

## Advances in alkaline batteries

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### Abstract

Alkaline rechargeable battery systems have been under development for more than 100 years yet. Different electrochemical couples of positive and negative materials have been subject of research and development, but only the nickel–cadmium system (NiCd) and, since about 10 years, the nickel–metal hydride system (NiMH) have achieved the stage of large volume production. Particularly, sealed NiCd and NiMH cells have been established in a variety of applications. Recent advances with the NiMH system have brought about portable batteries with energy storing capabilities coming close to those of alkaline primary cells. Although representing a technically interesting solution even for electric vehicles, relatively high cost will limit the use of rechargeable alkaline batteries to small high power batteries for hybrid electric vehicles. Basic technological developments for materials suitable for high energy and high power design are described.

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### 1. Introduction

Alkaline batteries have been playing an important role in the field of electric energy storing devices for more than 100 years. Since the discovery of the nickel–iron accumulator by Edison and of the nickel–cadmium battery system by Jungner [1,2], a multitude of inventions has contributed to make alkaline rechargeable electrochemical energy storing systems viable for a big market. This is particularly valid for the big consumer market driven by new electronic devices emerging since the last 20 years. The situation looks different for the traction and UPS market. Because of the considerably higher price in comparison to lead-based batteries, these systems—most of them based on nickel as cathode material—have been mainly used for those applications where lead–acid batteries exhibited weak behaviour. This mainly means high continuous power capability, fast recharge and long service life, particularly in terms of energy turnover.

In general, there are five different systems which have been under development for a long time in the last century. The NiCd system first developed by Jungner is still present in the market. Especially, the realisation of maintenance-free sealed NiCd cells by Neumann et al. [3] in 1950s made this system dominating the market for portable accumulators for more than 30 years. NiFe batteries played a less important role. Because of the instability of the Fe anode, no sealed and

maintenance-free battery could be realised hence limiting the use of NiFe accumulators to some traction and UPS applications. Despite a lot of efforts also the NiZn system could not be developed successfully to a rechargeable battery system. Lacking stability of the negative electrode with the tendency of growing Zn dendrites is the main reason for limited service life [1].

The only rechargeable alkaline system using a cathode other than a Ni-based material is the manganese/zinc system. Considerable efforts have been taken to bring this system to the market place [4]. Its most interesting features are high specific energy and relatively low cost. Nonetheless, lacking stability in terms of capacity turnover kept this interesting system from penetrating the market on large scale.

By end of the 1980s, the nickel–metal hydride system appeared in the market [5,6]. Main change to the other nickel-based rechargeable system is the replacement of the anode by a material capable of reversibly storing hydrogen. This development was enabled by the availability of new hydrogen-storing alloys which are stable under exposure to strong caustic media and a high number of charge/discharge cycles [7,8]. Increased specific capacities and high capacity densities of the negative electrode resulting from the employment of these hydride materials have been the reason for a considerable increase of energy storing capacity of cells manufactured therewith. Particularly, the increased energy density has been highly desired by the upcoming market of new portable applications in the last decade bringing about a variety of new electronic products as are notebook computers, mobile phones, consumer electronics, etc. NiMH bat-

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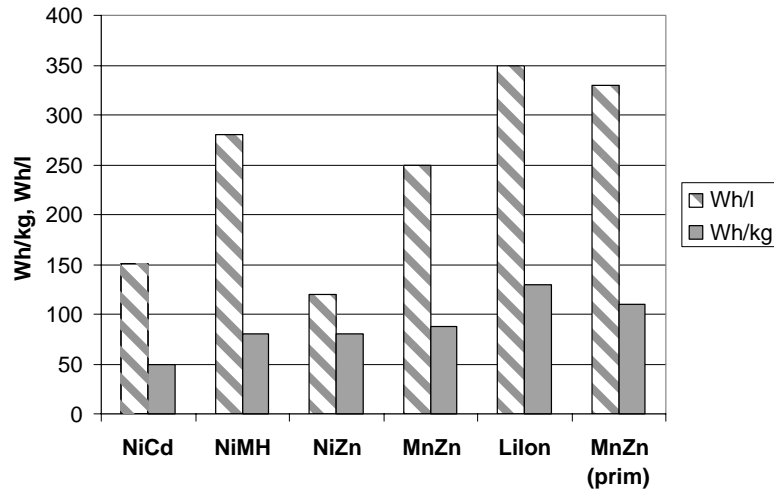


Fig. 1. Specific energy and energy density of various portable battery systems (cell based).

teries have continuously taken over the biggest part of the NiCd market since. Besides the significantly better technical properties, the lacking of poisonous heavy metals as, e.g. cadmium is another important argument. However, the further spreading of NiMH batteries runs under the strong competition by the rechargeable Li-ion system, which has a considerable advantage in terms of specific energy.

