

The World of Batteries

Function, Systems, Disposal



Stiftung
Gemeinsames
Rücknahmesystem
Batterien

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Preface

Portable energy sources are having an ever greater impact on our modern lives and this is probably one of the reasons why our brochure “The World of Batteries” has become progressively popular over the years.

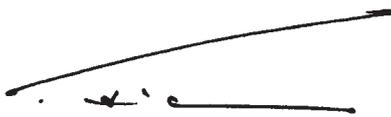
Electronic devices increasingly require higher power from ever lighter batteries/accumulators and consequently batteries and accumulators have been and are being adapted to meet the latest technological advances. Sales figures for alkaline manganese and lithium systems provide indisputable evidence for this.

However, even today, there is still no such thing as a “wonder battery” incorporating all the desired characteristics of a battery; energy density, light construction, safe handling and the ability to undergo thousands of recharge cycles. For this reason, there will continue to be many different battery systems and battery types which fulfill the particular operation requirements of a device.

“Recycling processes for batteries” has been given higher priority in this brochure as currently 90 % of all batteries are recycled to recover their metal content.

The brochure has been thoroughly revised to bring it up to date with the latest advances in mobile power provision.

We are pleased to be able to present to you with our 2nd completely revised issue of the “World of Batteries”.



Dr. Jürgen Fricke
Chairman GRS Batteries

Hamburg, December 2007

First Section: The Development and Functionality of Consumer Batteries

Beginnings 1789

The history of electro-chemical energy storage began with scientific investigations into electricity. Names such as Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827) are associated with this work and live on today in terms such as “galvanic cell” and “volt”. In 1789, while conducting an experiment, Galvani noticed that the legs of a frog began to twitch when they came into contact with two different types of metal. He concluded there was a connection between electricity and muscle activity.

Ten years later, Volta constructed the first simple battery. He put together alternating discs of copper and zinc in a column, with a sheet of paper soaked in a salt solution inserted between each of the layers. The “Voltaic pile” produced electricity when the plates were connected together with wire. Higher voltage could be extracted when several piles were connected in series.

Johann Wilhelm Ritter (1776-1810), who worked with Goethe in the area of natural science, developed a battery in 1802, the so-called “Ritterian pile”. The pile consisted of layers of copper and cardboard soaked in a table salt (sodium chloride) solution. The device could be charged with electricity and released current on discharge. The pile is considered to be the fore-runner of the accumulator, the rechargeable battery.

In the following centuries work on galvanic elements continued intensively and by the dawn of the 20th century, the original battery, which could only be operated while stationary, had been developed into a supremely practical dry element. The French engineer Georges Leclanché, the German physician Dr Carl Gassner (1855-1942) and Paul Schmidt (1868-1948) were instrumental in its development. Leclanché invented the manganese dioxide zinc cell with ammonium chloride acting as the electrolyte. The cell is still in wide use today. At a later date, Gassner and Schmidt succeeded in thickening the previously liquid electrolytes, hence laying the foundations for transportable batteries.

History of the development of the battery

| | | |
|------|--------------------------------|--|
| 1600 | Gilbert (England) | First electro-chemical experimentation |
| 1789 | Galvani (Italy) | Discovery of electricity while experimenting with animals/frogs |
| 1800 | Volta (Italy) | Discovery of the Volta cell/“Voltaic pile” |
| 1802 | Cruikshank (England) | First electric battery for mass production |
| 1802 | Ritter (Germany) | First accumulator “Ritterian pile” |
| 1820 | Ampère (France) | Discoverer of electromagnetism |
| 1833 | Faraday (England) | Publication of Faraday's Law |
| 1836 | Daniell (England) | Discovery of the “Daniell elements”/galvanic cell |
| 1859 | Planté (France) | Invention of the lead acid battery |
| 1860 | Leclanché (France) | Invention of the “Leclanché cell” manganese dioxide zinc element |
| 1888 | Gassner / Schmidt (Germany) | Invention of dry cells |
| 1899 | Jungner (Sweden) | Invention of the nickel-cadmium battery |
| 1901 | Edison (USA) | Invention of the nickel metal hydride battery |
| 1932 | Schlecht & Ackermann (Germany) | Invention of sintered electrodes |
| 1947 | Neumann (France) | Successful sealing of the nickel cadmium battery |
| 1960 | Union Carbide (USA) | Development of the alkaline manganese battery |
| 1970 | | Development of the valve-regulated lead acid battery |
| 1990 | | Commercialisation of nickel metal hydride battery (e.g. for vehicles) |
| 1992 | Kordesh (Canada) | Commercialisation of rechargeable alkaline manganese batteries |
| 1999 | | Commercialisation of lithium ion polymer batteries |
| 2002 | | Limited manufacture of fuel cells (PEM, for consumer batteries and vehicles) |
| 2006 | | First MP3 player with “bacteria batteries” (not yet commercially viable) |
| 2007 | | First “paper batteries” (not yet commercially viable) |

The principle of chemical storage of electrical energy is probably very much older. As early as approx. 250 BC, the Parthians were using clay pots, into which was inserted a copper plate and iron rod. This has been proposed as evidence that even then man had some understanding of galvanisation. The Egyptians are said to have manufactured copper plating galvanized with antimony some 4,300 years ago.

Operation Principles

The principle of a battery or accumulator can be demonstrated with two containers of water placed at different heights. If water is poured into the upper container and the two containers are connected by a tube, the flow of water can turn a wheel. When the upper container is empty, it can either be refilled with fresh water or the water from the lower container can be poured into the upper container. In effect, a battery functions just like these two water containers.

In a battery, the containers are called electrodes and instead of water, electrons flow between the electrodes. The electrons are “stored” in the electrodes and rather than turning a wheel, they power a mobile phone or MP3 player. The difference between a battery and an accumulator is that when the electrode (upper container) is empty, either the old battery is replaced by a new battery (filled with fresh water) or an accumulator is recharged (the water from the lower container is poured into the upper container). The higher the container, the steeper the connecting water tube and the faster the water wheel turns.



The “Ritterian Pile”, developed by Ritter in 1802, is considered to be the forerunner of the accumulator.

In batteries, height is called voltage and the flow of water current. The greater the voltage, (the higher the position of the water container) the more work the battery or accumulator can perform (for two containers of the same size). The bigger the water containers, the longer the water wheel can turn. In batteries, the size of the water container is its capacity. It indicates how many electrons can be stored in the electrodes. The greater the capacity the longer the MP3 player can play.

It is preferable to talk about electrical power rather than current when referring to batteries, as the current always has the same voltage and current multiplied by voltage is power. Power multiplied by time is energy. A battery is an electro-chemical energy converter, which can directly convert stored chemical energy into electrical energy. In other words, the minus pole releases electrons in large quantities at a “high” pressure and the plus pole “hoovers” them away. The “pressure difference” is the battery voltage; the flow of electrons per unit of time is the current.

The power capability of a battery is defined by its voltage in volts (determined by the chemical configuration of the battery) and its capacity in amp-hours (determined by the quantity of active material).

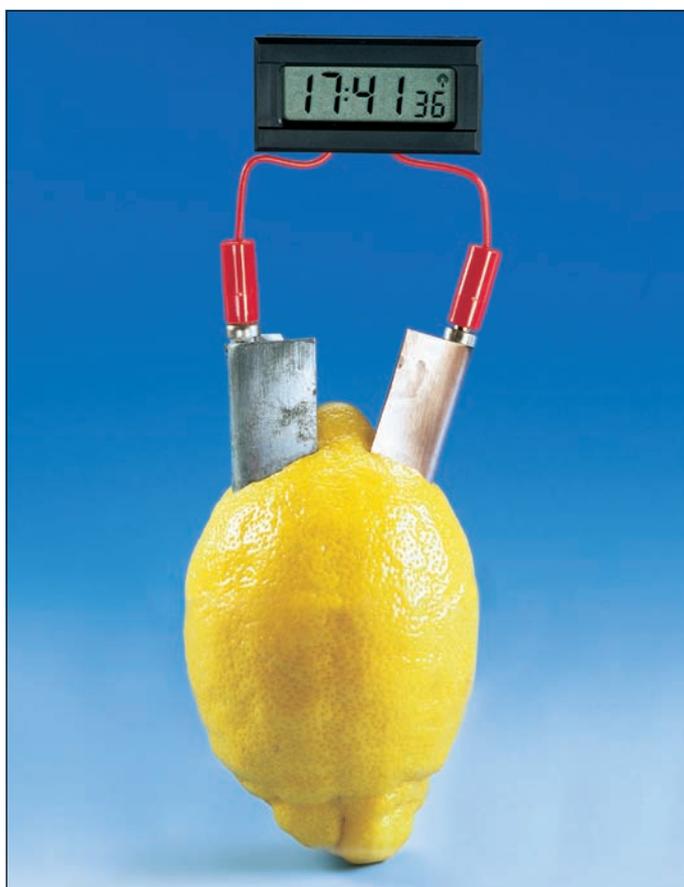
A MP3 player needs more energy per unit of time than a clock, hence there is a demand for different designs of battery producing the same power.

Differences between Primary and Secondary Systems

Needless to say, current does not stop at the poles. There is always a complete current cycle in batteries. The current of ions “flows” through the electrolyte fluid from one electrode to the other electrode. The attendant electro-chemical reactions take place during the flow. A variety of electrode materials release electrons (minus pole) and other materials “hoover” them away (plus pole). Pocket torches and television remote controls typically use manganese dioxide zinc batteries. There are two types of manganese dioxide zinc batteries, the “zinc carbon” and “alkaline manganese” also termed “alkaline”. In both of these battery types, zinc is the material supplying the minus pole with electrons because zinc likes to release its electrons as fast as possible. The plus pole is made of manganese dioxide, which assimilates the electrons.

