

Metal hydride electrodes and Ni/MH batteries for automotive high power applications

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Abstract

Nickel–metal hydride (Ni/MH) batteries are nowadays the most promising system, in the mid-term, for hybrid vehicles. Battery power requirements for the hybrid vehicle application are quite high, both for acceleration and for an effective quick battery recharging. This paper deals with the design and development of metal hydride electrodes and of prismatic Ni/MH batteries for high power automotive applications: hybrid vehicle and energy systems for the future 42 V electrical network in conventional ICE vehicles.

Electrode studies have focused on the substrate characteristics, the electrode preparation conditions and the additives to improve the performance of the active material, in terms of conductivity and avoidance of the active material shedding. The 25 Ah Ni/MH batteries have been designed to achieve maximum power drain (minimum electrical resistance), with a minimum weight and a valve regulated maintenance-free system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of Ni/MH batteries [1] has spread quickly for consumer applications, mainly for portable electronic equipment. However, power capability should be improved to answer the increased interest worldwide for the different types of hybrid vehicles, and even for the future conventional cars with 42 V electrical systems. The final acceptance of electric and hybrid cars will depend on the performance/cost ratio achieved in comparison to the outcome of competing technologies for other low and no-emission vehicles, including efforts to reduce emissions in conventional gasoline combustion engines and the development of low emission vehicles using alternative fuels, such as natural gas.

2. Experimental

2.1. Electrode development

Besides material electrochemical properties and kinetics, electrode morphology [2] and cell design are important

factors involved in the performance of batteries for high power applications. Electrode studies have focused on the current collector characteristics, the electrode preparation conditions and the additives to improve the performance of the active material in terms of conductivity and avoidance of the active material shedding. The substrate characteristics and the conductive additives affect strongly the internal resistance of the electrodes and thus the performance under high power requirements.

The electroactive materials used in this study (Fig. 1) were non-commercial samples of metal hydride AB₅ alloys developed under an EU funded project [3,4]. They had a model composition LaMM Ni_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3} (50% La/MM²) and specific surface treatments (mechanical grinding) to provide fast kinetics capability.

The studies concerning the electrode development have been carried out at the electrode scale, with a negative limited half-cell configuration. The electrodes were sized 50 mm × 50 mm, and have been prepared according to the variables studied. Up-scaling to electrodes sized 70 mm × 90 mm was also tested in order to achieve a comparison basis for alloys to be used later in cells and batteries. Two overdimensioned nickel hydroxide plates were used as counterelectrodes, a polyamide non-woven

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² MM: Misch metal, a natural mixture of rare earth elements, containing mainly La, Ce, Nd and Pr. LaMM denotes that La is the major component.

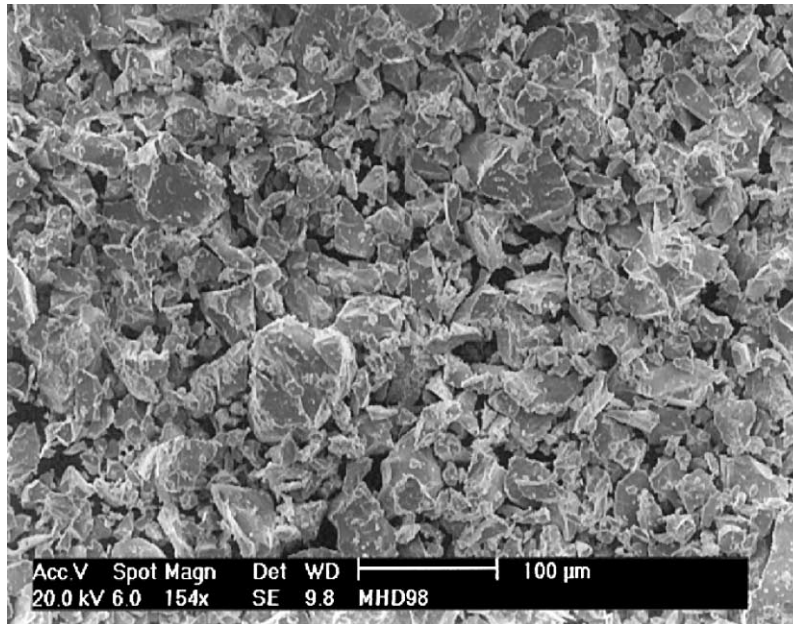


Fig. 1. SEM micrograph of the MH alloy.

as separator, and an excess of KOH solution 1.20 g/cm^3 as electrolyte.

