

# Nickel–metal hydride batteries. The preferred batteries of the future?

Paul Ruetschi, Felix Meli, Johann Desilvestro

*Leclanché S.A., 1400 Yverdon-les-Bains, Switzerland*

## Abstract

Construction, performance, cost and environmental aspects of nickel–metal hydride batteries are briefly reviewed. Comparisons with other rechargeable battery systems lead to the conclusion that nickel–metal hydride batteries will dominate the market for small, portable rechargeable batteries in the near future.

*Keywords:* Nickel–metal hydride batteries; Environment

## 1. Introduction

Nickel–metal hydride (Ni–MH) batteries are rapidly conquering an important share of the rechargeable (nickel–cadmium) battery market. The remarkable success of this new system is due to the fact, that it can be marketed as a cadmium-free, environmentally less objectionable product, and that it offers more energy per unit volume or weight than corresponding nickel–cadmium types.

Since the development of the lead/acid battery by Gaston Planté in 1860, and the development of the nickel–cadmium battery by Thomas Alva Edison and by Waldemar Junger in 1901, no other new rechargeable battery system has, up to very recently, gained commercial importance.

Although multiple research efforts on rechargeable Ni–MH batteries have been carried out, starting in the 1950s already, the break-through for commercial use was realized only in the 1980s, as a result of the development of cobalt–aluminium modified LaNi<sub>5</sub> hydrogen storage alloys [1]. The cost of these alloys can be reduced considerably by using ‘Mischmetal’ (Mm), instead of lanthanum [2]. Mischmetal is a mixture of rare earth elements; its composition corresponds to that of natural ores. It contains 50–55% cerium, 18–28% lanthanum, 12–18% neodymium, 4–6% praseodymium and other rare earth elements in small quantities, as well as metallic impurities. In Ni–MH batteries, one often employs lanthanum-enriched Mischmetal, for example 50% lanthanum, 30% cerium, 14% neodymium and other rare earth metals. A typical composition [3] of a presently used AB<sub>5</sub>-type hydrogen storage alloy is MmNi<sub>3.5</sub>Co<sub>0.7</sub>Mn<sub>0.4</sub>Al<sub>0.3</sub>.

Parallel to the above-described development, another class of hydrogen storage alloys has emerged, namely the AB<sub>2</sub>-

based alloys [4]. In this formula A stands for a hydride-forming element, such as zirconium or titanium, and B for another metal, such as nickel, cobalt, vanadium, manganese, aluminium or chromium.

One reported defined composition is, for example, [5]:  
Vr<sub>1.5</sub>Ti<sub>1.5</sub>Zr<sub>2.0</sub>Ni<sub>2.8</sub>Cr<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>0.6</sub>Mn<sub>0.6</sub>.

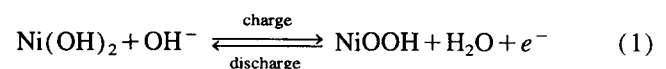
Today, a majority of battery manufacturers prefers the AB<sub>5</sub>-type alloys.

In very recent years, rechargeable lithium batteries (Li-ion batteries) have appeared on the market as the latest generation of portable, rechargeable energy sources. As will be discussed later, they have impressive characteristics and largely surpass Ni–MH batteries regarding energy delivered per unit weight or volume. However, they are considerably more costly to produce. Will the Ni–MH battery, having intermediate performance between nickel–cadmium and rechargeable lithium batteries, play an important role as the preferred battery of the future? The present paper analyses technical performance, environmental aspects and commercial competitiveness of Ni–MH batteries with regard to other rechargeable battery systems.

## 2. Technology and performance of Ni–MH batteries

The electrode reactions in a Ni–MH cell may be formulated in a simplified way as follows:

(i) at the positive electrode:



(ii) at the negative electrode:

