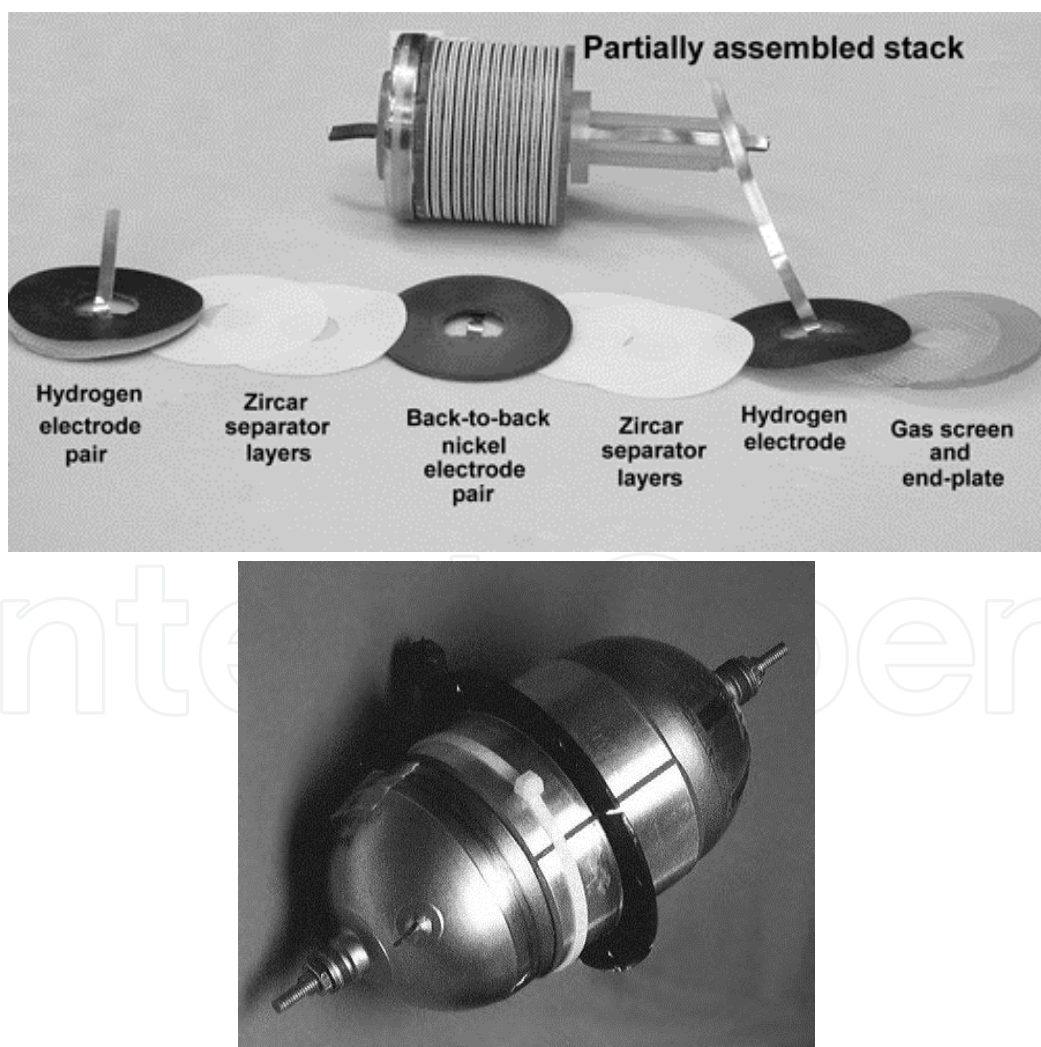


Figure 11. Scheme of a nickel-hydrogen battery (Zimmerman, 2009)

The battery has a sintered, nickel-oxide positive electrode and a negative electrode from platinum black catalyst supported with Teflon bonding dispersed on carbon paper. Two types of the separators are being used. First is formed from a porous ceramic paper, made from fibres of yttria-stabilized zirconia, second from asbestos paper (Linden & Reddy, 2002). Separators absorb the potassium hydroxide electrolyte. The battery was developed to replace Ni-Cd battery in space applications and it has some higher specific energy (50 Wh/kg) together with a very long cycle life. Standard voltage of the Ni-H₂ cell is 1.32 V.