The positive electrodes were prepared by electrochemical impregnation [5]: the active material is nickel hydroxide precipitated within the fibres by cathodic polarisation of the substrate in a concentrate nickel nitrate bath. The cobalt content coprecipitated in the active material is around 4%. In order to eliminate nitrate ions which are deleterious for the battery performance due to the self-discharge caused by a nitrate–nitrite–ammonia shuttle mechanism [6], the electrodes were polarised cathodically in a 5 M KOH bath. This type of electrodes is specially suited for high power applications, due to both the high nickel content (1700 g/m^2) and the small pore size distribution of the substrate. These facts allow for a close contact between the current collector and the active material during high rate charges and discharges.

Negative electrode testing included maximum capacity, cycling capability and high rate performance. Electrical testing has been carried out with a computer controlled cycling equipment Bitrode LCN-3-100-12 with modules CSM-6-100-12 for testing individual cells. In all cases, testing conditions and results have been referred to the weight of alloy: current is indicated as mA/g MH alloy and the capacity obtained as mAh/g MH alloy, to be able to compare the different electrode configurations and dimensions.

Concerning the current collector for the negative electrode, different metallic substrates can be used: nickel mesh, nickel-plated perforated steel sheets, nickel foam and nickel fibre mats. The substrate characteristics affect strongly the electrode performance, weight and cost. Three dimensional (3-D) substrates (nickel fibre mats, nickel foam substrates) have been considered the best options to achieve the

electrode performance needed for high power applications due to the closer contact between the conductive network and the active material particles. High porosity nickel fibre mats had been used previously in Ni/Cd batteries for high power industrial applications, showing excellent properties in terms of high rate charging and discharging capability [7,8].

Several nickel fibre and nickel foam substrates have been studied. Morphological characteristics of the substrates, such as total porosity and pore size distribution and the total nickel content and nickel weight distribution were considered critical parameters for the high power application and were thus studied with standard active material formulations. The electrode configuration has been optimised taking into account the high power application requirements: lug design and substrate-lug welding procedures.

The work on the paste composition has focused on the optimisation of the formulation [9,10] using commercial and cost effective raw materials as additives to improve the high rate performance and to avoid active material shedding during charge–discharge cycling. Some natural and synthetic resins have been tested as binders [11] and carbon, under different morphologies, as conductivity enhancer.

2.2. Cell development

The 25 Ah Ni/MH batteries, sized $80 \text{ mm} \times 34 \text{ mm} \times 137 \text{ mm}$, have been designed and assembled. Fig. 2 shows a photograph of one of the cells. All the cell components have been specially designed to achieve maximum power drain (minimum electrical resistance), with a minimum weight and a valve regulated maintenance-free system. The capacity of the negative electrodes was overdimensioned



Fig. 2. The 25 Ah Ni/MH cell.

20–40% with respect to the positive electrodes to promote adequate oxygen and hydrogen recombination within the cells during overcharge and overdischarge (charge and discharge reserves) [12], and therefore, to avoid electrolyte loss due to gas release through the valve.

A special non-woven grafted polyolefine mat has been chosen as separator [13] due to its low electrical resistance, its chemical stability and electrolyte absorption under the battery working conditions and because it shows enough wettability and ionic exchange capability during the battery operation, thus, allowing low internal resistance values. The vents have been designed to assure a high recombination level in the cell, for maintenance-free operation. The valve opening pressure is 0.8 bar. For this reason, prismatic metallic containers were used.

The electrical testing of single Ni/MH cells has been carried out with a computer controlled cycling equipment Bitrode LCN-3-100-12 with modules CSM-6-100-12 for testing individual cells. High rate discharges have been performed with a Digatron UBT, BTS-500, mod HEW 2000-6BTS. Data acquisition was performed with the software available (Bitrode and Digatron) and with a data logger Datataker 505.

The formation of the cells has been performed in two cycles, charging at the $C/5$ rate during 12 h and discharging at $C/5$ A down to 1.0 V per cell, C being the initially rated capacity, according to the electrode testing results. After each cycle, the electrolyte has been changed and the stack washed in KOH to eliminate any possible ammonia coming

from residual nitrates in the positive electrochemically impregnated plates.