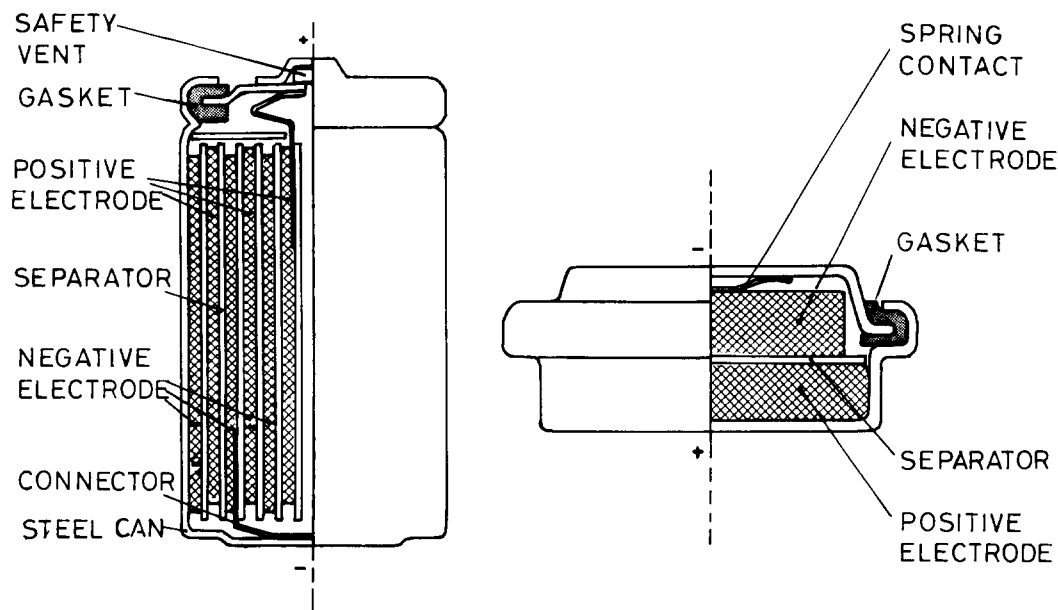
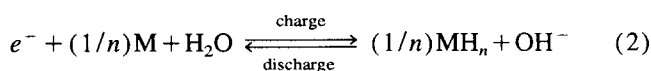
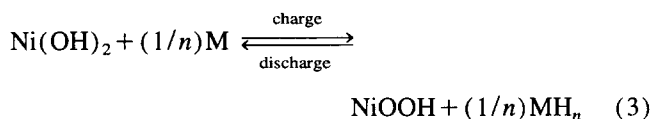


Fig. 1. Cross-sectional drawings of a Ni-MH button cell and a Ni-MH cylindrical cell.



The cell reaction is thus:



where, M stands for the hydrogen storage alloy and  $n$  is the maximum stoichiometric number for H in the hydrogen storage alloy. In the case of  $LaNi_5$ , for example,  $n = 6$ . The saturation composition therefore  $LaNi_5H_6$ , and the theoretical capacity per unit weight becomes 370 mAh/g.

The theoretical electrode potential of a hydride electrode is that of a reversible hydrogen electrode at the effective partial hydrogen equilibrium pressure of the hydrogen storage alloy. The hydrogen pressure depends on the alloy compo-

sition and the degree of hydrogen saturation. The practically used hydrogen storage alloys have (plateau) equilibrium pressures of about 1 bar (or below). A decrease in equilibrium hydrogen pressure by a factor of 10 would result in an increase in the theoretical electrode potential (and thus in a decrease in the cell voltage) by 29 mV only. With an approximate potential of 0.490 V for the  $Ni(OH)_2/NiOOH$  electrode, and a potential of  $-0.828$  V for a hydride electrode having an equilibrium hydrogen pressure of 1 bar, one calculates under these conditions a theoretical cell voltage of 1.318 V [6].

Ni-MH batteries have been developed in a variety of sizes, ranging from button cells, with a capacity of a few mAh, to large prismatic cells, with a capacity of up to 200 Ah [7,8]. The construction of Ni-MH cells is very similar to that of corresponding nickel-cadmium types. Cross-sectional drawings of a button cell and of a cylindrical cell are shown in Fig. 1.

### 2.1. Button cells

Button cells make, in most cases, use of pressed powder-type electrodes, which are enveloped by means of a nickel screen. The positive electrode is pressed from a mixture of nickel hydroxide, cobalt oxide, other metal oxide additives [9] and conducting agents, such as graphite or nickel powder. The negative electrode is pressed from a hydrogen storage alloy usually of the  $AB_5$ -type, mixed with additives and binders. Button cells range in diameter from 8 to 35 mm, in height from 3.5 to 9 mm, in weight from 0.7 to 14 g, and in capacity from 15 to 500 mAh. Pressed powder-type electrodes used in button cells are relatively thick and their high-rate performance is thus limited (Fig. 2). On the other hand, they have a relatively low self-discharge rate (Fig. 3) and they are inexpensive to manufacture.