Fig. 1 displays specific energies and energy densities for the various systems. Because of the described technical limitations only NiCd and NiMH batteries will be considered for future applications. Mid term, the use of NiCd batteries is expected to be limited to special applications which NiMH batteries cannot serve.

## 2. Alkaline battery systems for different applications

Besides portable applications, it is mainly the market for current and future traction which is challenging the development of alkaline rechargeable systems. While for high portable applications high energy storing capability is in the

focus of development, traction and vehicle applications are requesting especially high power capability and long service life in terms of calendar endurance and capacity turnover.

The realisation of cells with high capacities, and high energy storing capability was enabled by a couple of different basic developments in the past. At the positive polarity, the replacement of the positive Ni sinter electrode with the Ni foam electrode has brought about an around 50% volumetric capacity increase. This technical achievement was enabled by the considerably higher void volume fraction of the foam electrode and the employment of new high density types of nickel hydroxides. While Ni sinter electrodes typically have capacity densities of approximately  $450 \text{ mAh/cm}^3$ , nickel foam type electrodes reach values up to  $700 \text{ mAh/cm}^3$  (Fig. 2). The technical progress on the negative polarity was even more impressive. The change from the originally used Cd sinter electrode to the negative slurry electrode resulted in a some 30% volumetric capacity increase. A more drastic increase, however, was achieved by replacing cadmium hydroxide at the negative electrode with hydride-forming metal alloys. Up to 150% higher volumetric

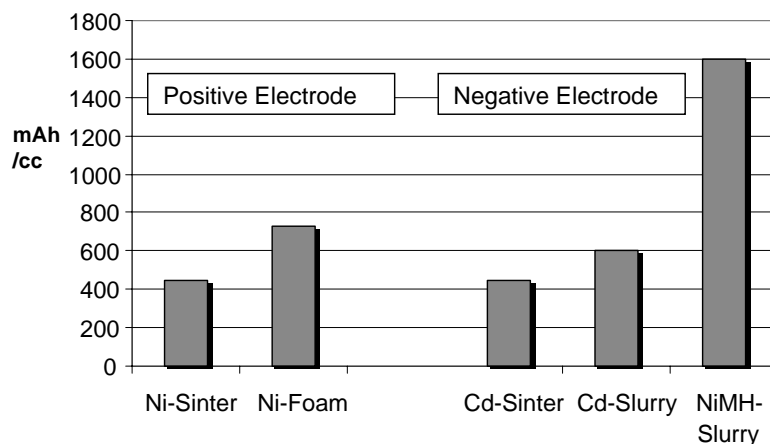


Fig. 2. Capacity densities of positive nickel electrodes, negative cadmium and metal hydride electrodes.

capacities have been achieved meanwhile (Fig. 2). This is the main reason why NiMH cells on the portable market available these days have an about 60% higher storage capability than corresponding NiCd cells have. Besides the improvements with the electrodes other achievements as are thinner separator materials, new electrode design and special electrolyte compositions have also contributed to technical progress.

The main advantage of alkaline batteries in vehicles is their high charge and discharge power capability and their excellent long term endurance. Both features are essential for future vehicle applications. This is especially true for hybrid electric vehicles (HEVs) which are very likely to come to the market place on larger scale within the next years, but also for new vehicle electric supply systems. The electric power supply systems will be based on an increased voltage level for supplying a multitude of new energy and power demanding vehicle functions. Alkaline batteries for pure electric vehicles (EVs) will remain a small niche market, because of the still limited driving range even with these advanced batteries and the relatively high cost. Both make these cars little interesting for a mass market. Over the last years, a couple of different products were developed. By use of advanced materials and optimised electrode and cell design, specific power capability up to 1300 W/kg could be demonstrated. Life testing exhibited results demonstrating the chance of realising power systems which may reach the life endurance of typical cars (10 years, more than 200,000 km).