The electrical testing programme included:

1. Initial cycling at the $C/5$ rate to establish real cell capacity: charging during 7 h and discharging down to 1.0 V (10 cycles).
2. Constant current discharges at different rates and room temperature. After charging the cells at the $C/5$ rate (C being the nominal capacity) during 7 h, they were discharged at the xC rate (where $x = 0.2, 0.5, 1, 2, 3, 5, 8$ and 10), down to a cut-off voltage defined according to the discharge rate. After each discharge, a residual discharge at the $C/5$ rate down to 1.0 V was carried out.
3. Constant current charges at different rates and room temperature, to obtain the charging curves. After each charge at the yC rate (where $y = 0.2, 0.5, 1, 2, 3$ and 5 and C is the nominal capacity) with a charge factor of 120%, the cells were discharged at the $C/5$ rate down to 1.0 V.
4. Charging efficiency for different states of charge has been calculated recharging the cells at the $1C$ rate and then discharging at the $C/5$ rate down to 1.0 V. Recharge factors were 50, 80, 90, 100, 110 and 120%.
5. Cycle life. Ni/MH cells have been cycled under constant current conditions at the $C/5$ and $1C$ rates, with a recharge factor of 120% and a discharge cut-off voltage of 1.0 V.
6. Recombination efficiency of the valve regulated design, measuring the weight loss during cell overcharge at the $C/20$ rate, after a complete charge at the $C/5$ rate, with $C = 25$ Ah.

3. Results and discussion

3.1. Electrode development

3.1.1. Current collector

Table 1 shows the rate capability of three types of nickel substrates: two fibre mats with different nickel contents (950 and 700 g/m^2) and a nickel foam with a lower nickel content (500 g/m^2). The discharge rates and the capacity of the electrodes has been referred to the weight of alloy. The results obtained show that there is a clear influence of the substrate type (fibre versus foam) on the electrode capacity: nickel fibre substrates lead to higher capacity values due to the closer contact of the active materials with the metallic current collector (nickel fibres). Also, the higher the nickel content in the substrate, the better the electrode high rate performance at current values over 1500 mA/g ($>5C$ rate).

The nominal characteristics of the nickel fibre substrate finally chosen as electrode support for further testing are as follows: 2.0 mm thickness, 95% porosity and with 950 g/m^2 . Fig. 3 shows an SEM micrograph of the substrate.

Table 1
Rate capability of negative MH electrodes with different substrates

Substrate (g/m ²)	Capacity at 100 mA/g (mAh/g MH alloy)	Capacity at 1500 mA/g (mAh/g MH alloy)	Capacity at 2750 mA/g (mAh/g MH alloy)
Foam 500	195	40	2
Fibre 700	277	214	52
Fibre 950	280	220	87

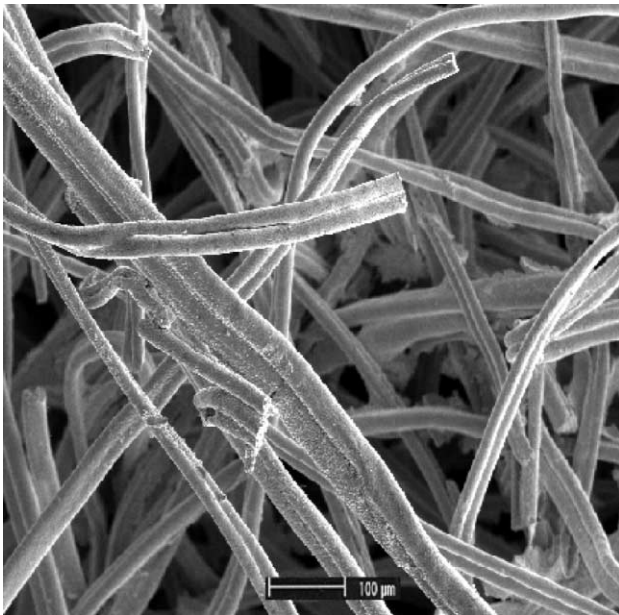


Fig. 3. SEM micrograph of the nickel fibre substrate.

3.1.2. Additives

Several commercial polytetrafluorethylene (PTFE) compounds containing carbon and graphite as fillers, in the range 15–32% in weight, have been tested, with a wide-spread range of results, trying to adjust the binder composition and the preparation conditions. However, the powder compounds showed poor mixing characteristics due to the hydrophobic characteristics of the materials, and poor adherence of the active materials to the current collector, leading to the shedding of the active material during the activation process.