The electrode materials are called “active mass” and must not touch in the battery or a short circuit will be created and the battery will automatically discharge. A separator is used to separate the active mass. This is made from a type of paper soaked in electrolyte solution. Ions from the manganese dioxide flow through the pores in the paper to the zinc – and so the cycle of current is completed.

Rechargeable batteries (also known as secondary batteries, accumulators or accu packs) allow spent chemical energy to be restored by recharging. A recharger device pumps electrons from the plus pole back to the minus pole. This recharges and reacti-



If you pierce a lemon with a copper plate and a zinc plate, without the plates touching, a voltage of about 1 V can be measured between the plates. The voltage is sufficient to run an electric clock. The metal strips are referred to as electrodes. The chemical reactions take place at the electrodes. Instead of energy being released as heat or light, it is emitted in the form of electrical energy.

The lemon could be replaced by table salt solution or any other conductive solution. If you dip two different metals in a conductive solution, you will always be able to measure a voltage.

The lemon battery shows that electricity can be produced from chemical reactions. Without such electrochemical processes, there would be no batteries or accumulators.

vates the electrode mass. The discharge/recharge process can be repeated up to a thousand times. Primary batteries can only be discharged once.

The lemon battery demonstrates how electricity can be produced by a chemical reaction. Without such electro-chemical reactions, there would be no batteries or accumulators.

There are significant differences between the specific storable energy, resilience and self discharge of primary and secondary batteries. The weight and volume related energy density of primary batteries is usually appreciably greater than that for secondary batteries. Energy density is the energy stored in a battery or cell. It is either referred to terms of mass (specific energy – watt hours per gram) or by volume (energy density – watt hours per cubic centimeter).

Regarding resilience, rechargeable systems produce better results. However, in terms of the general energy density rule, there is one exception, the lithium ion accumulator. Of all the accumulator systems, these batteries can store the most energy per volume/weight and maintain this over many discharge/recharge cycles. The electrochemical system with the highest energy content overall is the alkaline zinc air primary cell. When equipment is switched off, the battery also becomes inactive and the discharging process comes to a halt. Under these conditions the positive electrode and the negative electrode come into equilibrium. The equilibrium is linked to a given system with a certain voltage (for example, zinc carbon 1.5 V per cell, lead battery 2 V per cell).

In practice, under these conditions, self discharging processes persist, but have a greater or lesser effect subject to the system. Self discharge is a temperature dependent process which takes place at the cell's electrodes and is unrelated to the appliance. Self discharge is minimal for primary batteries and the opposite for rechargeable systems. Rechargeable systems can produce messenger ions which encourage self-discharge, as is the case for nickel cadmium (NiCd) and nickel metal hydride (NiMH) accumulators. The messenger ions wander backwards and forwards between the electrodes transporting charges (experts refer to this as a redox system). Further, the nickel (hydroxide) electrodes in NiCd and NiMH systems cannot be stored long-term. Self discharge at a maximum rate of 30 % per month is normal for these systems. Present-day standard accumulators are “empty” after about three months.

This explains why it is not advisable to use standard accumulators in torches or warning lights. The batteries are guaranteed to be dead when the torch or warning lights were needed. Primary batteries of the zinc carbon or alkaline manganese systems would be a far better choice of battery for this use.

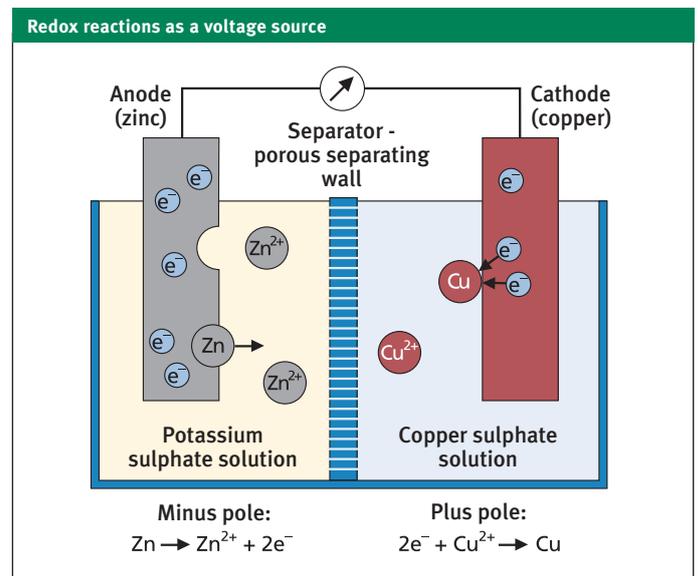
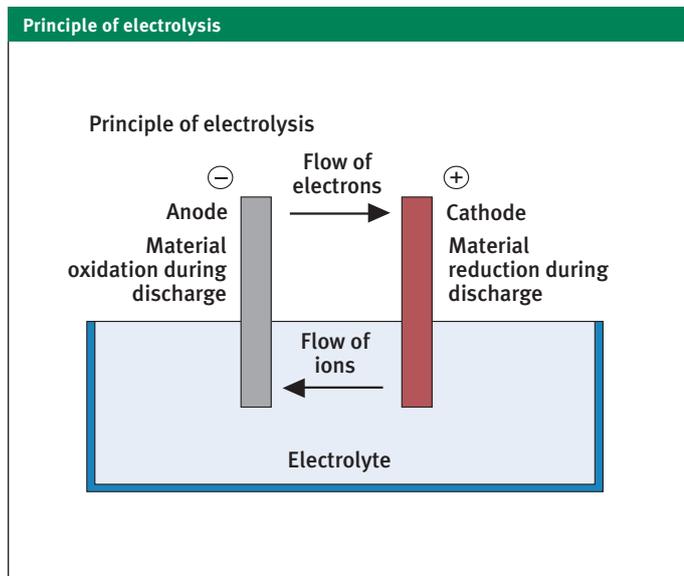
For a few years now advanced NiMH batteries have been available, marketed as “low self discharge” or “ready to use” batteries. These accumulators will be about 70 % “full” after about one year of storage. The degree of self discharge is considerably higher for accumulators than for primary batteries. Exceptions, again, are the lithium ion and lithium polymer batteries. They have the advantage of low self dis-

charge combined with high energy content and high resilience.

Self discharge from primary batteries is minimal. At room temperature they self discharge at a rate significantly lower than two percent a year.

However, there are also processes which increase internal resistance during storage. These processes also reduce resilience.

Loss of useable energy is often only noticed during intense usage (motor applications, flash lights) but this effect has nothing to do with electrochemical self discharge. An increase in internal resistance has not been detected during storage where there is low level discharge.



When electrical energy is extracted from a battery, zinc atoms (minus pole) release electrons (oxidation) which move as zinc ions in solution. The electrons flow along an external conductor to the appliance (for example a pocket torch) and then to the plus pole of the battery. At the plus pole, copper ions absorb the electrons (reduction). In technical terms, the transfer of electrons is a redox reaction. The circuit is completed by ions wandering between the electrodes through the electrolytes (ion flow). The exchange of electrons between appropriate reaction partners is thus the source of electric voltage in batteries. Reduction takes place at the cathode and oxidation at the anode.

Summary of characteristics and examples of the use of standard battery systems

| Type | Zinc Carbon | Alkaline Manganese | Silver Oxide | Lithium | Nickel Metal Hydride | Nickel Cadmium Accumulators | Lithium Ion |
|--------------------------|---|---|--|---|--------------------------------------|-----------------------------|--|
| Voltage | 1,5 V | 1,5 V | 1,55 V | 3 V | 1,2 V | 1,2 V | 3,6 V |
| Minus Pole Anode | zinc | zinc | zinc | lithium | water storing metal alloy | cadmium | lithium cobalt compound |
| Plus pole Cathode | manganese dioxide | manganese dioxide | silver oxide | manganese dioxide | nickel hydroxide | nickel hydroxide | graphite |
| Electrolyte | ammonium chloride or zinc chloride | potassium hydroxide | potassium hydroxide | lithium compound in org. solution | potassium hydroxide | potassium hydroxide | lithium compound in org. solution |
| Characteristics | voltage sinks significantly when discharging, cheap | leak proof, high performance, long-life | voltage constant for long time, very long life | very long storage, voltage stays constant for long time | high resilience, rechargeable | rechargeable, cheap | high resilience, high energy density, rechargeable |
| Use | pocket torches | radios, cameras, toys | watches, calculators, cameras | remote controls, calculator, back-up systems | cordless telephones, digital cameras | video cameras, tools | mobile phones, laptops, digital cameras |

Terminology

The smallest electrochemical unit of a battery is called a cell. A cell has no casing, no contacts and is usually connected to a neighbouring cell in the battery with soldered or welded contacts.

A battery can be recognised by its ready-to-use casing. It has secure connectors and is labeled with manufacturer and type details, battery voltage and other information.