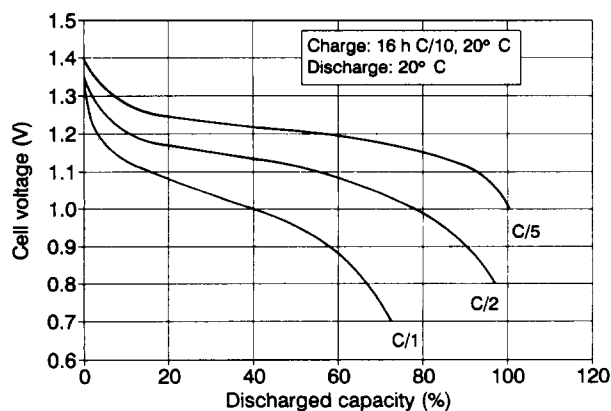


Fig. 2. Discharge curves at the 0.2C, 0.5C and C rate of a Ni-MH button cell, Leclanché-type H-95, with nominal capacity (0.2C) of 85 mAh, diameter 15.5 mm and height 6.2 mm.

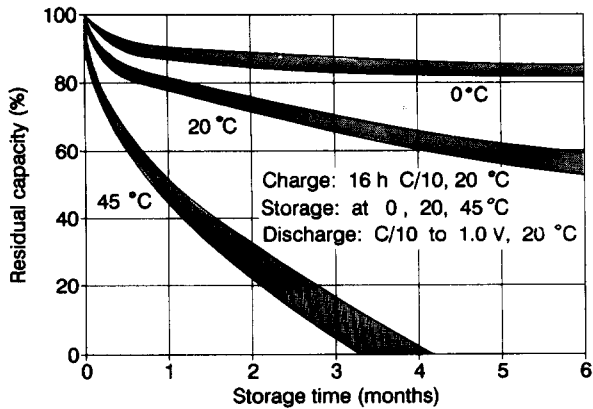


Fig. 3. Storage characteristics of a Ni-MH Leclanché-type H-95 button cell; dimensions see Fig. 2.

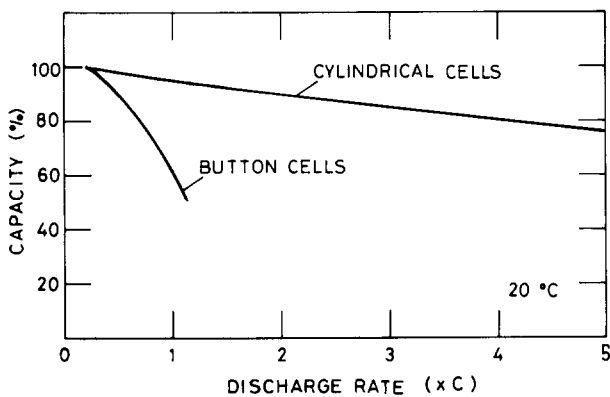


Fig. 4. Capacity vs. discharge rate for a cylindrical AA-cell (diameter 14.5 mm, length 50 mm) and for a button cell (diameter 15.5 mm, height 6.2 mm).

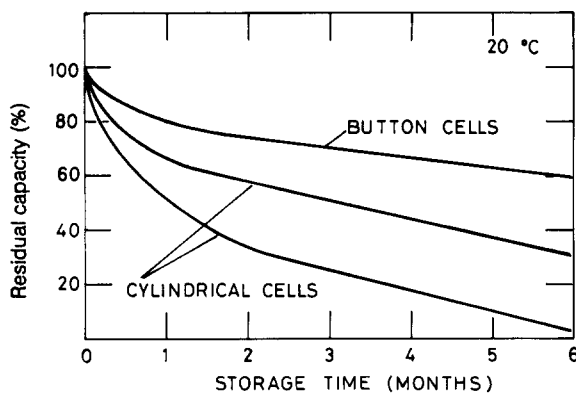


Fig. 5. Self-discharge behaviour of cylindrical cells and button cells (dimensions see Fig. 4). For cylindrical cells, data vary widely between cells of different manufacturers.

### 2.2. Cylindrical cells

Cylindrical cells are constructed with thin, flexible, spirally wound electrodes. Positives are either of the conventional-sintered type, or manufactured by applying a paste containing nickel hydroxide, cobalt oxide, other additives [9] and a conducting agent into a highly porous substrate of nickel foam or nickel felt. After drying, the electrodes are roll-

compacted and cut to size. Other manufacturing techniques, avoiding the use of expensive foam or felt, are also under development, such as direct roll-compacting of a mixture of nickel hydroxide with very fine nickel powder, onto screens or perforated sheets.