On the other hand, different commercial conductive carbon blacks were studied. The best results were obtained with an extra-conductive carbon black, characterised by a very high specific surface (>950 m²/g). This fact provides a high active surface to the electrodes so prepared, according to the results obtained in the electrode BET analysis. Furthermore, the hydrophobic properties of the carbon black promote gas diffusion through the negative active material, thus, improving the electrochemical processes. Fig. 4 shows the results obtained in the electrical testing of electrodes prepared with

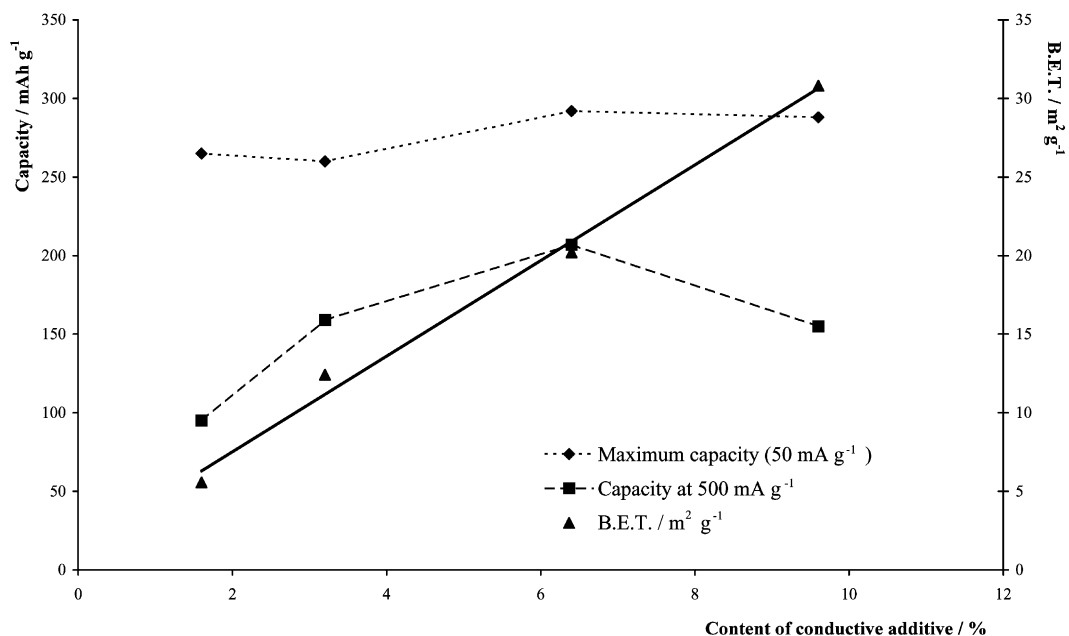


Fig. 4. Capacity and specific surface of negative electrodes with different carbon black contents.

different contents of extra-conductive black as electrode conductivity enhancer: when the carbon content increases, the electrode capacity measured at the 50 mA/g rate shows only a slight increase whereas the high rate capability increases up to 200 mAh/g alloy when 6.4% of conductive black is used. Higher values led to a decrease both of the capacity and the high rate capability. This drop in battery performance after an optimum point if the carbon content is further increased has been previously described in the literature [14] and was attributed to a resulting decrease in electrolyte absorption capacity.

Several natural and synthetic resins and different contents of them, have been tested to avoid the active material shedding during the manufacturing and electrical testing of the electrodes: PTFE (1–5%), arabic gum (0.2–1%), polyvinylalcohol (PVA, 0.2–0.5%) and carboxymethyl-cellulose (CMC 0.2–1%) were tested at different stages of the project both in aqueous and alcoholic media. The natural and synthetic polysaccharides allow one to adjust the rheological properties of the active material, thus, providing the adequate paste viscosity for the electrode mechanical preparation. A mixture of PTFE and PVA (1.8%, with a 8:1 ratio) was finally chosen, as they promoted the optimum working conditions for electrode preparation and active material retention. The binder concentration was adjusted to achieve adequate active material retention without disturbing the electrode conductivity and to obtain maximum capacity values in terms of total electrode weight.