In the following sections, the considerations for future rechargeable alkaline systems will be limited to recent developments with the nickel–metal hydride system. The development of the active storing electrode materials on both polarities and their influence on the electrochemical cell performance will be in the focus.

### 3. Experimental

X-ray diffraction analysis of electrode materials was performed with a Siemens D500 diffractometer with Cu K $\alpha$  radiation. Scan rate was 0.01° (2 $\theta$ ), step time was 0.3 s. The samples were measured and analysed four times, the peak broadening (full width at half maximum (FWHM)) was determined via a Siemens software. The degree of disorder was calculated from the line width of the (1 0 1) line according to [9], lattice parameters were calculated via Siemens software. X-ray diffraction of the hydride phase of hydrogen storage alloys was performed in a hydrogen pressure cell under hydrogen loading. The lattice parameters were determined after Rietveld refinement. Pressure–composition–temperature (PCT) curves were obtained from the alloy supplier. Thermal analysis was performed with the thermal analysis unit DSC 200 from Netzsch. For the electrochemical examinations, positive electrodes were made from the nickel hydroxide samples consisting of said nickel hydroxide, a cobalt source like cobalt hydroxide or cobalt oxide and PTFE as a

binder. A polyolefin foil was used as a separator. The negative electrode consists of a hydrogen storage alloy and a conductive carbon/PTFE mixture. A mixture of 6.5 mol/l KOH and 0.5 mol/l LiOH was used as an electrolyte. The capacity of the NiMH cells was limited by the positive electrode. The capacity was measured after 10 charge/discharge cycles at a C/5 rate. From discharge curves with various discharge currents, the average discharge voltage was obtained, characterising the rate capability. Hydrogen storage alloys were also examined in cylindrical NiMH cells using a foam type positive electrode.

## 4. Results and discussion

### 4.1. Effect of nickel hydroxide material on the performance of NiMH batteries

The nickel hydroxide materials used in this study had a spherical or nearly spherical shape. The materials differ in surface area, powder morphology as well as in crystallite size and in the degree of disorder in the crystal structure. The structure of  $\beta$ -nickel hydroxide consists of Ni(OH) $_2$  slabs from which protons can be deintercalated during electrochemical cycling to yield  $\beta$ -NiOOH. This process is reversible, thus  $\beta$ -nickel hydroxide can be cycled between  $\beta$ -Ni(OH) $_2$  and  $\beta$ -NiOOH. During overcharge  $\beta$ -NiOOH may be transferred to  $\gamma$ -NiOOH, where water (inter-slab water) and alkali ions are intercalated between the NiOOH slabs in the  $\gamma$ -phase [10,11]. Crystal imperfections due to stacking mistakes of the Ni(OH) $_2$  slabs or growth defects lead to a so called disordered material.

The decomposition of the nickel hydroxide samples was performed thermally in aluminum crucibles in the DSC apparatus under an inert gas atmosphere. When beginning the heating process at room temperature, the materials lose surface water up to 100 °C. The amount of surface water often correlates with the surface area of the nickel hydroxide powder. Inter-slab water is removed between 100 and 230 °C. Above 270 °C, the nickel hydroxide begins to decompose, generating water and nickel oxide (see Fig. 3) [12].

A slight correlation was found between the decomposition temperature of the nickel hydroxide and the degree of disorder of the material (see Fig. 4). An explanation for this behaviour is given by Wronski et al. [9,10]. They suppose that the hydroxyl groups can be removed more easily as their mobility is increased by ordering defects in the host lattice.

Highly ordered materials with a degree of disorder below 10% show a DSC peak at about 325–335 °C, whereas materials with a higher degree of disorder of 20% decompose at a significantly lower temperature of 290–300 °C. The intercalation and release of protons into and from the nickel hydroxide host lattice is expected to be enhanced by crystal imperfection. There can be stacking defects as well as growth defects producing vacancies for enhanced proton hopping conduction in the host lattice. The utilisation