AB<sub>5</sub>-type negative electrodes are manufactured by pasting a mixture of hydrogen storage alloy, a conducting agent and a polymeric binder into nickel foam or nickel felt. Techniques to produce plastic-bonded negative electrodes, which will not require expensive porous substrates, have also been developed [10]. Other techniques include direct roll-compacting of the active material, mixed with ultra-fine nickel powder, without the use of a binder [11]. Negative electrodes with AB<sub>2</sub>-type hydrogen storage alloys can be manufactured by means of hot-pressing or sintering techniques, without the use of polymeric binders [8]. As will be discussed later, certain organic binder materials, such as polytetrafluoroethylene (PTFE), containing fluorine or chlorine, might lead to problems when it comes to recycling used batteries.

Cylindrical cells with spirally wound electrodes have good high-rate performance (Fig. 4) but a relatively high self-discharge rate (Fig. 5). The latter is due to the instability of the nickel electrode, which loses oxygen during open-circuit storage. Addition of cobalt to the nickel hydroxide electrode improves its stability. On the other hand, self-discharge may be accelerated by impurities stemming from the hydrolysis of separators.

### 2.3. Prismatic cells

Although most Ni-MH cells, produced today, are of a cylindrical shape, the use of small prismatic cells with thin, flat electrodes, mounted in a deep-drawn steel casing, is rapidly increasing (Fig. 6). Prismatic cells, available on the

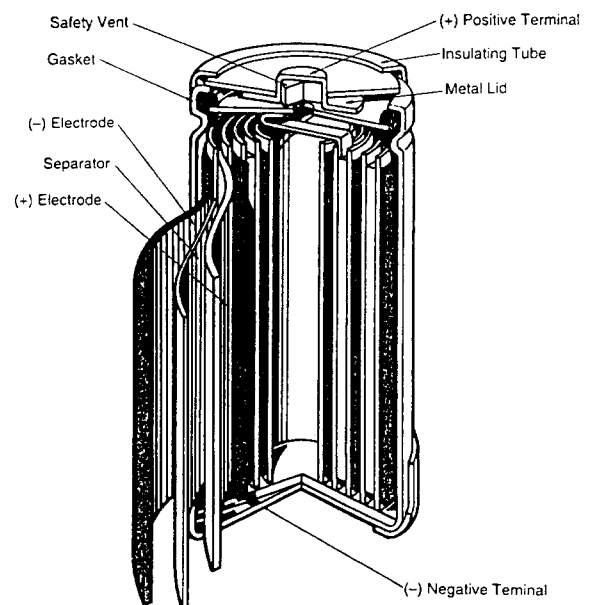


Fig. 6. Construction details of a small, prismatic Ni-MH cell.

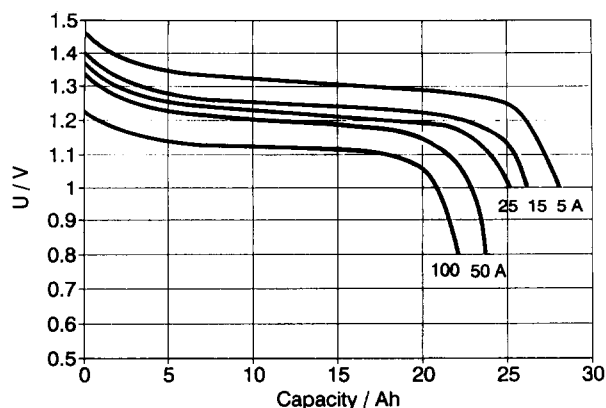


Fig. 7. Discharge curves for a large prismatic 25 Ah Ni-MH cell mounted in a plastic casing.

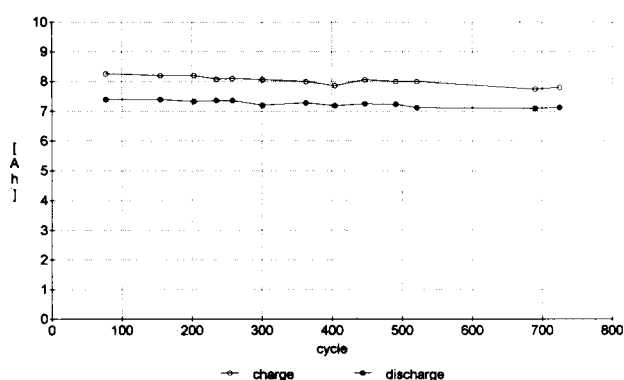


Fig. 8. Cycle-life data for a 9 Ah (C/5) prismatic Ni-MH cell mounted in a plastic casing: (○) charge, and (●) discharge.

market today, have a width of 14.5–22.6 mm, a length of 48–67 mm, a thickness of 5.6–14.4 mm and a weight of 12–76 g. Electrical characteristics are similar to those of corresponding cylindrical types.