3.1.3. Electrode preparation conditions

Concerning the process conditions, studies have focused on the development of a reliable method for electrode manufacturing. Different mixing conditions have been

tested, together with several procedures to spread the active materials on the substrate mechanically. In any case, the additives and liquid media used in the active material formulation affected the electrode preparation. Tests performed have shown the importance of two process parameters to assure the homogeneous distribution of the active material through the 3-D substrate:

- rheological properties, adjusted by means of an alcoholic media and PVA as hydrophilic binder, which enabled the spreading of the active material within the substrate pores; and
- the pressure applied to the electrode after spreading the active material on both sides of the substrate.

3.2. Cell development

Fig. 5 shows the constant current discharge curves of the cells at different rates, from $C/5$ up to $10C$, C being their nominal capacity (25 Ah). Discharge durations and average discharge voltages have been used to calculate the specific energy at the $C/5$ and $8C$ rates, which are respectively 41 Wh/kg and 24 Wh/kg. The calculated specific power is 205 W/kg at the $8C$ rate, and 335 W/kg for a peak power pulse (10 s). These values agree with the high specific power/moderate specific energy required for hybrid vehicle applications [15,16].

The rechargeability test included constant current charges at the $C/5$, $C/2$, $1C$, $2C$, $3C$ and $5C$ rates, C being the nominal capacity of 25 Ah, and the recharge factor was $1.2C$ in all cases. The discharged capacity (at the $C/5$ rate) obtained after each constant current charge is represented in Fig. 6, considering that the nominal capacity of the cells (25 Ah)

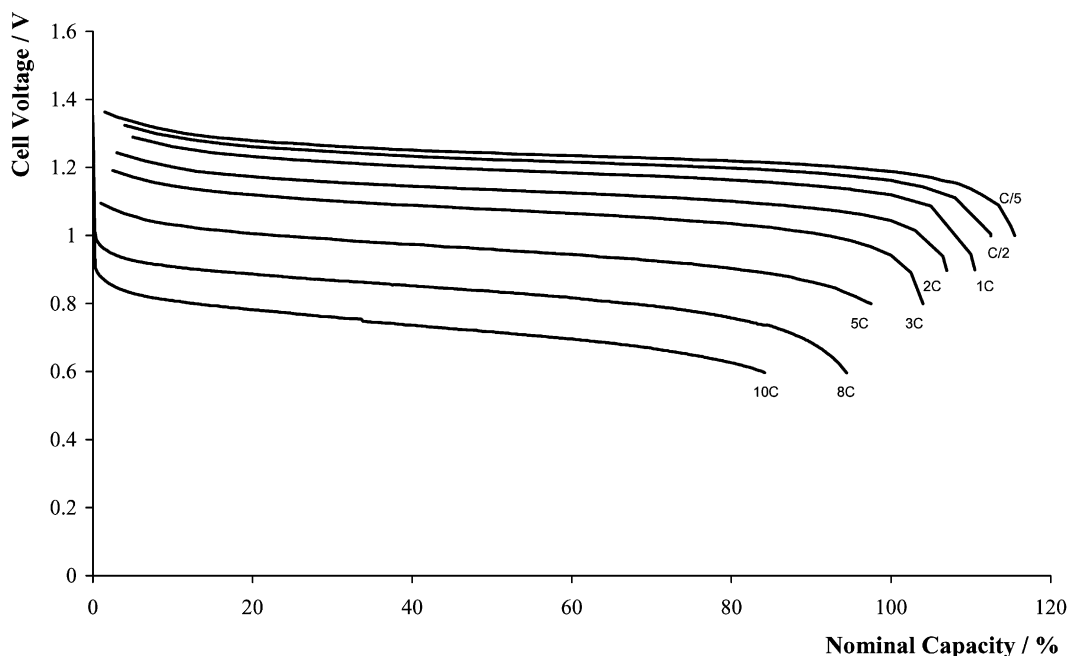


Fig. 5. Constant discharge curves of Ni/MH cells ($C = 25$ Ah).