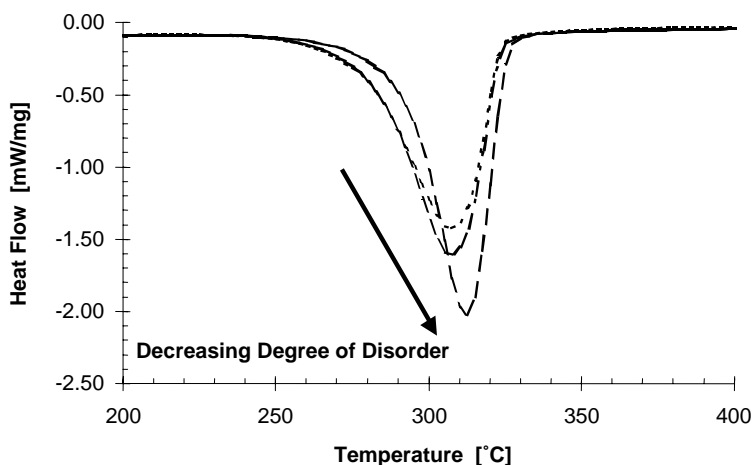


Fig. 3. DSC curves of different nickel hydroxides.

of nickel hydroxide often suffers from its low conductivity. Disorder may also result in an enhanced conductivity especially when cobalt is introduced into the lattice replacing nickel. Due to Guinier's theory of layered imperfect crystals, Wronski et al. [9] used the concept of the degree of disorder to quantify the defects in the stacking of basal planes. The broadening of the (1 0 1) line is used according to [9,10] for the calculation of the degree of disorder in the present work. Peak broadening is also related to a reduced crystallite size. The line broadening due to the size effect is therefore overlaying the line broadening due to disorder in the arrangement of the lattice planes. A correlation between the specific capacity and the width of the (1 0 1) line (FWHM) was found for various nickel hydroxide materials (see Fig. 5).

As has been discussed earlier, the broadening of the (1 0 1) line is mainly caused by disorder effects rather than by a decreased crystallite size. The latter mainly influences the (0 0 1) and (1 0 0) reflections [13]. Therefore, the increasing specific capacity of the various nickel hydroxide materials can be explained by an increasing degree of disorder in the stacking of the basal planes. Nickel hydroxides characterised

by a FWHM of the (1 0 1) line of  $0.5^\circ$  ( $2\theta$ ) or less exhibited a specific capacity of about 220–230 mAh/g. Less ordered materials showing a FWHM of the (1 0 1) line of  $0.9^\circ$  ( $2\theta$ ) or more had a specific capacity of about 270–280 mAh/g, which comes close to the theoretical value of 289 mAh/g  $\text{Ni}(\text{OH})_2$ . Taking into account that the studied nickel hydroxides were doped hydroxides substituting, e.g. some cobalt and zinc for nickel, the latter values correspond to a mass utilisation close to 100% of the theoretical value.

The specific capacity of the nickel hydroxide material is a main topic for high energy demands, since the capacity of nickel–metal hydride cells is determined by the positive electrode and its active material. A good high power capability on the other hand is also important especially for applications in the field of electric vehicles and hybrid vehicles. Therefore, the high power capability of different nickel hydroxides was also evaluated (see Fig. 6).

A correlation between the average discharge voltage at a discharge rate of 10C, measured at a complete NiMH cell (corresponding to a discharge time of 6 min) and the line width of the (1 0 1) line in the X-ray diffraction pattern was

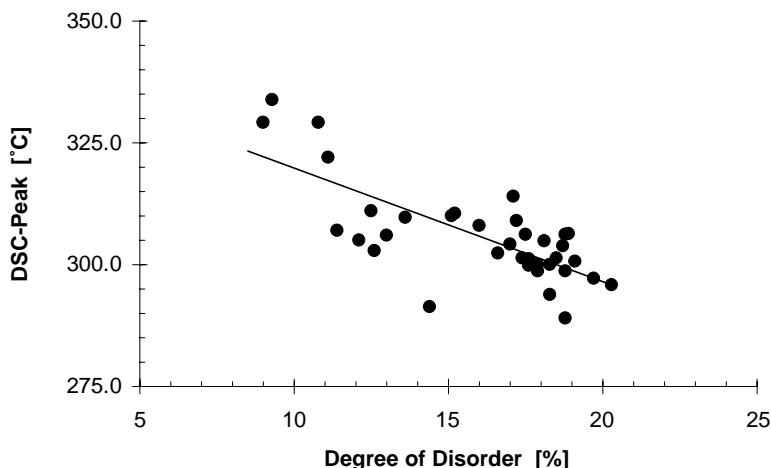


Fig. 4. Correlation between decomposition temperature and the degree of disorder of various nickel hydroxides.

