

Batteries
ACME Faculty, EHVE course
B.Sc. Studies, III year, V semester
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Nickel-Metal Hydride batteries

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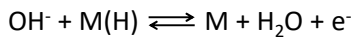
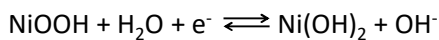
- In 1969 it has been discovered, that LaNi_5 alloy can reversibly absorb in form of a hydride gaseous hydrogen formed as a result of water electrolysis (experiments at Batelle, Switzerland).
- In 1978 the first cell containing LaNi_5 has been manufactured as well as other cells with nickel-lanthanides alloys (however they had short cycle life).
- At the end of 80s the first cells with the more sophisticated electrodes were designed: the single metals were substituted with doped alloys. It enabled cheap manufacturing of cells with long cycle life. They were made available on the market in 1989.

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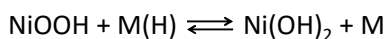
Nickel-Metal Hydride batteries



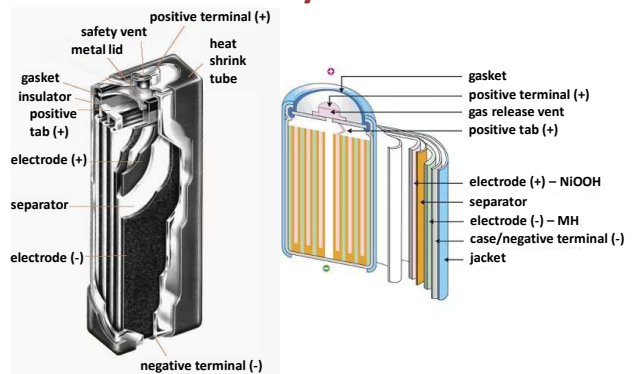
Reactions at electrodes (discharge to the right):



Overall reaction:



Nickel-Metal Hydride batteries

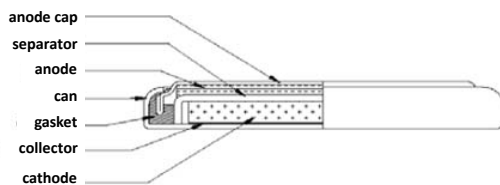


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Nickel-Metal Hydride batteries



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NiMH: design

- Anode usually consists of two metals alloy with stoichiometry of a A_2B , AB , AB_2 or AB_5 type. Usually one can absorb hydrogen exothermally and the other one can absorb it in endothermic process.
- Metal A is usually a lanthanide or other transition metal that can form a stable hydride as a result of electrochemical reaction with hydrogen formed in water electrolysis. Metal A has to release hydrogen easily due to the electrochemical reaction, so the hydrogen ions can recombine with hydroxide ions. Also, metal has to absorb hydrogen to a large extent.

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NiMH: design

- Metal B is a metal (usually transition one), that is corrosion resistant (protects metal A against conditions inside the cell, namely hydrogen and strong base presence) and possess catalytic properties (decrease activation energy of the absorption process).
- Whole alloy need to have not only high capacity for hydrogen absorption, but also absorb it at relatively low pressure, just not very low – the alloy that forms too stable hydride also cannot easily release hydrogen. The alloy should not degrade with the cycles of absorption and desorption. It is important that metal catalyzes hydrogen formation from water in the strongly basic environment. Obviously, good diffusion of hydrogen through an alloy is a basic requirement.

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NiMH: design

- Cathode is made of nickel oxyhydroxide;
- Electrolyte is a concentrated (ca. 6 mol dm^{-3}) water solution of potassium hydroxide (usually) – KOH.
- Separator is made of hydrophilic unwoven fabric, usually of polyolefines such as polypropylene, which is resistant to concentrated bases.
- Electrodes are soaked with electrolyte as much as it is possible, however not the separator, as it should enable gas exchange and their diffusion.
- Cases are made of steels resistant to bases.

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NiMH: manufacturing

The designs of NiMH cells are similar to those of NiCd cells. Thus, all contemporary cell designs such as:

- coin / button;
- prismatic;
- cylindrical.

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NiMH: pros and cons

Advantages of NiMH cells:

- 1.5x higher energy density compared to NiCd;
- High resistance to overcharging and deep discharge; almost unlimited resistance apart from too fast (dis)charge;
- Proper operation and good capacity even when cycled fast;
- Possibility of faster discharge than NiCd;
- Cycle life of up to 1000;
- Materials relatively neutral towards environment;
- Compared to NiCd almost no memory effect;
- Cheaper than Li-ion cells.

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NiMH: pros and cons

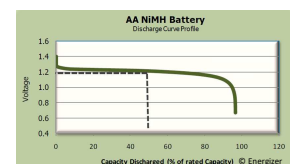
Disadvantages:

- Poor operation (low capacity) at low temperatures; unreliable below -20°C ;
- Fast self-discharge – 3x faster than that of NiCd;
- Lower energy density compared to Li-ion;
- More expensive than NiCd.