A cylinder is still the most common cell shape. It is easy to produce, has the largest energy density and is mechanically very stable. A cylinder is also a good shape to resist internal pressure. Other standard forms are button cells, round cells, prism cells and flexible sheet cells.

| General Description (Type) | IEC Term | ANSI Standard | BS Standard | Average Weight in g | Dimensions in mm |
|----------------------------|----------------|---------------|-------------|---------------------|--------------------|
| | AlMn/ZnC | AlMn/ZnC | AlMn/ZnC | AlMn/ZnC | |
| Micro | LR 3/R 3 | AAA | AM4 /UM4 | 11/9 | Ø 10.5 x 44.5 |
| Mignon | LR 6 R 6 | AA | AM3 /UM3 | 23/17 | Ø 14.5 x 50.5 |
| Baby | LR 14/R 14 | C | AM2/UM2 | 69/46 | Ø 26.2 x 50.0 |
| Mono | LR 20/R 20 | D | AM1/UM1 | 141/95 | Ø 34.2 x 61.5 |
| 9 V Block | 6 LR 61/6 F 22 | 1604 D | 6AM6/006P | 46/37 | 26.5 x 17.5 x 48.5 |

Second Section: The Technology and Production of Primary Battery Systems

Zinc carbon ZnC

The French engineer Georges Leclanché (1839-1882) invented the manganese dioxide zinc cell with ammonium chloride electrolytes in 1860. Even today, several billion of the galvanic elements named after Leclanché are produced annually across the world. The classic zinc carbon battery continues to be a cheap alternative to alkaline manganese batteries and rechargeable battery systems. Increasing demand for greater capacity and performance will slowly eliminate this battery type.

The zinc carbon element ought, in fact, to be called the “manganese dioxide zinc system with ammonium chloride or zinc chloride electrolytes”. However, what its name actually refers to is its carbon conductor (for the positive electrode, i.e. cathode) and zinc content (for the negative electrode, i.e. anode). Both the negative electrode material and the cell’s housing are zinc.

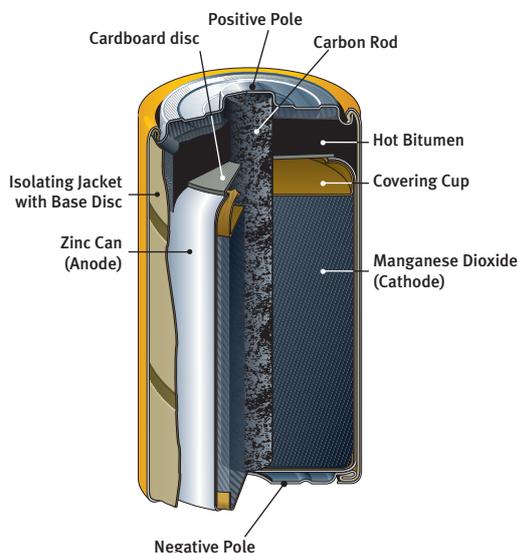
The positive electrode consists of a manganese dioxide mass with a centrally positioned carbon rod as conductor. Depending on the particular system, either an ammonium chloride or a zinc chloride solution acts as the electrolyte. The zinc chloride system is the better quality system.



Zinc Carbon / ZnC

Use of the zinc carbon battery is primarily aimed at appliances which have no real requirement for long-life battery performance, for example, alarm clocks, television remote controls and pocket calculators. As ever more appliances need high performance batteries for their operation, these batteries are increasingly being superseded by batteries from the alkaline manganese system. Although sales of zinc carbon batteries are regressing, they still form a significant percentage of the batteries entering the waste stream. Nearly all zinc carbon batteries are manufactured in five standard sizes, which are present in the waste stream in the following percentages: 2 % AAA, 40 % AA, 24 % C, 28 % D and 6 % 9 V blocks.

Zinc Carbon/ZnC



Alkaline Manganese **AlMn**

Since the Second World War, it has been known that battery systems with an alkaline electrolyte have a relatively high energy density and are relatively resilient. Researchers in the USA at that time were involved in constructing a manganese dioxide zinc cell with an alkaline electrolyte. This type of cell was initially developed solely for military use. By the beginning of the 70s it was beginning to make inroads into a limited civilian market.

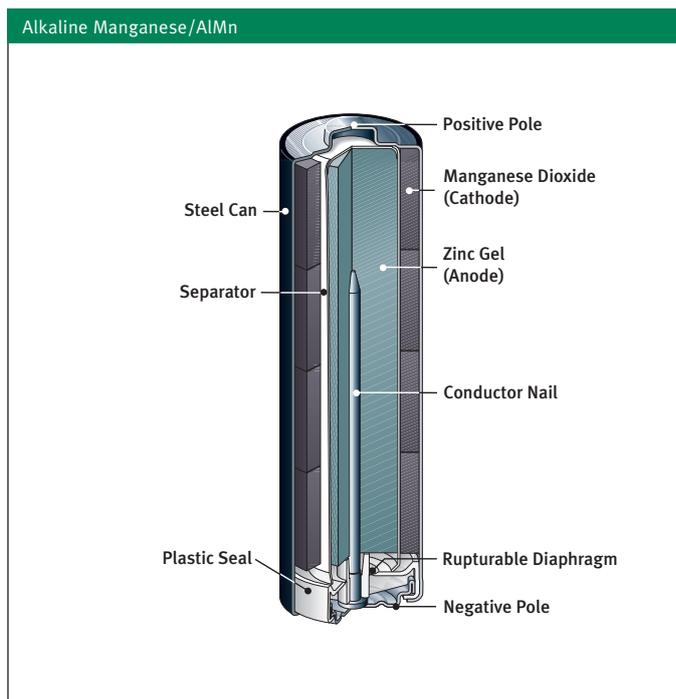
The picture has now changed entirely. Since the mid-eighties, sales of alkaline round cells in Europe have far exceeded those of zinc carbon cells.

As neither the alkaline nor manganese component forms the battery's active material, the alkaline manganese battery ought to be described as the "manganese zinc element with an alkaline electrolyte". In this system the cathode is made from a mixture of manganese dioxide and graphite and the anode is powdered zinc. Both cathode, separator and anode are soaked in the electrolyte potassium hydroxide.



Many mains-independent devices such as MP3 players, organisers (PDA) and digital cameras require high quality batteries with particularly large current reserves. Improved alkaline manganese batteries are now available for high current applications.

The increase in power has come from greater active mass in a denser cathode, more internal cell volume and an improved electrolyte with superior conductivity. The improved alkaline manganese battery performs about 15 times better than the equivalent zinc carbon battery.



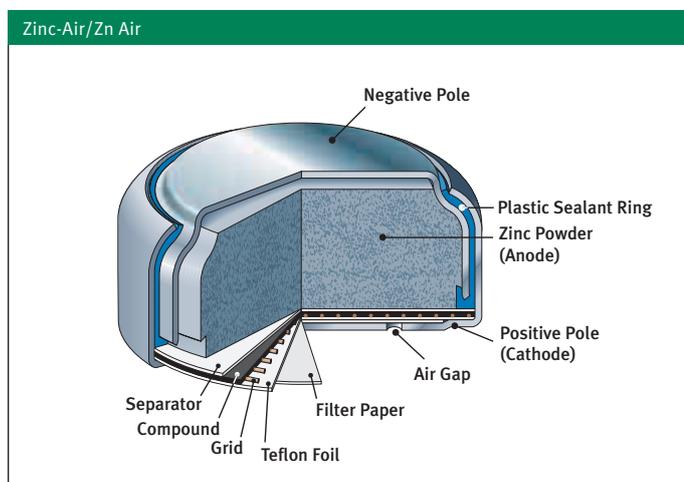
Alkaline manganese batteries are the most ubiquitous battery system of today – two thirds of all batteries and accumulators sold in Germany are from this system. They are available in all sizes from the button cell to heavy industrial batteries weighing several kilograms. The life time of an AlMn battery depends on its application. Every AlMn battery currently entering the waste stream is five or more years old. Round cells used to contain up to 2 % mercury. Unlike cadmium and lead, mercury was never an active participant in the redox reaction. It had a variety of passive functions including preventing the formation of dendrites from amalgamation of zinc. Today, all AlMn batteries are mercury-free, apart from button cells.

Zinc Air ZnAir

In this type of battery, oxygen from the air reacts with a catalytic cathode and zinc anode. The cathode (positive pole) is very thin, leaving a lot of space for anode material (zinc powder). Alkaline zinc air cells have the highest energy density, the highest specific energy and capacity of all the electrochemical systems. Hearing aids are a typical application area.

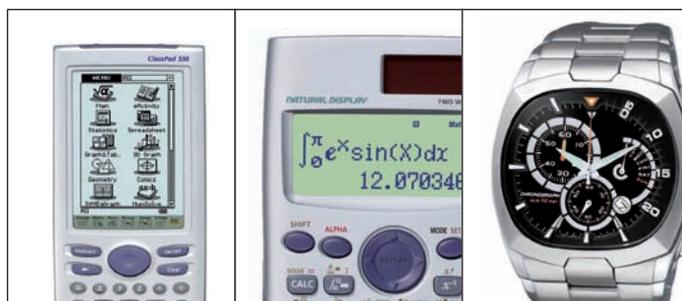


A hearing aid requires a battery with small dimensions, high capacity and a flat discharge surface. Zinc air systems can only be stored for a limited time once activated (after the adhesive foil has been removed when exposed to the air). It is essential that this type of battery be kept hermetically sealed until used. Once the foil has been removed, the cells discharge over a maximum period of 500 hours. Batteries in a dry atmosphere (heated rooms) lose their power even faster as they dry out relatively quickly. Sealed zinc air batteries can be kept for an almost unlimited time period.