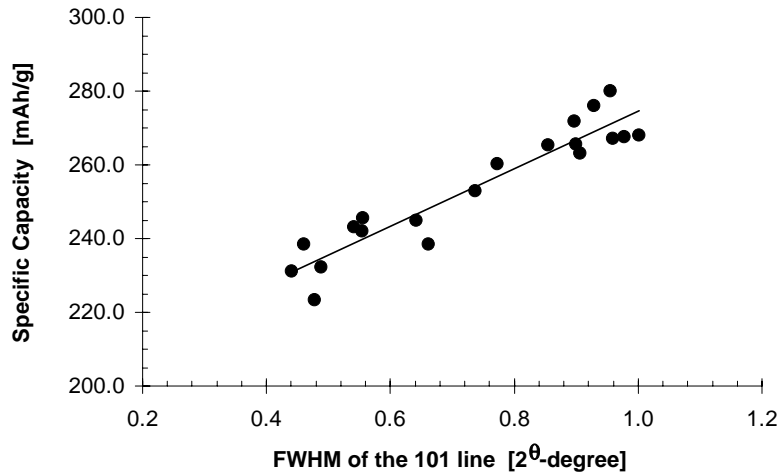


Fig. 5. Correlation between the FWHM of the (101) peak and the specific capacity of the nickel hydroxide material.

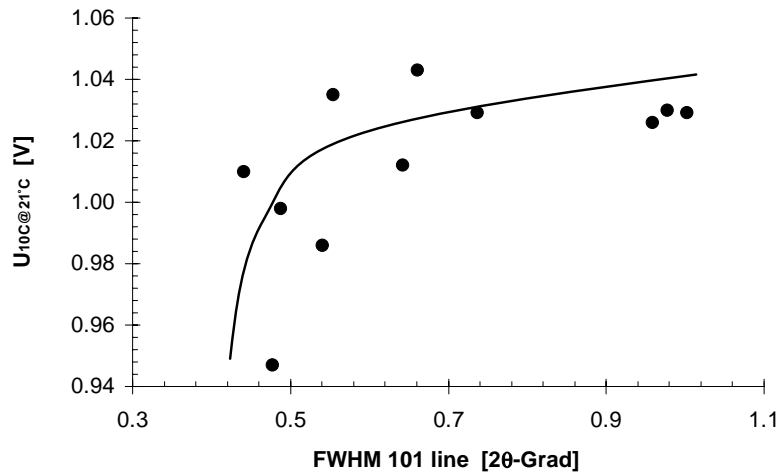


Fig. 6. Correlation between the average discharge voltage for a 10C discharge rate at 21 °C and the line width of the (101) line.

found (Fig. 6). As the line broadening of the (101) peak is mainly caused by stacking mistakes of the basal planes, the increasing discharge voltage at high rate discharge currents is ascribed to improved proton diffusion by disorder effects. Nickel hydroxides with a higher degree of disorder represented by a higher broadening of the (101) peak, show an average discharge voltage at a 10C discharge which is 60–100 mV higher than that of corresponding materials with higher ordered structure.

#### 4.2. Effect of hydrogen storage alloy material on the performance of NiMH batteries

The absorption and desorption equilibrium of hydrogen by AB<sub>5</sub> alloys is represented by PCT isotherms [14] as are shown schematically in Fig. 7.

Prior to the formation of the hydride phase or β-phase, a so called α-phase is built, this is describing the solid solution of hydrogen in the alloy host lattice. A further increase of the hydrogen concentration in the host lattice leads to the

formation of the β-phase resulting in a two phase region, where the equilibrium pressure remains constant. After the β-phase formation is completed, a further increase of the hydrogen concentration results in a solid solution of hydrogen in the β-phase, which is characterised by further increasing

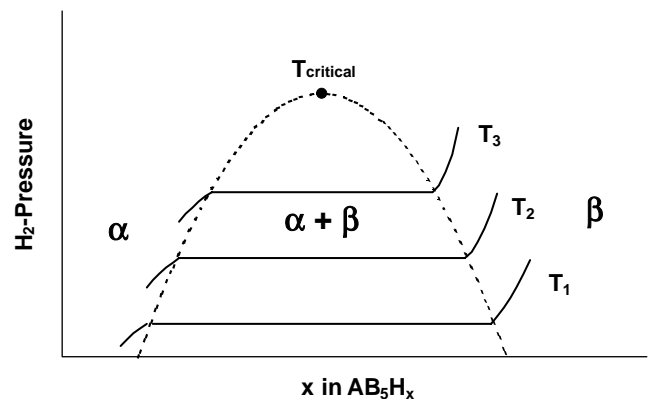


Fig. 7. PCT diagram of a AB<sub>5</sub> type hydrogen storage alloy.