4.2.2. Principle of operation

The overall reaction during discharge:



The hydrogen gas liberated on charging is stored under pressure within the cell pressure vessel. Shape of the vessel is cylindrical with hemi-spherical end caps made from thin, Inconel alloy. Pressure of hydrogen inside the vessel grows to 4 MPa during charge whereas in the discharged state falls to 0.2 MPa. The cells may be overcharged because liberated oxygen from the positive electrode recombines rapidly at the negative electrode into the water.

5. Flow batteries

Flow batteries store and release electrical energy with help of reversible electrochemical reactions in two liquid electrolytes. An electrochemical cell has two loops physically separated by an ion or proton exchange membrane. Electrolytes flow into and out of the cell through separate loops and undergo chemical reaction inside the cell, with ion or proton exchange through the membrane and electron exchange through the external electric circuit. There are some advantages to using the flow battery when compared with a conventional secondary battery. The capacity of the system is possible to scale by increasing the amount of solution in electrolyte tanks. The battery can be fully discharged and has little loss of electrolyte during cycling. Because the electrolytes are stored separately, flow batteries have a low selfdischarge. Disadvantage is a low energy density and specific energy.

5.1. Br₂-Zn battery

5.1.1. Battery composition and construction

The zinc-bromine cell is composed from the bipolar electrodes. The bipolar electrode is from a lightweight, carbon-plastic composite material. Microporous plastic separator between electrodes allows the ions to pass through it. Cells are series-connected and the battery has a positive and a negative electrode loop. The electrolyte in each storage tank is circulated through the appropriate loop.

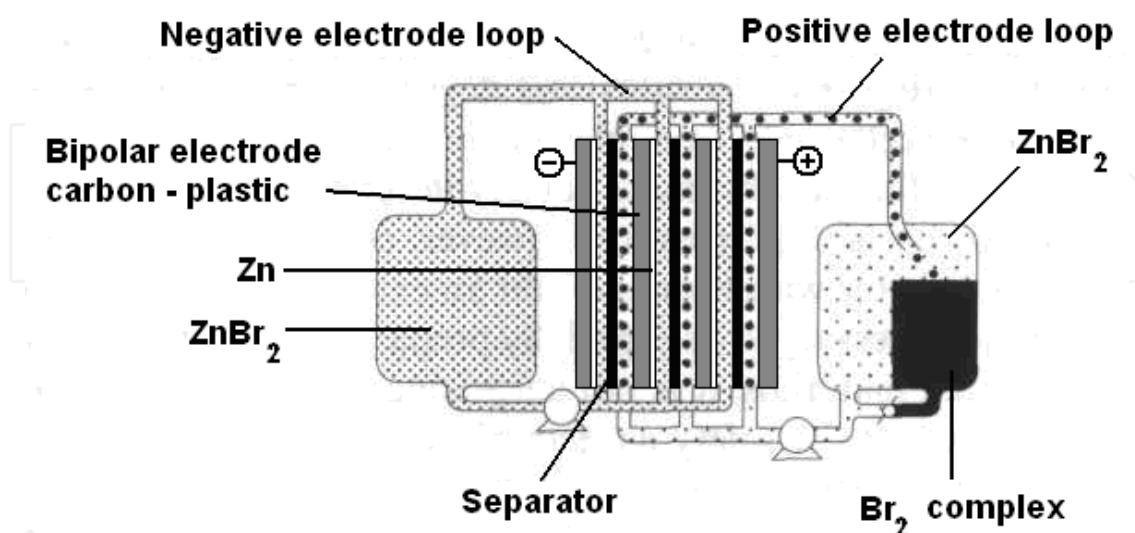
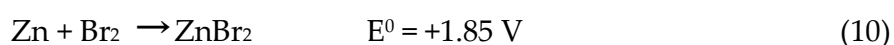


Figure 12. Scheme of zinc-bromine battery (Dell & Rand, 2001)

5.1.2. Principle of operation

The overall chemical reaction during discharge:



During discharge product of reaction, the soluble zinc bromide is stored, along with the rest of the electrolyte, in the two loops and external tanks. During charge, bromine is liberated on the positive electrode and zinc is deposited on the negative electrode. Bromine is then complexed with an organic agent to form a dense, oily liquid polybromide complex. It is produced as droplets and these are separated from the aqueous electrolyte on the bottom of the tank in positive electrode loop. During discharge, bromine in positive electrode loop is again returned to the cell electrolyte in the form of a dispersion of the polybromide oil.