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NiMH: operation conditions

- OCV is ca. 1.2 V;
- Operation range from 1.4 V (charged) to 0.9 V (discharged);

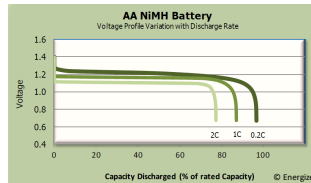


- Electrolyte does not participate in an overall cell reaction, so it does not change its composition during operation of the cell; Thus, it maintains high conductivity and does not change operation conditions; due to that, cell does not require any maintenance (refilling);

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NiMH: operation conditions

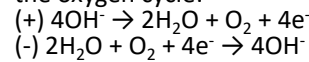
- Optimal charge rate ranges from C/12 to C/3. Rate above 1C can speed up cell ageing. Priming/formatting rate should be of ca. C/40.
- Discharge can be anything below 1C. Possible up to 4C, but with a distinctly lower capacity. Discharge with the rate over 4C is not beneficial to the cell.



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NiMH: operation conditions

Overcharging would trigger the oxygen cycle:



Total sum of the cycle is null. However, a lot of heat is generated as a result which shortens cell life;

Anode capacity is bigger than that of a cathode, so oxygen recombines with H^+ ions forming in an excess (results in water). When overcharging is too intensive (large current exceeding cathode maximum rate of oxygen generation), then it might come to the free hydrogen generation and inner cell pressure increase.

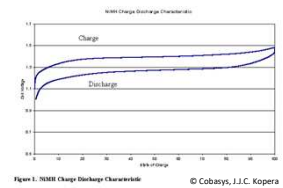
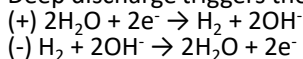


Figure 1. NiMH Charge Discharge Characteristics © Cobasys, J.J.C. Kopeck

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NiMH: operation conditions

Deep discharge triggers the hydrogen cycle:



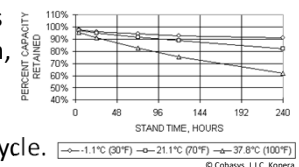
As in the oxygen cycle, the main hazard is heat generation. As before, too high current may disrupt the cycle and generate gaseous product.

Too deep discharge may lead to the cell polarization reversal in case there are multiple cells operating together as a battery. One of the cells then works reversed (too small potential difference leads to the outweigh by the rest of cells) by discharging irreversibly to zero capacity and whole battery is not working properly any more.

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NiMH: operation conditions

- Self-discharge: NiMH cells lose capacity by their own, mainly due to hydrogen desorption from anode and through the oxygen cycle.



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The higher temperature is, the faster self-discharge is. Typical self-discharge at the room temperature is 1-3% a day (relative to the nominal capacity), but during the first day it may be even up to 5 times that. Temperature increase by 10°C increases self-discharge rate 1.5-2x.

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NiMH: operation conditions

- Partial charging results in memory-like effect, to a much smaller extent than it was the case with NiCd cells, however. In case of NiMH the most important factor towards memory effect is a formation of the wrong crystalline structure of NiOOH (γ instead of β) at the interface of not fully discharged phase with that freshly charged. Priming/formatting the cell can remove the memory effect, though.

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NiMH: storage conditions

Optimal storage conditions:

- Low temperature (below room temperature);
- Not shorted and not connected to the circuit;
- Charged;

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NiMH: modifications

Anode alloys compositions:

- A_2B A: Mg or Ti; *e.g.* Ti_2Ni (old prototypes)
 B: Ni;
- AB A: Zr, Ti; *e.g.* $ZrNi$ (old prototypes)
 B: Ni, Fe, Cr, V;
- AB_2 A: V, Ti; *e.g.* $ZrNi_2$ (rarely is use)
 B: Zr, Ni; (30% higher capacity than
 AB_5 , but less stable)
- AB_5 A: La, Ce, Ti, *e.g.* $LaNi_5$
 Mischmetal;
 B: Ni, Co, Mn, Al; (the most popular in industry)

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NiMH: modifications

Modifications consist not only in metals choice, but also their doping. Naturally doped alloy is a Mischmetal ($Ce_{0.48}La_{0.25}Nd_{0.17}Pr_{0.05}+0.05$ of other lanthanides), which is a residue of monazite processing, after removing thorium and radium (which monazite is ore of). For instance, in AB_2 type alloys the nickel is doped with iron, chromium, cobalt or manganese.

Dopants are also used for enhancing the alloy parameters, especially to obtain low volume changes during cycling, better catalytic properties and better hydrogen absorption.

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NiMH: modifications

- Electrolyte can also be modified. The most important modification is an addition of LiOH to enhance mechanical stability of electrodes, notably cathode. NaOH is also added sometimes to enhance the electrolyte performance at the high temperatures, however, its addition shortens cell's lifespan;
- Separators are modified for their better wettability (hydrophilicity). It is achieved with sulfonation (addition of sulfate groups on fibers) or acrylic acid addition.
- In whole cells special alloys can be used that can recombine oxygen and hydrogen resulting from oxygen and hydrogen cycles.

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NiMH: applications

- Electronic devices – the same applications as lithium-ion cells (that once substituted NiMH cells) phones, cameras, music players; Compatible with most of devices due to similar voltage to alkaline and NiCd cells.
- Hybrid cars, with notable example of Toyota Prius, that was the first mass-produced hybrid car. This model still possess the title of the biggest number of vehicles produced (>3.5 million).

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