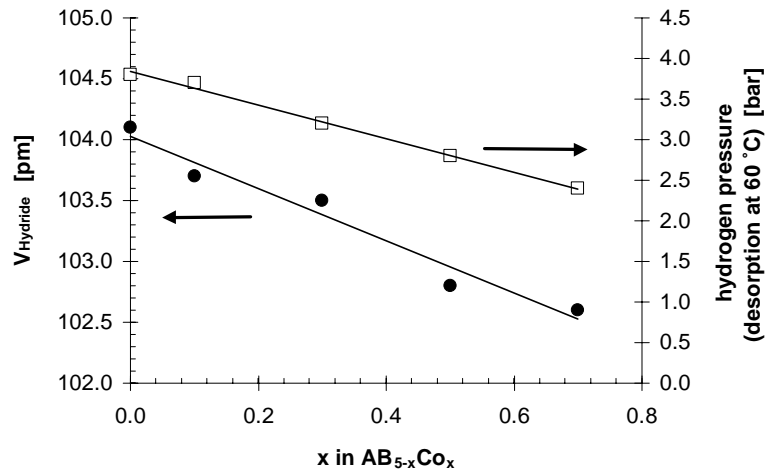


Fig. 8. Influence of the cobalt content in a  $AB_5$  type hydrogen storage alloy on the unit cell volume of the hydride phase (●) and the hydrogen equilibrium pressure at 60 °C (□).

pressure. The hydrogen concentration in the alloy lattice depends on the temperature.

$AB_5$  alloys for battery applications must be able to take up hydrogen not only from hydrogen gas phase but also electrochemically. An equilibrium pressure compatible with the mechanical stability of the cell case is a key issue. Electrochemical stability against a strong caustic medium as well as fast electron and hydrogen transfer reactions at the particle surface enabling rapid charging and discharging are crucial for the cell performance.

The formation of the hydride phase goes along with an increase of the unit cell volume. The volume expansion as well as the hydrogen equilibrium pressure are related to the alloy composition. In a series, an  $AB_{5-x}Co_x$  hydrogen storage alloys with B consisting of a mixture of nickel and other elements like aluminum or manganese or others and with Co substituting for nickel, the volume of the hydride phase as well as the hydrogen equilibrium pressure were found to decrease with an increasing cobalt content (Fig. 8).

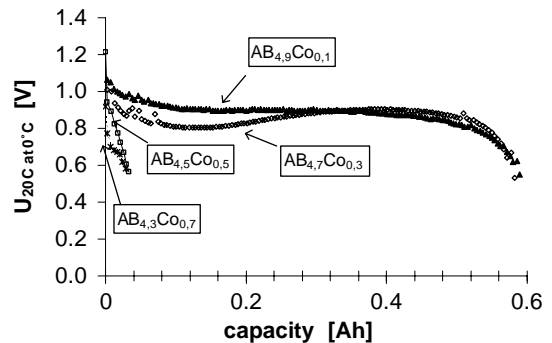


Fig. 9. Influence of the cobalt content in  $AB_{5-x}Co_x$  alloys on the average discharge voltage for a 20C discharge rate at 0 °C.

In this series of different hydrogen storage alloy compositions, a correlation between the cobalt content  $x$  in  $AB_{5-x}Co_x$  and the average discharge voltage was observed. This is especially valid for high discharge currents (see