5.2. Vanadium redox battery

5.2.1. Battery composition and construction

A vanadium redox battery is another type of a flow battery in which electrolytes in two loops are separated by a proton exchange membrane (PEM). The electrolyte is prepared by dissolving of vanadium pentoxide (V_2O_5) in sulphuric acid (H_2SO_4). The electrolyte in the positive electrolyte loop contains $(\text{VO}_2)^+$ - (V^{5+}) and $(\text{VO})^{2+}$ - (V^{4+}) ions, the electrolyte in the negative electrolyte loop, V^{3+} and V^{2+} ions. Chemical reactions proceed on the carbon electrodes.

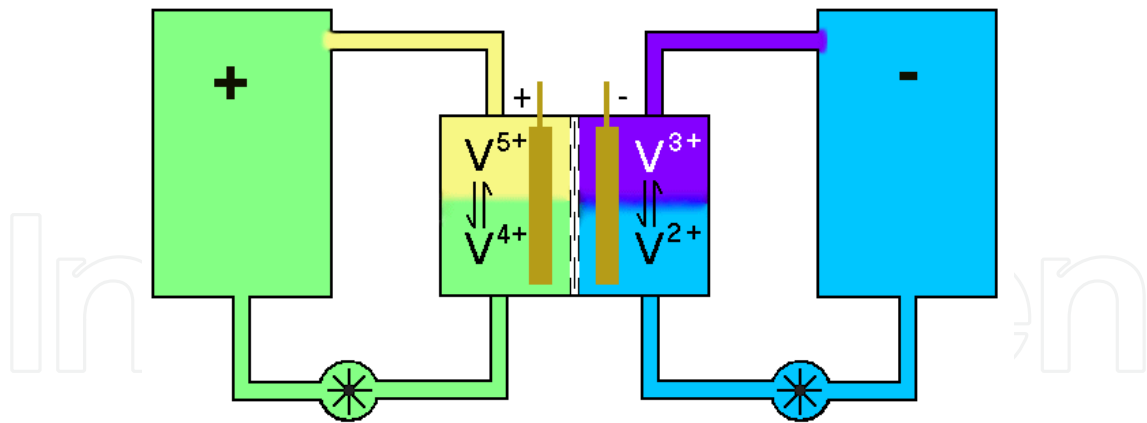
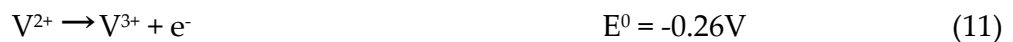


Figure 13. Scheme of vanadium redox battery

5.2.2. Principle of operation

In the vanadium redox cell, the following half-cell reactions are involved during discharge:

At the negative electrode:



At the positive electrode:



Under actual cell conditions, an open circuit voltage of 1.4 Volts is observed at 50% state of charge, while a fully charged cell produces over 1.6 Volts at open-circuit, fully discharged cell 1.0 Volt.

The extremely large capacities possible from vanadium redox batteries make them well suited to use in large RAPS applications, where they could average out the production of highly unstable power sources such as wind or solar power. The extremely rapid response times make them suitable for UPS type applications, where they can be used to replace lead acid batteries. Disadvantage of vanadium redox batteries is a low energy density of about 25 Wh/kg of electrolyte, low charge efficiency (necessity using of pumps) and a high price.

6. High temperature batteries

6.1. Na-S battery

6.1.1. Battery composition and construction

Sodium, just like lithium, has many advantages as a negative-electrode material. Sodium has a high reduction potential of -2.71V and a low atomic weight (23.0). These properties allow to make a battery with a high specific energy (100-200 Wh/kg). Sodium salts are highly found in nature, they are cheap and non-toxic. Sulphur is the positive electrode

material which can be used in combination with sodium to form a cell. Sulphur is also highly available in nature and very cheap.