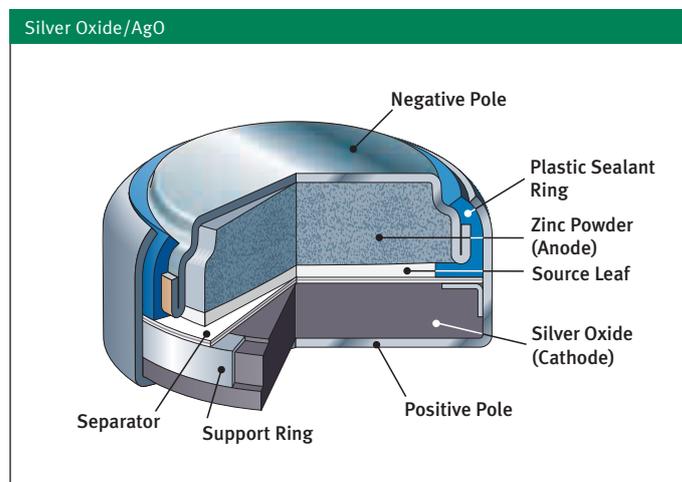


Silver Oxide AgO

This system is used mainly in the manufacture of button cells, the smallest button cells can be very small indeed. Their design is similar to that of alkaline manganese cells, but the manganese dioxide is replaced by silver oxide in tablet form as the cathode material. The anode is zinc powder.



This type of battery uses very expensive raw materials and as such, its application area will continue to be limited to micro devices requiring a battery with high energy content that is highly resilient.



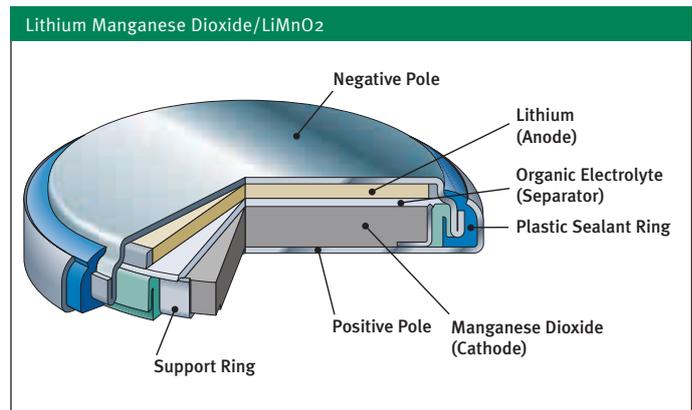
LiMnO₂

Lithium Manganese Dioxide

Researchers and developers working in the last century experimented with just about all the possible combinations of electrodes and electrolytes. Lithium attracted sustained interest as a negative electrode. Lithium is a light metal with a high specific capacity (3.86 Ah/g) and unique electrochemical characteristics. Right from the start developers faced the problem of finding a positive electrode suitable for the negative lithium electrode. Lithium is also difficult to handle, it reacts with moist air and particularly intensively with water. It melts at a temperature of only 180°C.

The strong reaction potential of lithium means that only water-free (anhydrous) materials can be used in its cells. Unlike the standard battery systems, only water-free electrolytes can be used. The electrolytes are often organic or inorganic solvents. The addition of certain salts increases conductivity.

There are several types of primary lithium batteries in a wide range of sizes. Lithium batteries vary in the configuration of the electrolyte and the active substance of the positive electrode, that is, the substance reduced during discharge. This can either be fluid or solid as in lithium manganese dioxide cells. The negative electrode in lithium manganese dioxide cells is lithium and the positive electrode manganese dioxide. The lithium manganese dioxide system is the most widespread of all the systems. The advantages of the lithium cell include high voltage,



high energy density, flat discharge surface, very good storage behaviour and the fact that it can be used over a wide temperature range. In addition, it is available in all construction shapes. Lithium batteries have minimal self discharge which makes them suitable for long-term applications in electronics, telecommunications and metrology. They are also frequently used in photographic equipment, e.g. in automatic film transport, adaptive lighting and flash units.

A new development is the thin lithium flat cell, also known as lithium paper. This battery measures less than 0.4 millimeter and is perfect to fit in bank card-sized intelligent smartcards. Smart cards are active cards with a battery operated microchip and integrated display.



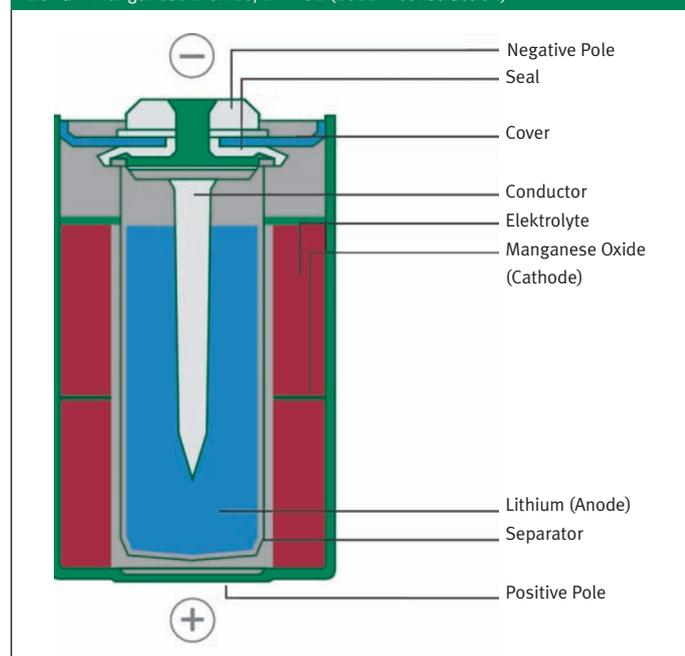
Their transponder functions would not be possible over large distances without the battery in the card. The term transponder is derived from a combination of its actions, transmitting (sending) and responding. Smartcards do not just open doors, they can process entire payment procedures. No matter whether the payment is for train tickets, airplane tickets, motorway tolls or car park tickets, a “smartcard” can perform all these tasks. The new flat cell is also perfect for other applications requiring a very flat, low construction height battery.

Lithium systems are increasingly finding their way into other areas of the consumer market. The combination of lithium with an electrolyte with a low freezing point such as non-inflammable thionylchloride (SOCl_2) produces a high energy density, low weight and low self discharge and the ability to function under extreme conditions. Depending on the particular type of cell and its design, LiSOCl_2 cells may be used in a variety of applications, e.g. back-up systems, supply meters, security systems, alarm systems or positioning systems.

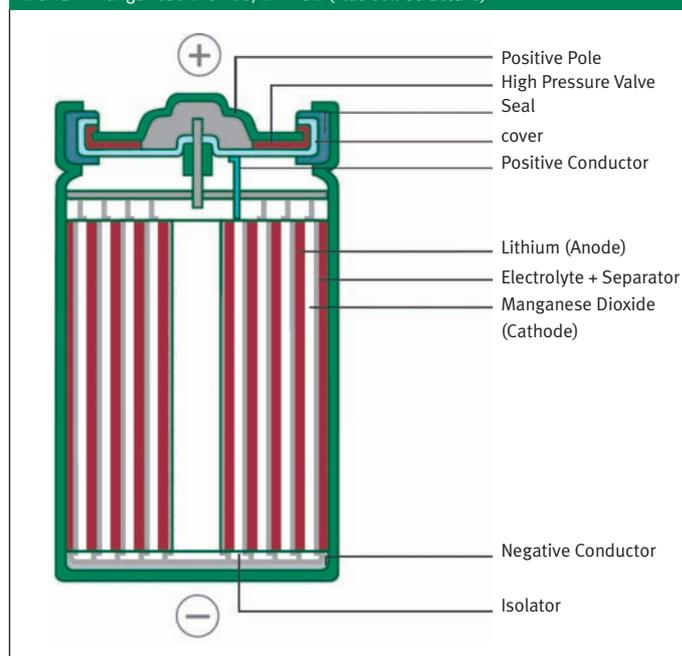
Lithium/Li

Lithium primary batteries come in a variety of construction types. In the bobbin structure, the cathode is cylindrical. The anode is rolled onto the internal housing wall, which has safety advantages as current from unintentional short circuiting cannot be very high. Heat which generates principally on the contact surface between the anode and cathode can be dispersed externally. High pressure build up cannot occur, whether or not a predetermined breakage point has been integrated in the design. In flat cell constructions, the anode is pressed onto the container base. The cathode is a disc positioned above the anode, separated from anode by the separator. This construction has the same safety advantages as the bobbin structure. Lithium button cells are similarly constructed, apart from the sealing system (plastic seal).

Lithium Manganese Dioxide/ LiMnO_2 (bobbin construction)



Lithium Manganese Dioxide/ LiMnO_2 (Flat Cell Structure)



The Technology and Production of Secondary Battery Systems

Nickel Cadmium NiCd

The active components of NiCd accumulators, when charged, are nickel hydroxide in the positive electrode and cadmium in the negative electrode. The electrolyte is potassium hydroxide. The advantages of this battery system, in comparison to the newer rechargeable systems, are its high resilience, fast recharge time and low-temperature durability to minus 15 °C. Hence NiCd rechargeable batteries are still widely used for cordless tools. However, its high cadmium content means there are other applications, such as cordless telephones, for which this system is no longer suitable and has been replaced by NiMH accumulators. Another drawback is its relatively low energy content compared to alkaline and lithium primary systems. Memory effect may also be a problem.