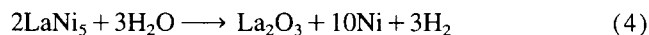
Large prismatic Ni-MH batteries in metallic or plastic casings have been developed for electric-traction applications. These batteries have excellent power characteristics. Fig. 7 shows data for a 25 Ah cell, built for a hybrid electric vehicle at Leclanché. Even at the 4C rate (100 A), the cell furnishes 80% of its nominal capacity. Heat management during charge is a major problem of large sealed Ni-MH batteries. All Ni-MH cells use separators in form of non-woven felts of wettable polymeric materials, such as polypropylene or polyamide. They are wetted with electrolyte, a 30% KOH solution containing a small amount of LiOH. All cylindrical and prismatic cells are equipped with a safety vent.

#### 2.4. Cycle life and ageing

The cycle life of Ni-MH batteries is excellent. As many as 2000 cycles have been achieved with various types of cells. Data obtained with a 9 Ah prismatic cell, developed at Leclanché for an electric bicycle, are shown in Fig. 8. The cycles consisted of a 4 A charge for 2 h and a 4.5 A discharge to an

end-point voltage of 0.8 V. The charge efficiency was 92% under these conditions.

Due to volume changes of the crystal lattice of hydrogen storage alloys during hydrogen uptake, one observes fracturing of the grains and a particle size decrease as a result of cycling. Hydrogen storage alloys of the AB<sub>5</sub>- or AB<sub>2</sub>-type may also age due to irreversible oxidation of the less noble metal components under formation of corresponding oxides or hydroxides. Fig. 9 shows scanning electron microscope (SEM) pictures of AB<sub>5</sub>-type electrode material, before and after cycling. The formation of fine-grained corrosion material is clearly visible after 1000 cycles. X-ray photoelectron spectroscopy (XPS) investigations show an enrichment of oxygen at the surface of the hydrogen storage alloy grains (Fig. 10). The corrosion process of AB<sub>5</sub>-type alloys may be described either as a reaction with water, under formation of hydrogen:



or as a reaction with oxygen, evolved at the positive electrode during charge:

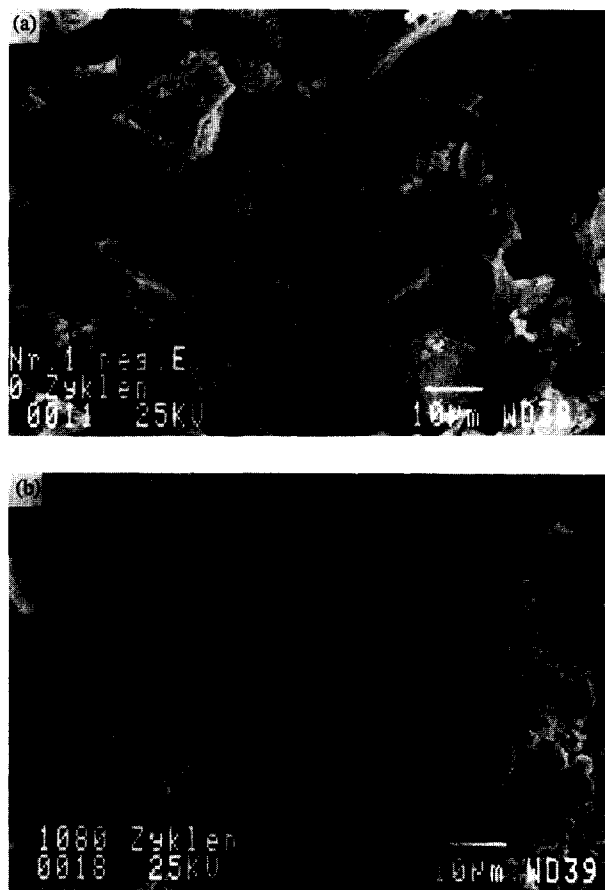
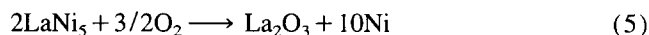


Fig. 9. SEM pictures of AB<sub>5</sub>-type hydrogen storage alloy. (a) Before cycling, (b) after 1080 cycles to 40% depth-of-discharge, using a charge factor of 150% (button cell tests).