The problem of a sodium-sulphur cell is to find a suitable electrolyte. Aqueous electrolytes cannot be used and, unlike the lithium, no suitable polymer was found. That is why a ceramic material beta-alumina ($\beta\text{-Al}_2\text{O}_3$) was used as electrolyte. It is an electronic insulator, but above 300 °C it has a high ionic conductivity for sodium ions.

In each cell, the negative electrode (molten sodium) was contained in a vertical tube (diameter from 1 to 2 cm). The positive electrode (molten sulphur) is absorbed into the pores of carbon felt (serves as the current-collector) and inserted into the annulus between the ceramic beta-alumina electrolyte tube and the cylindrical steel case (Fig. 14). Between molten sodium and beta-alumina electrolyte also could be found a safety liner with a pin-hole in its base.

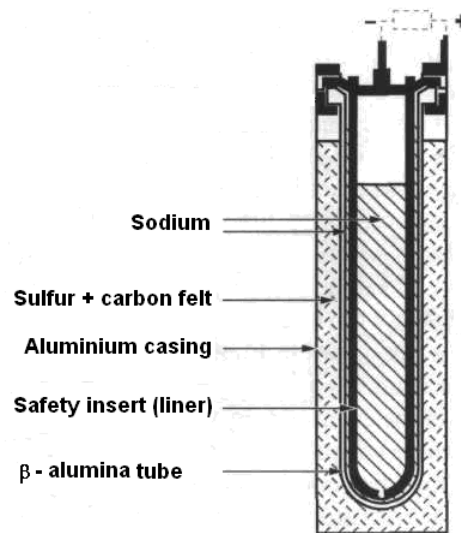


Figure 14. Schematic cross-section of Na-S cell (Dell & Rand, 2001)

6.1.2. Principle of operation

The cell discharges at 300 to 400 °C. Sodium ions pass from the sodium negative electrode, through the beta-alumina electrolyte, to the sulphur positive electrode. There they react with the sulphur to form sodium polysulphides. Standard voltage of the cell is about 2 V.

The cell discharges in two steps:



Uncontrolled chemical reaction of molten sodium and sulphur could cause a fire and corrosion inside the cell and consequently destruction of the cell. It often happens after the fracture of the electrolyte tube. This problem is solved by inserting of safety liner to the beta-

alumina tube. This allows a normal flow of sodium to the inner wall of the beta-alumina electrolyte, but prevents the flow in the case of tube fracture.

6.2. Na-metalchloride battery

6.2.1. Battery composition and construction

In the sodium-metalchloride battery the sulphur positive electrode there is replaced by nickel chloride or by a mixture of nickel chloride (NiCl_2) and ferrous chloride (FeCl_2) – see Fig. 15. The specific energy is 100-200 Wh/kg.

The negative electrode is from molten sodium, positive electrode from metalchloride and electrolyte from the ceramic beta-alumina (the same as in the sodium-sulphur battery). The second electrolyte, to make good ionic contact between the positive electrode and the electrolyte from beta-alumina, is molten sodium chloraluminate (NaAlCl_4).

The positive electrode is from a mixture of metal powder (Ni or Fe) and sodium chloride (NaCl). During charge, these materials are converted into the corresponding metal chloride and sodium. Iron powder is cheaper than nickel powder, but nickel cells have higher voltage and could operate over a wider temperature range (200 to 400 °C) than iron cells (200 to 300 °C) (Dell & Rand, 2001).