The classic memory effect is related to the negative cadmium electrode and only a problem with nickel cadmium accumulators. A phenomenon of accumulators is that they are very easy to incapacitate if incorrectly handled. The technical explanation is that metal crystals gather at the negative electrode during lengthy charging with low current or during premature charging, started before the accumulator has completely discharged. The crystals increasingly encroach on the available

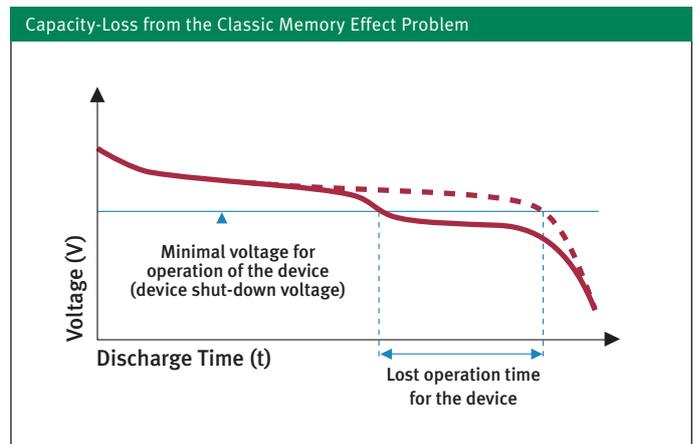
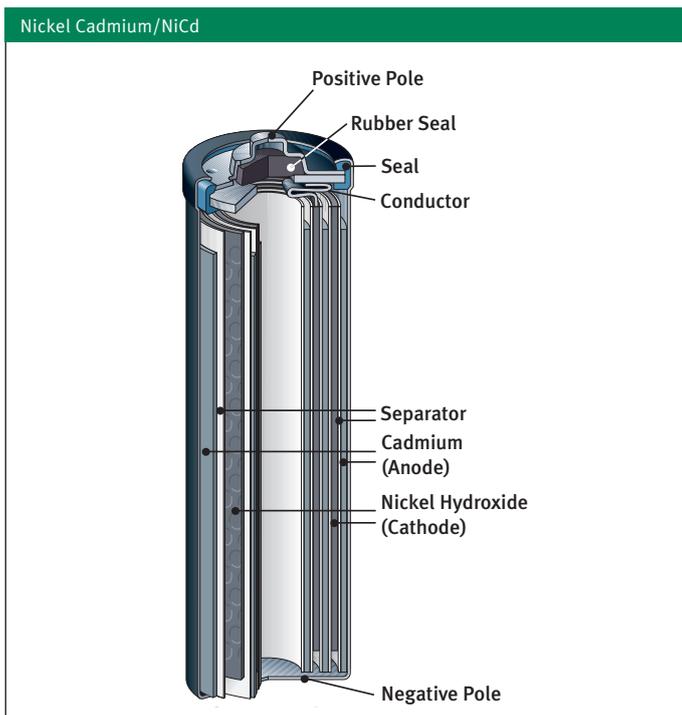


capacity of the negative electrode until the accumulator can only supply the specified voltage for a few minutes. These days, the recommendation is never to top-up recharge, but to wait until the accumulators have discharged to the extent that the appliance can no longer function. At this stage the “shut-down voltage” for the device has been reached and the recharging process can begin.

An accumulator can easily be discharged by using the appliance until it no longer receives sufficient voltage, but an even better method is to use a recharger with a discharge function. If a

NiCd accumulator is ever incapacitated by the classic memory effect, it can be reactivated with a special refreshing device, which will entirely discharge the accumulator before recharging it. The classic memory effect problem is thus reversible.

Modern rechargers avoid the memory effect problem by measuring the exact charge state before recharging as well as indicating when the maximum capacity limit has been reached.



Lead Pb

The lead accumulator is one of the oldest accumulator systems, it has been around since the middle of the 19th century. It will not be discussed in any detail in this brochure as its main application area is cars, driving batteries and industrial batteries. Unlike other accumulators, one cell produces 2 V. A lead accumulator is not subject to the memory effect problem, that is, it can always be recharged regardless of its charge status. It exists mainly in two construction forms:

Open cells: can be refilled with water (e.g. starter batteries or emergency power systems)

Closed cells (maintenance-free cells): These cells have a high pressure valve to keep the operational pressure within acceptable limits. The electrolyte is incorporated into either a gel cushion or a mat. Lead accumulators using the mat technology are becoming increasingly important in the market.

Positive Electrode: $\text{PbO}_2 + 3 \text{H}^+ + \text{HSO}_4^- + 2 \text{e}^- = \text{PbSO}_4 + 2 \text{H}_2\text{O}$

Negative Electrode: $\text{Pb} + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{H}^+ + 2 \text{e}^-$

Total Reaction: $\text{Pb} + \text{PbO}_2 + 2 \text{H}_2\text{SO}_4 = 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$

Nickel Metal Hydride NiMH

Batteries from this system (in a charged state) consist of the following main components: a positive nickel hydroxide electrode, a negative electrode of a hydrogen-storing alloy and an alkaline electrolyte. The key difference between NiMH and NiCd batteries is that a hydrogen-storing alloy entirely replaces the cadmium. Fast innovation cycles have meant that the energy density per volume of NiMH accumulators is nowadays higher than that of standard NiCd accumulators.

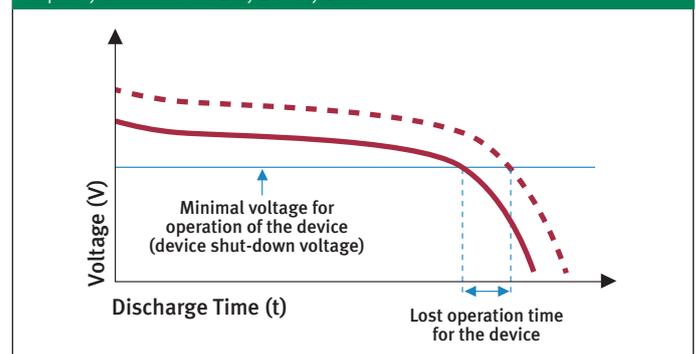


Nickel metal hydride batteries are developing in several directions at once. Advances in electrodes and electrolytes have improved the number of potential recharge cycles to the extent that they now approaches that for nickel cadmium cells. At the same time, cells are being developed with very little internal resistance lowering heat output while simultaneously increasing performance. These cells are used in electro-bikes, which occasionally have to supply 30 Amps or more over a long period – a long uphill haul. A further advance is the development of a NiMH cell able to function at high temperatures. These cells are integrated into emergency lights or back-up applications and have the advantage of taking up considerably less volume than nickel cadmium batteries of a similar capacity. NiMH batteries are an option for many applications which traditionally would have used NiCd batteries – the primary construction of both the batteries is identical.

The lazy-battery effect, comparable to the classic memory effect, can occur with NiMH technology. This problem can likewise be entirely remedied. In principle the causes are the same as those for the classic memory effect (permanent recharging or partial recharging), but in this case effects the positive nickel hydroxide electrode. The discharge voltage drops only slightly and, in fact, the same revitalisation treatment solves the problem, i.e. entirely discharging the accumulator from time to time, preferable two to three times in a row.

A recharger with a discharge function is a help for this process. The consequences of the lazy battery effect are entirely reversible and an accumulator can regain its old performance. The lazy battery effect is far less serious than the classic memory effect. The voltage drops somewhat lower than normal, but the usage time remains virtually the same and, as with the memory effect, the accumulator is not damaged.

Capacity-Loss from the Lazy Battery Effect



Lithium Ion Li Ion

Attempts to develop a lithium battery were made very early on in the history of the battery. Today lithium ion batteries have many applications and are the system of choice if a high energy density is required. Rechargeable lithium batteries do not contain lithium in its metal form. Their main use is in telecommunications and portable computers. As industrial batteries, the lithium ion system is used in hybrid electrical vehicles and vehicles with the new wire harnesses. Lithium ion accumulators are not compatible with NiCd or NiMH accumulators; they require a specific method of charging and cell management.



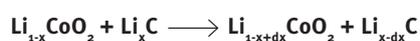
Although lithium batteries also function like galvanic cells, the active materials do not react chemically. Instead, lithium ions are incorporated into the positive electrode and the negative electrode. During charging, ions are in effect pumped from one electrode to the other. They are, so to say, swapped between the positive and negative interface material.

This system is a safe alternative to lithium metal galvanization. The energy density is mainly determined by the cathode material – cobalt oxide is commonly used today, which is suitable for a maximum of 180 watt hours per kilogramme. Lithium nickel cobalt (LiNiCo) can produce an energy density of maximum 240 Wh/kg. The principal reaction equation can be represented as:

Initial charge:



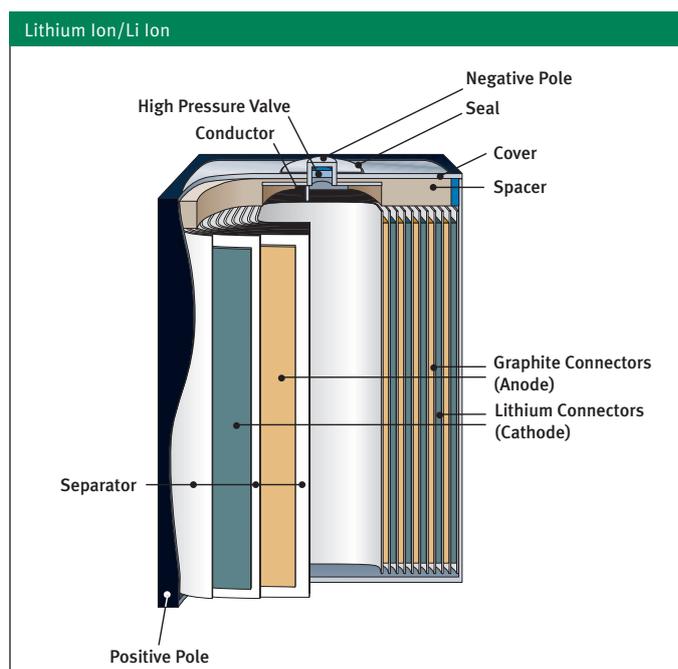
The reverse reaction occurs upon discharge. Lithium ions are released from the negative material and return to the positive material.