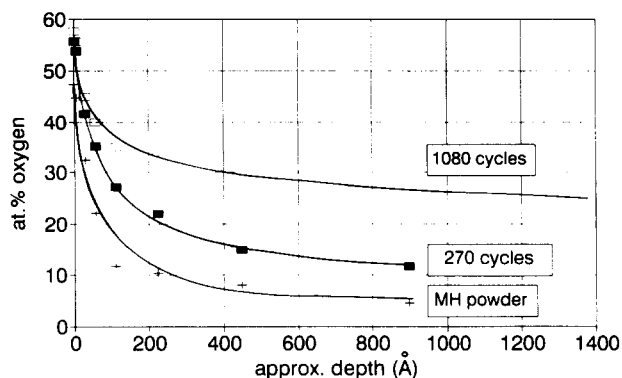


Fig. 10. Oxygen enrichment, as derived from XPS investigations, at the surface of a hydrogen storage electrode with AB<sub>5</sub>-type alloy, initially (MH powder), after 270 cycles and after 1080 cycles to 40% depth-of-discharge, using a charge factor of 150% (button cell tests).

However, these ageing processes are slow. The loss of hydrogen storage alloy by the above irreversible oxidation may be compensated by working with an initial excess of negative active material. The cycle life of Ni–MH batteries is thus more than satisfactory.

### 3. Comparison with other rechargeable battery systems

The energy per unit volume (Wh/l) and the energy per unit weight (Wh/kg) of Ni–MH batteries are compared with those of other rechargeable systems in Figs. 11 and 12. These Figures were derived from the mean discharge voltage and the discharge duration to a standard end of discharge voltage (1.7 V for lead/acid, 1.0 V for nickel–cadmium and Ni–MH, 2.5 V for lithium), as taken from technical brochures of various manufacturers.

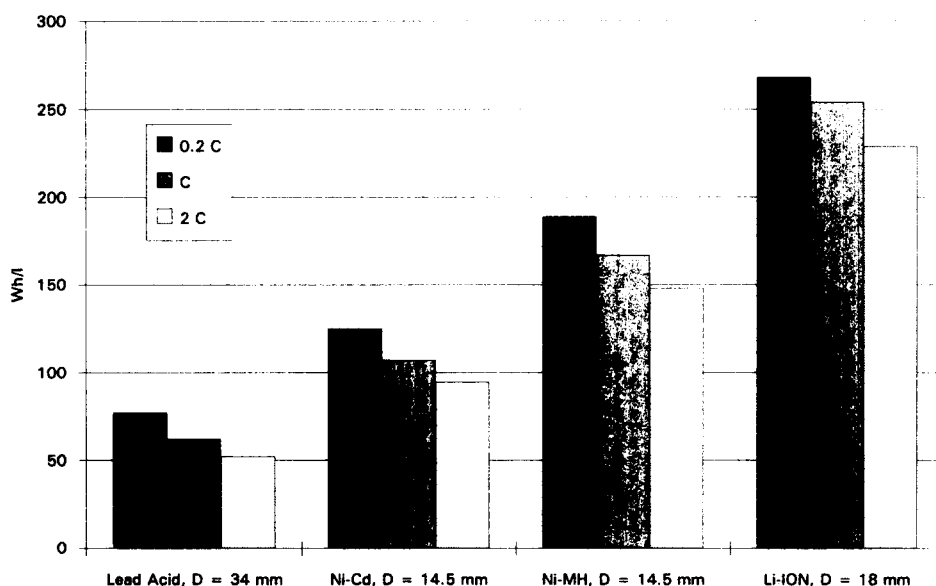


Fig. 11. Energy per unit volume for rechargeable, cylindrical cells of the lead/acid, nickel–cadmium, Ni–MH, and lithium-ion type. D indicates cell diameter.