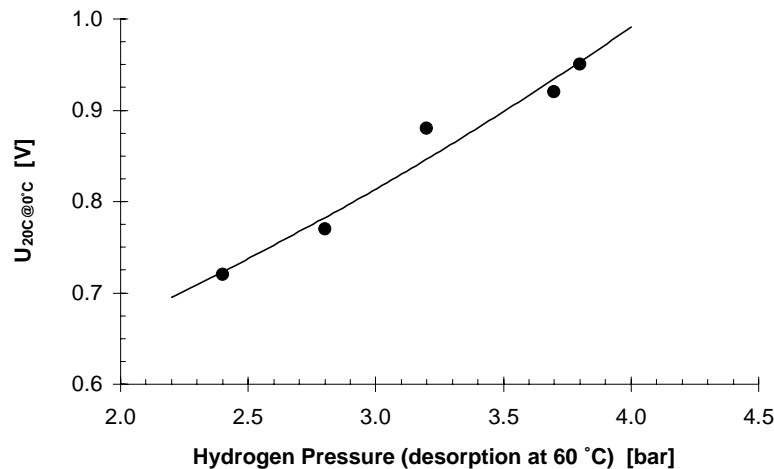


Fig. 10. Correlation between hydrogen equilibrium pressure for desorption at 60 °C and average discharge voltage for a discharge rate of 20C at 0 °C in a  $AB_{5-x}Co_x$  type hydrogen storage alloy.

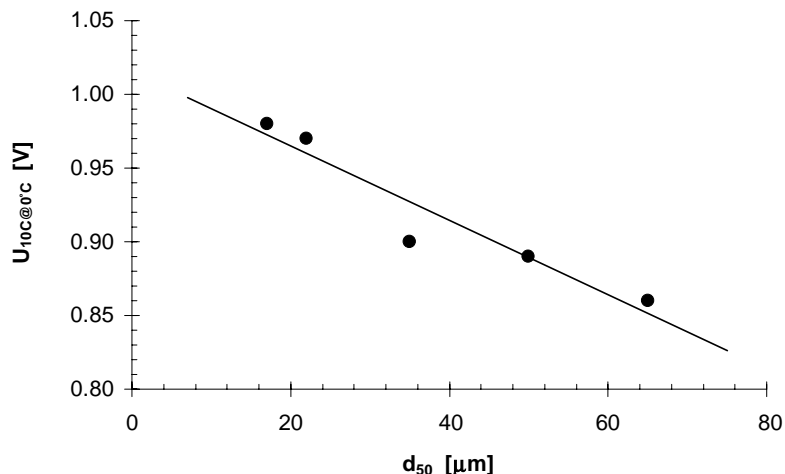


Fig. 11. Correlation between average discharge voltage at a 10C rate at 0°C and the average initial particle size of an AB<sub>5</sub> type hydrogen storage alloy.

Fig. 9), representing discharge voltages under 20C rate at 0°C.

The average discharge voltage of a 20C rate at 0°C as well as the discharge capacity decrease with increasing cobalt content. While the basic composition AB<sub>5</sub> shows a high average discharge voltage of about 950 mV under these conditions, the compound with the highest cobalt content (AB<sub>4.3</sub>Co<sub>0.7</sub>) exhibit a significantly lower average discharge voltage of 720 mV and an inferior capacity. From these data, a correlation between hydrogen equilibrium pressure and high rate capability can be deduced (Fig. 10).

The highest average discharge voltage for a 20C discharge rate at 0°C was found with the alloy having the highest hydrogen equilibrium pressure corresponding to the lowest cobalt content in the AB<sub>5-x</sub>Co<sub>x</sub> alloy series. High rate discharge voltages decrease with decreasing hydrogen equilibrium pressure.

The equilibrium pressure represents the thermodynamic stability of the hydride phase. The kinetics of electron and hydrogen transfer dominating the discharge capability, however, is determined also by other factors. The amount of the surface area as well as its catalytic activity are of great importance with respect to power performance. Particularly, the chemical composition of the hydrogen storage alloy may affect the hydrogen transportation and the electron transfer. Layers consisting of insulating oxides normally are formed by corrosion at the surface of the particles in alkaline medium. These surface layers may act as barriers for electron and hydrogen transfer. Studies of the surface structure of electrochemically cycled hydrogen storage alloys confirmed the evidence of surface layers consisting of rare earth oxides or hydroxides [7]. Underneath the oxide surface layer, a nickel-enriched layer was observed. Its presence is generally regarded responsible for high electrocatalytic activity for hydrogen and electron absorption and desorption. Stable hydrides are represented by a low equilibrium pressure due to a strong chemical binding of the hydrogen to the metal