Of all the rechargeable systems, lithium ion batteries have the greatest energy density per volume or weight. As with other secondary systems, the period between recharging depends on the application. The energy density of lithium ion batteries is typically double that of standard nickel cadmium batteries. In addition there is potential for even higher energy densities in the future. The resilience aspect is good and they are similar to nickel cadmium batteries regarding discharge. A high voltage of 3.6 V per cell means unicellular batteries can be constructed. Most mobile phones function with an unicell. A nickel based battery requires three 1.2 V cells in series to achieve the same voltage.

Rechargeable lithium batteries have no memory or lazy effect.

To store the batteries, the majority of manufacturers recommend 40 percent charge status and a cool environment.



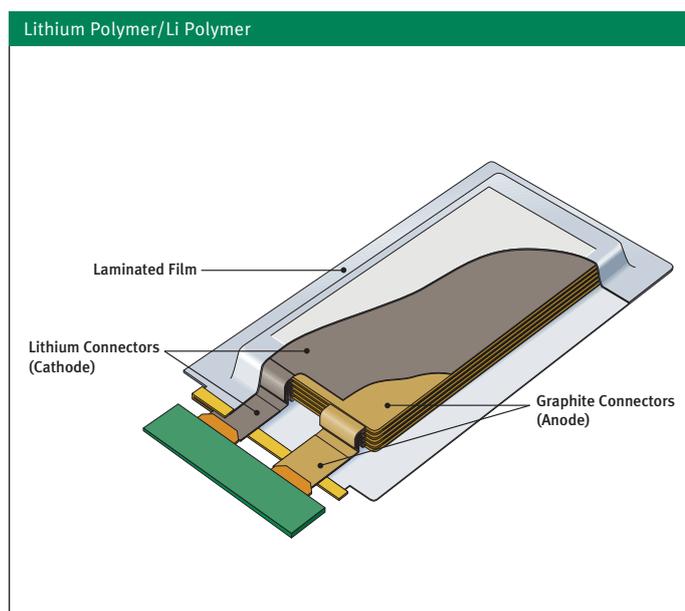
Lithium Polymer Li Polymer

For several years now, academic and industrial scientists have been working on polymer electrolytes to replace conventional liquid organic electrolytes and simultaneously make the classic separator redundant. The lithium polymer battery differs from other rechargeable lithium batteries by the electrolyte it uses. The electrolyte is a plastic-like layer, which cannot conduct electricity, but allows the exchange of ions (exchange of electrically charged atoms or groups of atoms).

The polymer electrolyte replaces the traditional porous separator element soaked in electrolyte. Without a liquid electrolyte these accumulators are absolutely leak-free and aluminium or metallic plastic foils can be used instead of a metal as housing for the cell.

The dry polymer solution simplifies manufacture, improves robustness, safety and also permits a slender form. It can be produced in any shape to occupy the empty space in appliances. Even extremely flat, foil-like shapes are possible. With a cell thickness of about one millimeter, device designers can let their imagination run wild when it comes to the shape, configuration and size of the battery.

However, the dry lithium polymer suffers from poor conductivity. Internal resistance is too high to deliver the power peaks necessary for modern communication devices, which leads to problems with the hard disc of portable computers. Heating the cells to 60°C or more improves conductivity, but is a specification which cannot be implemented in portable applications.



Most of the commercial lithium polymer batteries used in today's mobile phones are hybrid cells containing gel electrolytes. The correct term for these batteries is lithium ion polymer batteries. They are the only functioning polymer battery used in mobile phones. Although the characteristics and performance of both lithium ion types (lithium ion battery and lithium ion polymer battery) are similar, the lithium ion polymer battery is the only one in which a solid electrolyte replaces the porous separator element.

Gel electrolyte is inserted merely to improve ion conductivity. Lithium ion polymer batteries have their market niche in applications requiring ultra thin or flexible geometric shapes, for example, credit cards.

Third Section: Disposal

EU Battery Directive

The Battery Directive (directive on the return and disposal of used batteries and accumulators – BattV) came into effect in 1998. It has since been regularly revised to incorporate the new EU environmental regulations. Amendments have included a ban on the marketing of batteries exceeding the defined mercury, cadmium or lead content limits.

Batteries and accumulators may not be disposed of in the household waste, regardless of their electrochemical system or toxic material (heavy metal) content. Spent batteries and accumulators either must be returned to an outlet where batteries or accumulators are sold, or taken to a municipal collection point. Both retail and local governments have an (unpaid) obligation to take back batteries, regardless of brand or battery system. Manufacturers and importers of batteries in their turn are required to provide retail and municipalities with suitable collection containers and to take back the collected portable batteries at no cost.



Batteries do not belong in household waste

To ensure that the returns requirement is comprehensive, the Battery Directive offers manufacturers and importers two options. Either they install their own collection system for their batteries or they join a common collection system.

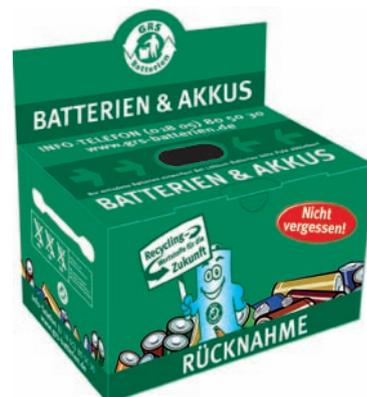
Stiftung GRS Batterien

The Foundation Common Collection System of Batteries (GRS Batterie) is a common collection system for manufacturers. It was set up in 1998 by Duracell, Energizer, Panasonic, Philips, Saft, Sanyo, Sony, Varta and the German Electrical and Electronic Manufacturers Association (ZVEI). As a foundation, GRS Batterien is a non-profit making organisation. Currently (end of 2007) 900 manufacturers and importers use GRS Batterie's services. They pay a disposal fee for the batteries and accumulators they market in Germany. The fee depends on weight and electrochemical system.

The manufacturers and importers who have a contract with GRS Batterie annually sell almost 1.5 billion batteries and accumulators. Their return collection is organised by GRS Batterie by providing collection and transport containers to all ubiquitous retailers, commercial and industrial users, public institutions and local municipalities. There are currently about 170,000 collection points for spent batteries and accumulators across Germany. GRS Batterie also organises the collection of full containers, sorting of the batteries and accumulators into the different electrochemical systems and disposal management (recycling or disposal).

In 2007 GRS Batterie collected 14,000 t of spent batteries. More than 90 % of those batteries and accumulators were recycled under the motto "Recycling- Wertstoffe für die Zukunft" (Recycling – resources for the future). The extensive documentation GRS Batterie has made of disposal services allows it undertake outcome evaluations for the regional authorities.

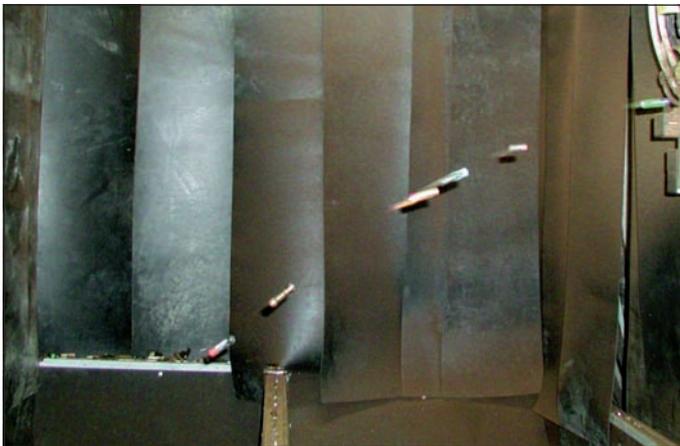
Recent figures and facts about the system are published regularly on our internet site www.grs-batterien.de.



Sorting Process

Portable batteries and accumulators are collected as a mixture as the consumer cannot be expected to pre-sort. Once collected, the batteries and accumulators are separated into the various electrochemical systems. This initial sort is important for the next step in recycling as the battery content determines the recycling method.

GRS Batterien uses two sorting methods:



The Electromagnetic Process

This method identifies magnetic round cell systems with an electromagnetic sensor. An adjacent magnetic field is disturbed depending on which electrochemical system is being transported over the sensor. The “disturbance” induces a measurable change in voltage. Up to six batteries can be isolated per second. The sorting purity is 98 % as a minimum.



The X-ray Process

Once the round cells have been sorted for size, they pass through a x-ray sensor. The various battery systems are recognised by the grey gradation on the x-ray image. More than 26 batteries can be recognised per second with a purity of more than 98 %.

The total capacity of the sorting plant is over 15,000 t/a.

Regardless of the first sorting process, all AlMn and ZnC batteries are put through a further sorting step, the UV sensor. Until 2005 European battery manufacturers used UV sensitive pigments in the paint of mercury-free AlMn batteries and some of the ZnC mercury-free batteries. The sensor recognises these batteries, which can be recycled cheaply as they are guaranteed mercury-free.