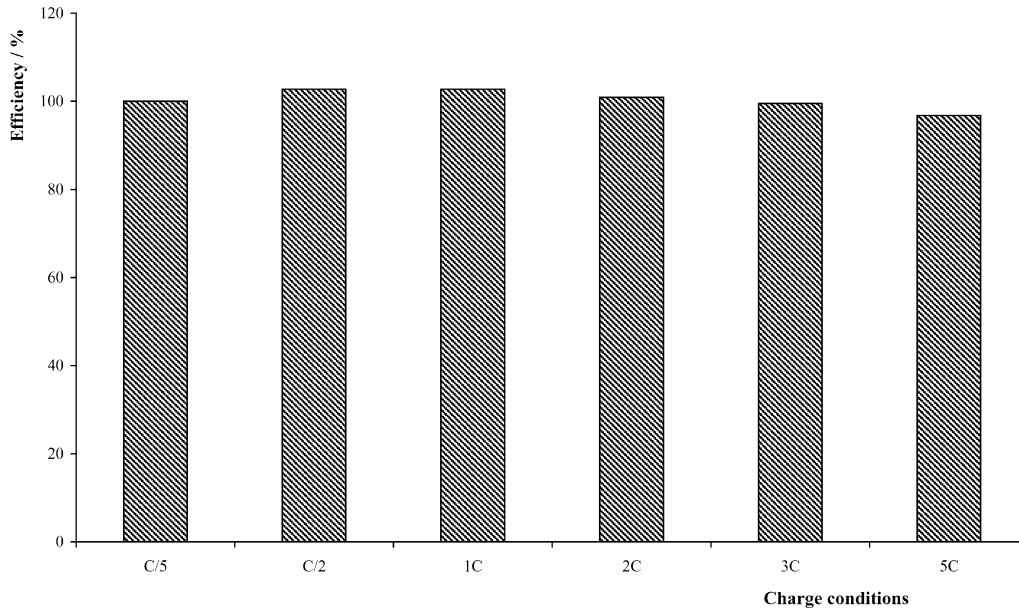


Fig. 6. Charging efficiency of Ni/MH cells under different charging regimes ($C = 25$ Ah).

corresponds to 100% efficiency and according to the following formula:

$$\text{Efficiency} = \frac{\text{Capacity (Ah) at the } xC \text{ rate}}{\text{Capacity (Ah) at the } C/5 \text{ rate}} \times 100$$

The figure clearly shows that the best charging efficiency is obtained when the cells are recharged at the 1C rate, and that up to the 3C rate the efficiency is over 100%. This fact enables the definition of a quick charge procedure, at least during a few minutes and 80% state of charge, to avoid temperature and internal pressure increase.

The charging efficiency for different states of charge has also been calculated charging the cells at the 1C rate and

then discharging at the $C/5$ rate down to 1.0 V. Fig. 7 shows the capacity discharged expressed as percentage of the nominal capacity after each partial charge. The charging efficiency obtained for the different charging ratios tested is higher than 95%, commonly 97–98%.

Cycling performance of the cells is satisfactory, both under constant current conditions and in special tests simulating the hybrid vehicle working conditions. More than 400 cycles have been achieved up to date discharging the cells at the $C/5$ rate down to 1.0 V (100% DOD) and charging at the $C/5$ rate and testing goes on. Ni/MH cells have also been cycled according to the power assist profile of the EUCAR specification for hybrid vehicles [17]. After 40 000 cycles

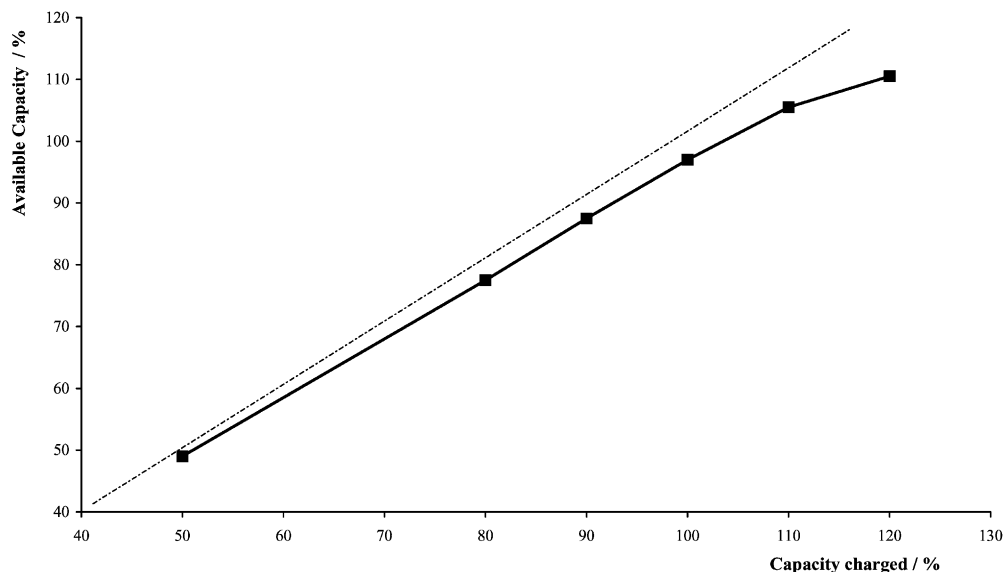


Fig. 7. Recharge efficiency test at the 1C rate of Ni/MH cells ($C = 25$ Ah).