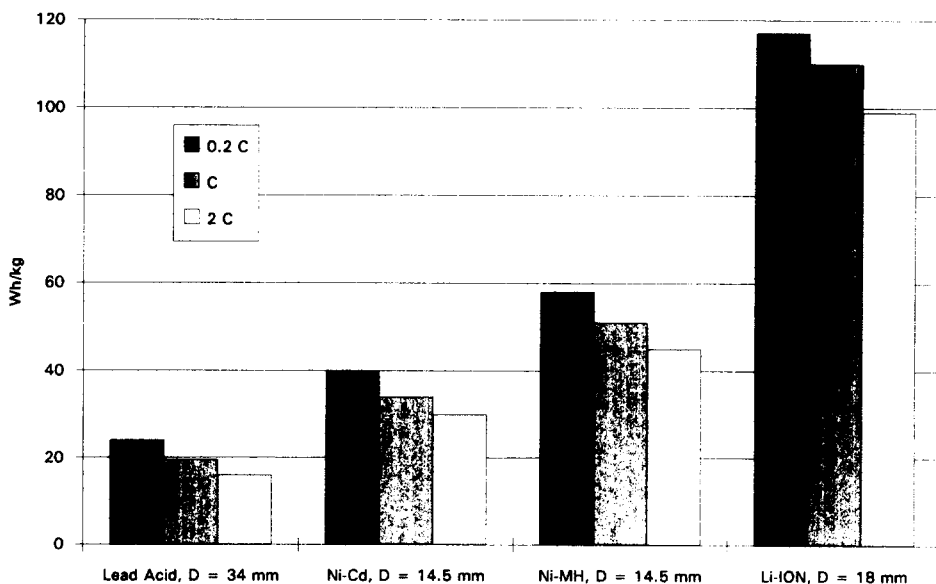


Fig. 12. Energy per unit weight for rechargeable, cylindrical cells of the lead/acid, nickel–cadmium, Ni–MH, and lithium-ion type. D indicates cell diameter.

Although Ni–MH batteries have superior specific energy than the other two aqueous electrolyte systems, they remain largely inferior to the new rechargeable lithium (Li-ion) batteries. However, lithium batteries are much more expensive to produce. It has been estimated [12] that the approximate cost (per Wh) for nickel–cadmium, Ni–MH and Li-ion batteries are in the ratios 1:1.35:2–3, respectively. In addition, lithium batteries cannot be operated for safety reasons without electronic control of each individual cell. Thus, Li-ion batteries will only be used in applications where it is imperative to have a maximum energy content.

For most uses, the Ni–MH battery system will be preferred. It is environment-friendly, and offers more energy per unit volume or weight than nickel–cadmium or lead/acid batteries. Only when it comes to large batteries, for electric-vehicle application, for example, Ni–MH batteries will encounter serious competition from the much lower-cost lead/acid batteries.

#### 4. Recycling of Ni–MH batteries

One important aspect to be considered, when trying to make forecasts as to the future success of a battery system, is the ease of recycling. Lead/acid batteries have the advantage of permitting recycling with relative ease, since lead is the major component of the battery, and it has a low melting point. It is estimated that in Europe more than 95% of all used lead/acid batteries are returned to smelters for recycling of the lead [13].

Collection of spent nickel–cadmium batteries is necessary because of the highly toxic nature of cadmium. The fraction of collected spent Ni–Cd batteries is relatively high in Switzerland, since they are collected together with dry cells and sorted out thereafter. In Sweden, the use of nickel–cadmium batteries has been curtailed by legislation.

The French Company SNAM operates a Ni–Cd battery recycling plant in St. Quentin-Fallavier and in Viviers, France. The process involves, firstly, a pyrolysis step at 350 °C for 14 h, whereby organic polymeric materials decompose. In a second step, the pyrolyzed batteries are heat-treated, together with waste cadmium electrodes from large spent industrial cells, under addition of charcoal, at 900 °C for 24 h. Hereby, cadmium and nickel are reduced to their metallic forms and cadmium is evaporated and condensed. The collected cadmium has a purity of 99.95%. In the oven remains a nickel-enriched iron scrap, which contains still about 0.1–0.5% Cd. There appears to be no difficulty in using this scrap for steel production.

Ni–MH batteries, being manufactured in the same physical dimensions as nickel–cadmium batteries, will naturally be collected after use together with the latter. Although Ni–MH batteries are cadmium-free, it will be unacceptable to have them end up in incinerators or landfill sites, because of their high heavy metal content. Automatic separation of Ni–MH batteries from nickel–cadmium batteries, for example on the basis of density, will be difficult. Densities are similar and, moreover, depend on grade and manufacturer. It is thus likely that Ni–MH and nickel–cadmium batteries will have to be recycled together.

If, in the future, nickel–cadmium batteries would be banned, because of their cadmium content, it might become possible to recycle collected, cadmium-free batteries directly, together with steel filter dusts or steel scrap, in large installations of the steel industry. However, the batteries should then be free of halogen-containing organic materials such as PTFE, because of the dangers regarding formation of dioxines.

The approximate weight composition of Ni–MH batteries is listed in Table 1. The recovery of cobalt, nickel, rare earth metals, zirconium, titanium, vanadium, etc., may be an incentive for the recycling the Ni–MH batteries by a wet-chemistry

Table 1  
Typical chemical composition of Ni–MH batteries (wt.%)

Element	Button cells AB <sub>5</sub> alloys	Cylindrical cells AB <sub>5</sub> alloys	Cylindrical cells AB <sub>2</sub> alloys	Prismatic large cells AB <sub>5</sub> alloys <sup>d</sup>
Ni	29–39	36–42	37–39	38–40
Fe	31–47	22–25	23–25	6–9
Co	2–3	3–4	1–2	2–3
La, Ce, Nd, Pr	6–8	8–10		7–8
Zr, Ti, V, Cr			13–14	
H and O <sup>a</sup>	8–10	15–17	15–17	16–18
C <sup>b</sup>	2–3	0–1		0–1
Plastics <sup>c</sup>	1–2	3–4	3–4	16–19
K	1–2	1–2	1–2	2–3
Others	2–3	2–3	1–2	3–4

<sup>a</sup> In water and oxides.