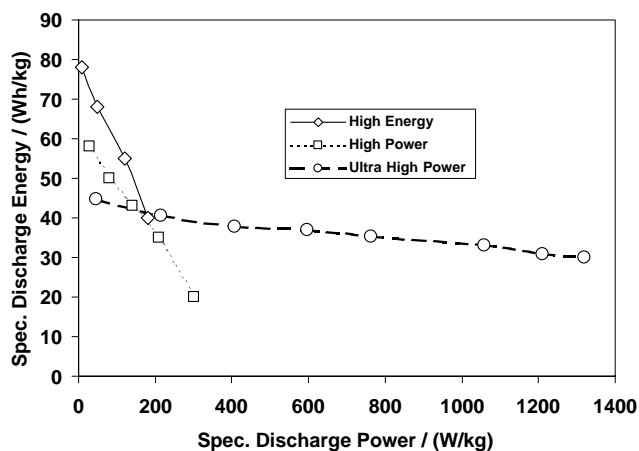


Fig. 12. Specific discharge energy vs. specific discharge power for different NiMH cell types.

alloy bulk. This goes along with a decreased kinetics of hydrogen release from the metallic solid phase. The effect of the surface area can be taken from Fig. 11. AB<sub>5</sub> type alloys with different particle sizes, characterised by their  $d_{50}$  value, were tested under high rate discharge conditions.

A discharge current corresponding to a 10C rate was applied at 0°C. An average discharge voltage of 0.98 V for cells with fine alloy particles (<20  $\mu\text{m}$ ) was observed. This is drastically higher in comparison to the value of 0.86 V measured at cells with relatively coarse particles (>60  $\mu\text{m}$ ). It is well known that hydride-forming metallic alloy particles break into finer pieces during electrochemical cycling, so increasing the intrinsic active surface area over cycling.

## 5. Conclusion

Technical progress with the nickel–metal hydride system triggered by the development of advanced positive and neg-

ative electrode materials has made most likely the replacement of NiCd batteries in almost all technical applications in not far future. Taylor-made basic material will play a major role for the future development. This is valid for batteries used for portable applications in the consumer market, but also for the wide range of the future traction battery market. Particularly, high performance batteries in terms of power capability and long term endurance will remain a field of interesting future materials and basic electrochemical research and development. The energy versus power plot in Fig. 12 demonstrates the technical achievements with NiMH cells in terms of energy storing capability and power performance.

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### References

- [1] C.D.S. Tuck (Ed.), *Modern Battery Technology*, Ellis Horwood, New York, 1991.
- [2] D. Berndt, *Maintenance Free Batteries*, Research Studies Press, Taunton, UK, 1997.
- [3] Varta Batterie AG, *Sealed Nickel Cadmium Batteries*, VDI Verlag, Duesseldorf, 1982.
- [4] J. Daniel-Ivad, K. Kordesch, E. Daniel-Ivad, L. Duong, in: *Proceedings of the 19th International Seminar Exhibit on Primary and Secondary Batteries*, Ft. Lauderdale, FL, 11–14 March 2002.
- [5] J.J.G. Willems, *Philips J. Res.* 39 (Suppl. 1) (1984).
- [6] H. Ogawa, M. Koma, H. Kawano, J. Matsumoto, *J. Power Sources* 12 (1988) 339.
- [7] F. Meli, L. Schlapbach, *J. Less Common Met.* 172 (1991) 1252.
- [8] F. Lichtenberg, U. Köhler, A. Fölzer, N.J.E. Adkins, A. Züttel, *J. Alloys Compd.* 2253–2254 (1997) 570.
- [9] Z.S. Wronski, G.J.C. Carpenter, D. Martineau, P.J. Kalal, *Electrochem. Soc. Proc.* 18 (1997) 804.
- [10] Z.S. Wronski, G.J.C. Carpenter, D. Martineau, P.J. Kalal, *Electrochem. Soc. Proc.* 14 (1996) 177.
- [11] H. Bode, K. Dehmelt, J. Witte, *Electrochim. Acta* 11 (1966) 1079.
- [12] O. Rademacher, K. Wiesener, E. Prikryl, *Z. Phys. Chem.* 257 (1976) 354.
- [13] C. Delmas, C. Faure, L. Gautier, L. Guerlou-Demourgues, A. Rougier, *Philos. Trans. R. Soc. Lond. A* 354 (1996) 1545.
- [14] C. Tessier, P.H. Haumesser, P. Bernard, C. Delmas, *J. Electrochem. Soc.* 146 (1999) 2059.