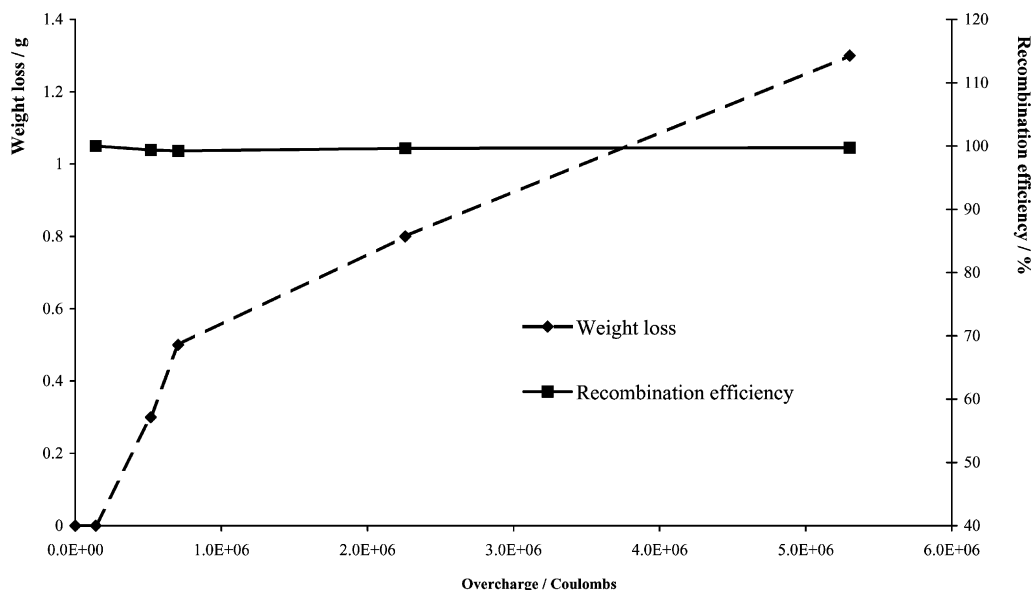


Fig. 8. Recombination efficiency of Ni/MH cells.

(equivalent to 2000 deep cycles) the cells did not show a significant capacity loss.

Finally, the recombination efficiency has been calculated, considering that in the water electrolysis process, each Ah charged represents a water consumption of 0.3361 g. The recombination efficiency values obtained when overcharging the battery at the $C/20$ rate are close to 100% as shown in Fig. 8. Moreover, the cell was further overcharged at increasing rates, thus, showing decreasing recombination efficiency values, ranging from 96.9% when overcharged at the $C/10$ rate to 78.2% during overcharge at the $1C$ rate.

4. Conclusions

The main factors affecting the high rate performance of the negative MH electrodes are:

- substrate type, nickel content and nickel distribution to assure a close contact substrate-active material;
- conductive additives with high specific surface area which provide increased active surface and connecting points between the alloy particles and between the alloy and substrate fibres;
- binders (PTFE and PVA) to avoid active material shedding during cycling, assuring high rate performance along the battery life: PVA also acts as surface agent, providing a homogeneous distribution of the active material through the substrate pores; and
- active material and electrode preparation conditions, through and adequate mixing of the components and final sizing of the electrodes with a press ($>1 \text{ t/cm}^2$).

Valve regulated Ni/MH prismatic cells rated 25 Ah and prepared with the high performance MH negative electrodes and positive electrodes impregnated electrochemically show

excellent high rate discharge capability and rechargeability. Recombination efficiency is nearly 100%, which allows for a maintenance-free operation.

Work performed up to date on the development of prismatic Ni/MH cells for high power applications encourages further studies in order to optimise energy and power battery ratios (Wh/kg and W/kg), thus, promoting their use for hybrid vehicles and 42 V automotive electrical network systems.

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