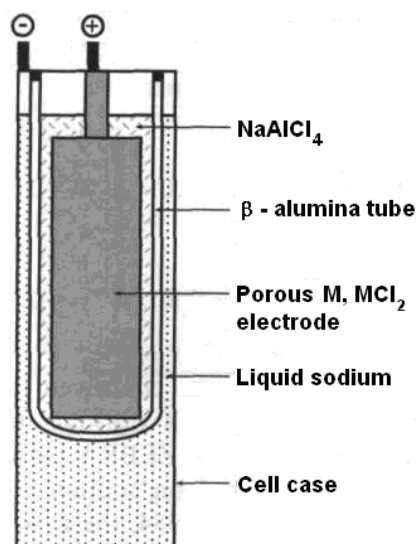


Figure 15. Schematic cross-section of Na-metalchloride cell (Rand, 1998)

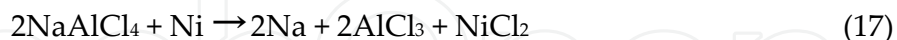
6.2.2. Principle of operation

The basic cell reactions during discharge are simple, i.e.



Advantage of the sodium metalchloride cell over the sodium sulphur cell is that there is possibility of both an overcharge and overdischarge reaction, when the second electrolyte (molten sodium chloraluminate) reacts with metal (overcharge) or with sodium (overdischarge).

Overcharge reaction for sodium nickelchloride cell:



Overdischarge reaction for sodium nickelchloride cell:



Another advantage of the sodium metalchloride system is safety of operation. When the beta-alumina electrolyte tube cracks in this system, the molten sodium first encounters the NaAlCl_4 electrolyte and reacts with it according the overdischarge reaction.

7. Conclusion

This chapter is focused on electrochemical storage or batteries that constitute a large group of technologies that are potentially suitable to meet a broad market needs. The five categories of electrochemical systems (secondary batteries) were selected and discussed in detail: standard batteries (lead acid, Ni-Cd) modern batteries (Ni-MH, Li-ion, Li-pol), special batteries (Ag-Zn, Ni-H₂), flow batteries (Br₂-Zn, vanadium redox) and high temperature batteries (Na-S, Na-metalchloride). These batteries appear to be promising to meet the requirements for end-user applications.

However, the use of secondary batteries involves some technical problems. Since their cells slowly self-discharge, batteries are mostly suitable for electricity storage only for limited periods of time. They also age, which results in a decreasing storage capacity.

For electrochemical energy storage, the specific energy and specific power are two important parameters. Other important parameters are ability to charge and discharge a large number of times, to retain charge as long time as possible and ability to charge and discharge over a wide range of temperatures.

Author details

Petr Krivik and Petr Baca

*The Faculty of Electrical Engineering and Communication,
Brno University of Technology, Czech Republic*

Acknowledgement

This chapter is supported by the EU project CZ.1.05/2.1.00/01.0014 and by the internal grant FEKT-S-11-7.

8. References

- Calabek, M. et al. (2001). A fundamental study of the effects of compression on the performance of lead accumulator plates, *J. Power Sources*, Vol. 95, 97 – 107, ISSN 0378-7753
- Dell, R.M. & Rand, D.A.J. (2001). *Understanding Batteries*, The Royal Society of Chemistry, ISBN 0-85404-605-4, Cambridge, UK
- Linden, D. & Reddy, T.B. (2002). *Handbook of Batteries, Third Edition*, McGraw-Hill, Two Penn Plaza, ISBN 0-07-135978-8, New York, USA
- Nelson, R. (2001). *The Basic Chemistry of Gas Recombination in Lead-Acid Batteries*, Santa Fe Drive, Denver, Colorado, USA
- Rand, D.A.J. et al. (1998). *Batteries for Electric Vehicles*, Research Studies Press Ltd., ISBN 0-86380-205-2, Taunton, Somerset, Great Britain
- Rand, D.A.J. et al. (2004). *Valve-regulated Lead-Acid Batteries*, Elsevier B.V., ISBN 0-444-50746-9, Netherlands
- Ruetschi, P. (2004). Aging mechanisms and service life of lead-acid batteries. *J. Power Sources*, Vol. 127, 33–44, ISSN 0378-7753
- Vincent, C.A. & Scrosati, B. (2003). *Modern Batteries*, Antony Rowe Ltd, ISBN 0-340-66278-6, Eastbourne, Great Britain
- Zimmerman, A.(2009). Nickel-Hydrogen Batteries: Principles and Practice, Available from <http://www.aero.org/publications/zimmerman/chapter2.html>