<sup>b</sup> Graphite.

<sup>c</sup> Polypropylene, polyamide, etc.

<sup>d</sup> With plastic casing.

separation process. Such processes are presently under investigation [14].

## 5. Conclusions

Nickel–metal hydride batteries have excellent electrical characteristics and cycle life. Although energies per unit weight and per unit volume are inferior to those of rechargeable lithium (Li-ion) batteries, they fulfill the needs for most applications. Their costs are only slightly higher – and in the future probably very similar – to those of nickel–cadmium batteries, and at least two to three times lower than that of lithium batteries. They are free of toxic heavy metals, such as cadmium, and can be considered as the preferred rechargeable batteries of the future, at least in the field of small portable energy sources.

## Acknowledgements

The authors express their thanks to Professor R. Giovanoli, University of Berne, and Professor L. Schlapbach, University of Fribourg, for their help in carrying out SEM and XPS measurements.

This study was partially supported by a grant from the Swiss Federal Department of Energy.

## References

- [1] J.R. van Beek, H.C. Donkersloot and J.J.G. Willems, in L.J. Pierce (ed.), *Power Sources 10*, 1985, pp. 317–338.
- [2] H. Ogawa, M. Ikoma, H. Kawano and I. Matsumoto, in T. Keily and B.W. Baxter (eds.), *Power Sources 12*, 1989, pp. 393–410.
- [3] G.D. Adzic, J.R. Johnson, S. Mukerjee, J. McBreen and J.J. Reilly, *Ext. Abstr., The Electrochemical Society Fall Meet., Miami Beach, FL, USA, 1994*, Abstr. No. 34, pp. 50–51.
- [4] M.A. Fetcenko, S. Venkatesan, K.C. Hong and B. Reichmann, in T. Keily and B.W. Baxter (eds.), *Power Sources 12*, 1989, pp. 411–431.
- [5] S.R. Ovshinski, M.A. Fetcenko and J. Ross, *Science*, 260 (1933) 176–181.
- [6] T. Sakai, K. Muta, H. Miyamura, N. Kuriyama and H. Ishikawa, *Proc. Symp. Hydrogen Storage Materials, Batteries and Electrochemistry, 1992*, Proc. Vol. 92-5, The Electrochemical Society, Pennington, NJ, USA, pp. 59–91.
- [7] J. Desilvestro, P. Reymond, J. Larcin and P. Ruetschi, *Ext. Abstr., The Electrochemical Society Meet., New Orleans, LA, USA, 1993*, Proc. Vol. 93-2, pp. 69–70.
- [8] M.A. Fetcenko, S. Venkatesan, S.R. Ovshinsky, *Proc. Symp. Hydrogen Storage Materials, Batteries and Electrochemistry*, Proc. Vol. 92-5, The Electrochemical Society, Pennington, NJ, USA, 1992, pp. 141–167.
- [9] K. Ohta, K. Hayashi, H. Matsuda, Y. Toyoguchi and M. Ikoma, *Ext. Abstr., The Electrochemical Society Meet., 1994*, Miami Beach, FL, USA, Abstr. No. 61, pp. 98–99.
- [10] T. Hara, N. Yasuda, Y. Takeuchi, T. Sakai, A. Uchiyama, H. Miyamura, N. Kuriyama and H. Ishikawa, *J. Electrochem. Soc.*, 140 (1993) 2450.
- [11] Z. Ye, T. Sakai, D. Noréus, E. Rosén and N.E. Bärning, *Ext. Abstr., The Electrochemical Society Fall Meet., Miami Beach, FL, USA, 1994*, Abstr. No. 52, p. 83.
- [12] A. Jamard, *Rep. NiCad 94 Conf., Geneva, Switzerland, 1995*, International Cadmium Association, London, pp. 104–107.
- [13] P. Ruetschi, *J. Power Sources*, 42 (1993) 1–7.
- [14] J.W. Lyman and G.R. Palmer, *Ext. Abstr., The Electrochemical Society Fall Meet., Miami Beach, FL, USA, 1994*, Abstr. No. 71, p. 113.