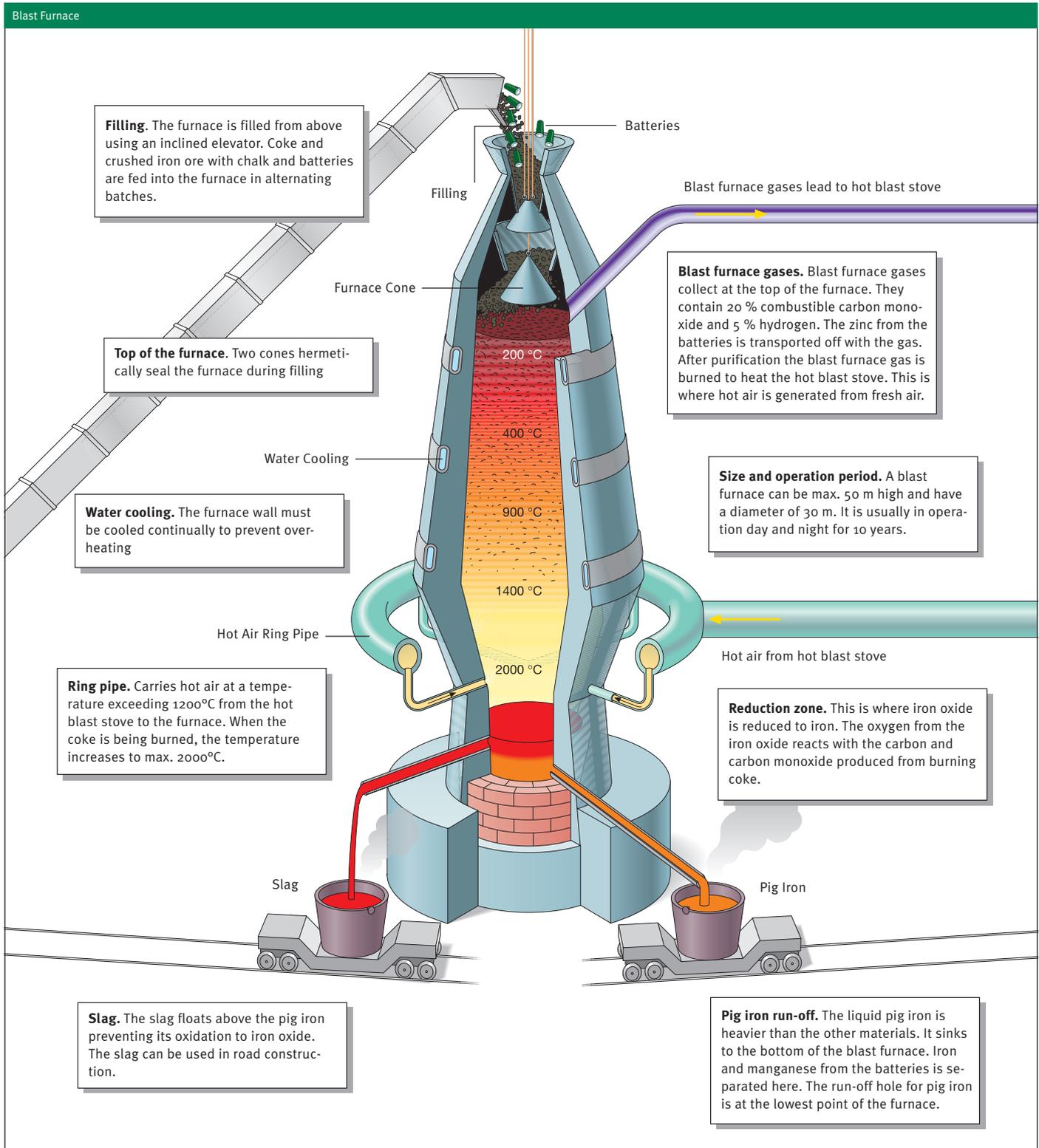
Although it has been illegal to market batteries containing mercury (apart from button cells) since 2001, older batteries always find their way into the waste stream. GRS Batterien regularly analyses the mercury content of collected AlMn and ZnC batteries. The results show that the mercury content is continually decreasing, making the UV sensitive pigment no longer necessary.

Hence the conditions are met for the number of batteries which can be recycled to continue increasing.

Recycling Processes

The percentage of batteries which can be recycled continues to rise. More than 90 % of isolated batteries can be recycled for their metal content and the trend is moving ever upward. Particular attention is being given to recycling processes producing high quality products.

One recycling method that guarantees high quality is recycling in a blast furnace. Alkaline manganese and zinc carbon batteries are recycled returning pig iron, zinc concentrate and slag.

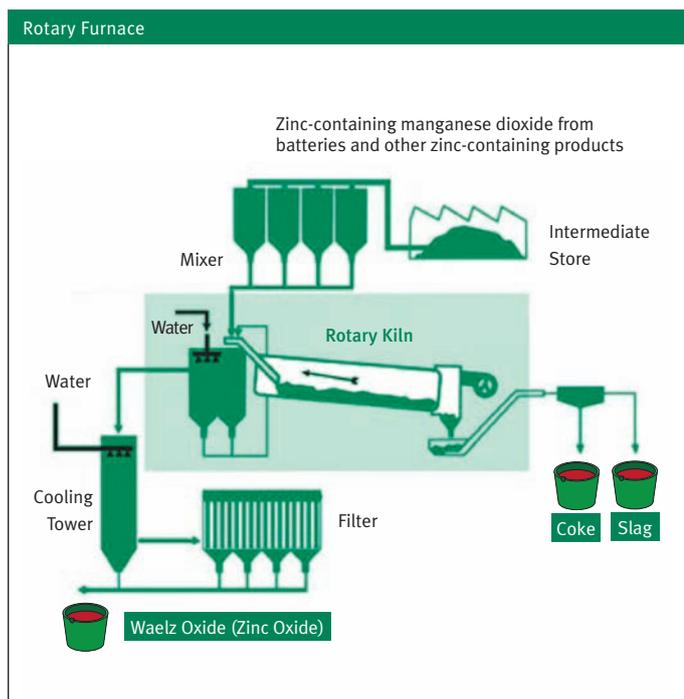


In the following pages a few recycling methods for specific battery systems are described in more detail.

AlMn and ZnC Batteries

In addition to recycling in the blast furnace process, other methods are also used.

1. For example, alkaline manganese and zinc carbon batteries can be cut into small pieces in a monitored process and the iron content separated from manganese oxide containing zinc. The iron part is returned to steel works and the manganese oxide containing zinc processed to zinc oxide in a rotary kiln.
2. The electric-arc furnace process produces ferro-manganese (among other substances) from batteries, zinc is recovered as powdered zinc. Incidental slag is used in path construction. Electrical heating is performed by an electric arc between two carbon electrodes or by resistive heating. Contamination by fuel or combustion gas can not occur. Liquid steel, termed soft steel is particularly pure when produced in electro-arc-furnaces.



NiCd Batteries

As a rule, cadmium is distilled while in a vacuum or inert atmosphere and the remaining steel nickel mixture used to produce steel. The recovered cadmium is usually used to manufacture new NiCd batteries.

NiMH Batteries

The focus here is on the recovery of nickel. There is the potential for the release of hydrogen while cutting up the NiMH batteries into small pieces, so the processing has to be monitored. Once the plastic content has been removed, a product with high nickel content is left, a product that is used as an important alloy component in the production of steel.

Lithium Batteries

GRS Batterien recycles lithium primary system batteries (LiMnO_2) using a vacuum distillation procedure. The focus of this procedure is on the recovery of nickel containing iron and ferro-manganese. Lithium acts as a reduction agent in this process. Rechargeable lithium systems (Li ion or Li polymer) are processed to recover the metal content, in particular cobalt, nickel and copper.

Mercury Button Cells

There are presently several methods in Germany to process mercury-containing button cells. The methods are aimed at recovering mercury from mercury-containing components. Mercury-containing waste is treated in a vacuum-thermal process. The mercury is evaporated at temperature between 350°C and 650°C , it is then condensed at a lower temperature and reintroduced to the economic cycle. The mercury-free “de-mercurised” steel is sold.

The following materials (amongst others) can be recovered by battery recycling:

Recovery of Primary Products during Battery Recycling

Iron

Iron in the battery
In battery engineering, iron is used as housing and as an alloy component, matrix or substrate for electrodes. Batteries with pure iron electrodes have been realised, but have not become established, e.g. the nickel iron accumulator.

Iron as a recyclable product
Iron is essential to the manufacture of steel. Steels are alloys of iron, which are produced from mixing (alloying) with other metals and non-metals (in particular carbon). Iron is the world's most used metal with excellent strength and durability characteristics when alloyed with other metals such as chrome, molybdenum and nickel. It is used in the manufacture of vehicles, ships and throughout the entire construction industry (steel concrete) and it is one of the three ferro-magnetic metals (in addition to cobalt and nickel), the characteristics of which allow it to be used industrially in generators, transformers and electro-motors.

Zinc

Zinc in the battery
Metal zinc is one of the most important negative electrode (anode) materials in non-rechargeable batteries. In ZnC battery systems, the zinc-containing outer housing also acts as a negative electrode, where zinc is oxidised to zinc oxide. Zinc has proved a reliable anode material in many primary battery systems. It produces a high voltage potential, is inexpensive, easily available and environmentally benign.

Zinc as a primary product
Zinc is a blue-white, base metal, which is quite brittle at both room temperature and above 200°C. Between 100°C and 200°C it is easy to shape. In air zinc forms a weather-proof layer of zinc oxide and zinc carbonate. Consequently, it is used in corrosion protection regardless of its base metal characteristics.

Manganese

Manganese in the battery
Manganese dioxide performs as both oxidation agent and electrode material in dry batteries. The principle of a ZnC battery was initially realised by the Frenchman Georges Leclanché in 1860. He encased a graphite cathode in manganese dioxide. In secondary battery engineering, manganese plays an important role as a component in the mixed metal alloy of NiMH accumulators and as the cathode material in Li ion accumulators.

Manganese as a primary product
Manganese is a grey white, hard and very brittle metal. Its high readiness to react with sulphur and oxygen and its material-improving characteristics make it very important for the metal industry. Manganese is used in desoxidation and desulphurisation or as a stability-enhancing alloy element in steels. After iron, manganese is the second most common metal.

Nickel

Nickel in the battery
Nickel is used mainly as cathode material. Since the development of Nickel cadmium accumulators in 1899 by Waldemar Junger, they have proved their worth in various accumulator systems (e.g. NiCd or NiMH). As nickel electrodes are unsatisfactory conductors in practice, the nickel component is usually sponge nickel on a good conductive matrix base.

Nickel as a primary product
Nickel is a silvery white metal. It is hard, malleable and easy to polish. Like iron and cobalt, it is ferromagnetic. Nickel is an important alloy metal principally used in the purification of steel. It makes steel non-corrosive and increases its hardness, durability and malleability. Steel alloyed with nickel is used in highly corrosive environments.

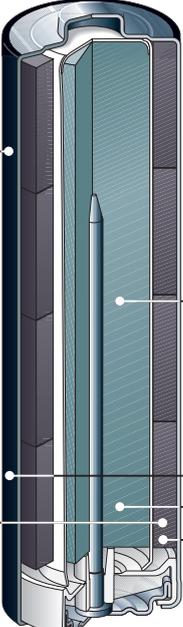


Figure: Alkaline Manganese Battery

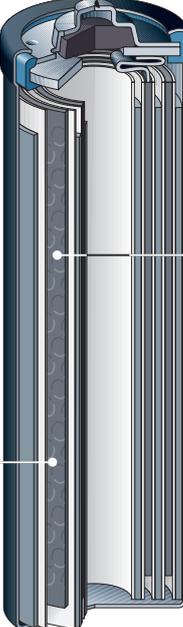


Figure: Nickel Cadmium Battery

Fourth Section: The Future

The future of today

The periodic table has only a limited number of elements suitable for making a battery and as such, there are not going to be any new battery systems in the near future. But there can always be an exception to the rule and for sometime now, nickel zinc has become increasingly popular, ousting in part the alkaline manganese battery in high current applications. Nickel zinc (abbreviation ZR) is an alkaline system in which its positive mass is primarily nickel hydroxide and its negative mass zinc. The trend towards miniaturisation has been prevalent for several years. Smaller and smaller devices require ever more complex energy management in an increasingly diminutive space. There are currently rechargeable lithium polymer batteries on the market weighing only 8g.



It is almost impossible to get through a day without using battery power in one form or another and now there is a demand for portable energy supplies from virtually all application areas. The battery operated electrically powered milk frother is no longer a novelty, but there are any number of other “hidden” batteries operating in our service. Electronic controlled elements permanently measure the tire pressure of quality vehicles and are also vital in heating meters and back-up systems. Intelligent clothes are meanwhile nothing new and flashing kids’ shoes have long since been surpassed by the battery-powered clothing now conquering the international fashion world. Going by the name “Wearable Technologies”, just about every designer has intelligent clothing in their portfolio. The clothing itself can supply the electrical power. There

are jackets with mobile phones stitched into the jacket’s arms with solar cells in its collar to recharge the accumulator. The jacket’s wearer is unlikely to find his mobile needs recharging, at least not when the sky is cloudless. Shoes have been transformed into a communication design by not only protecting your feet but also recording your pulse via sensors while you run. Clothes of the future not only will keep you warm, but will also provide a controlled climate. Hidden in the back of your jacket will be a computer weighing only a few grammes managing your telephone calls or recording your pulse rate, heart rate or “felt” climate data.

The future of tomorrow

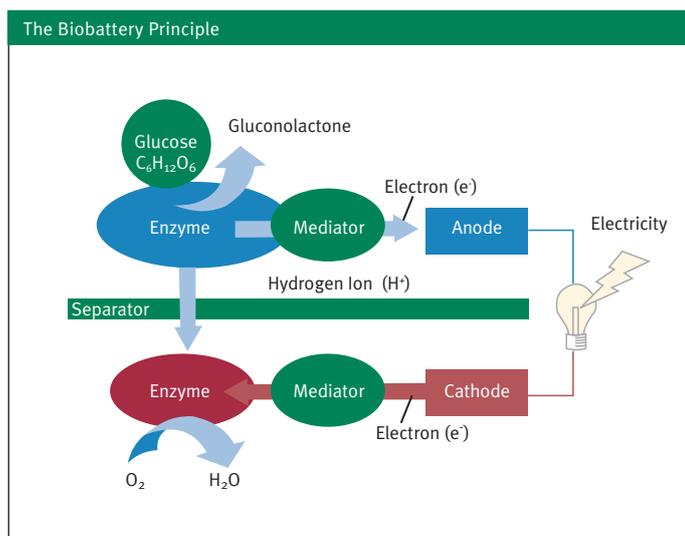
Not just clothing will be intelligent. Smartcards have been around for some years now. They might look like a standard credit card but in fact have numerous extra functions and are able to upload and store a limited amount of new information. This is made possible with a 0.4 millimetre thin lithium battery. The innovation flood is seemingly unending. “Intelligent” newspapers with organic electronic components, batteries and displays embedded in the newspaper are doubtless going to be a huge application area. Newspapers of the future will be a chimaera between the digital and printed world. Who wouldn’t enjoy animated photos waving at you from the newspaper, mini-videos showing replays of the finest goals from the latest football games or an article that reads itself out loud.



The future of the day after tomorrow

Electricity from sugar? A battery powered by sugar to appeal to environmentally concerned consumers? A prototype of such a battery can already produce up to 50 milliwatts.

A sugar-containing fitness drink will no longer be drunk, but instead used to supply enough current to power an MP3 player. Power is generated from sugar by enzymes and a conductive metal. The enzymes operate close to the anode. A newly developed cathode structure is responsible for supplying adequate oxygen to the system and ensuring that the requisite amount of water is retained. An optimised electrolyte is responsible for achieving a comparatively high energy level.



The researchers took their inspiration from photosynthesis in plants. Sugar is broken down into its components by enzymes at the centre of the battery. Electrons and hydrogen are released during the process, which then combine with oxygen from the air. The energy released is stored by the electronic mini device.

Needless to say, “sugar batteries” are entirely biodegradable. The carbohydrates used in the manufacture of the battery can easily be extracted from plants the world over. However, it is too early to market the battery. The edge of a single cube-shaped module of the battery measures 4 centimetres. Four cubes have to be connected together before a single sound can be extracted from, e.g. an MP3 player.

A lot has happened since Galvanis’ twitching frog’s leg about 220 years ago, but the history of the battery is no where near its end. Who knows what is waiting around the corner? The brochure “The World of Batteries” will keep your readers up-to-date.

Fifth Section: Addendum

Glossary

Active Mass: the substance in the electrodes involved in the charge and discharge reactions.

Anode*: during discharge, the negative electrode of any electrochemical current source. In batteries the anode is a metal, for example zinc or lead, which during discharge is “burnt cold”, that is, oxidised.

Cathode*: term for the positive electrode of any electrochemical current source during discharge. In charged batteries/accumulators the cathode is a metal oxide.

Electrode: usually a metallic conductor which serves to conduct carriers of electric charge in a liquid, in a gas, in a vacuum or on the surface of a solid body, e.g. during electrolysis.

Electrolysis: the separation of an ion conducting fluid (electrolyte) while connected to a sufficiently high voltage. The products of electrolysis of a water system are the gases hydrogen and oxygen.

Electrolyte: Ion-conducting fluid inside a battery/accumulator which provides the requisite medium for charge and material transport between the electrodes. Liquids, pastes or solid electrolytes are used.

Electron: negatively charged particle

Inert gas: non-reactive gas

Ion: electric charged particle

Secondary battery: rechargeable battery, accumulator

Self discharge: cell capacity loss during storage. The degree of self discharge is affected by the ambient temperature.

Vacuum distillation: temperature-dependent separation of the individual components of a chemical mixture taking place in a vacuum.

* The negative electrode is always the anode and the positive electrode is always the cathode in primary systems. The same is only applicable to accumulators during discharge.

Abbreviations

AgO: silver oxide

AlMn: alkaline manganese

ANSI: American National Standards Institute. Us American agency for industrial procedure standards. The German equivalent is the Deutsche Institut für Normung e.V. (DIN)

BattV: Battery Directive on the collection and disposal of spent batteries and accumulators (German Version)

Hg-free: mercury-free

Hg-containing: mercury-containing

HgO: mercury oxide

IEC: International Electrotechnical Commission, international standards commission for electro-technology and electronics, located in Geneva

JIS: Japanese Industrial Standard

Li, primary: lithium, non-rechargeable lithium system

Li ion/Li polymer: lithium ion, lithium polymer, rechargeable lithium system

NiCd: nickel cadmium

NiMH: nickel metal hydride

ppm: parts per million (for example one milligramme per kilogramme)

Zn air: Zinc air

ZnC: Zinc carbon

Sources

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Recycling –

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