

High Performance Metal Hydride Alloy for Rechargeable Battery Technology

PLATINUM METALS ENHANCE ALLOY SURFACE PERFORMANCE

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Nickel metal hydride (NiMH) rechargeable battery technology is currently the major competitor to well-established nickel cadmium (NiCad) technology. Due to new legislation in the European Union and elsewhere, NiCad cells are gradually being replaced to reduce the use of toxic cadmium, and NiMH cells are predicted to be a reliable alternative. NiMH batteries provide a higher energy density and are environmentally more acceptable than NiCad cells. In addition they have a low memory effect, allowing easy charging and discharging. However, current NiMH technology has limitations, particularly when cells are rapidly charged/discharged, and the lifetime of a cell is ~ 500 cycles, compared to ~ 1000 cycles for NiCad. Here, we report advances enabling rapid charging/discharging to be achieved by the modification of the surface of the metal hydride alloy with platinum group metals. This enhances the rates of sorption of hydrogen within the alloy, and the alloy is shown to be stable in air. An overview of NiMH battery technology is presented and developments resulting in high performance cells are described.

The basis of the application of metal hydrides to secondary or rechargeable batteries has been established for well over 100 years, with Thomas Graham being the first to observe the reversible hydrogen absorption/desorption reaction in palladium (1). He found that when a current was applied to palladium and then reversed, that hydrogen was absorbed and then desorbed from the metal (1, 2).

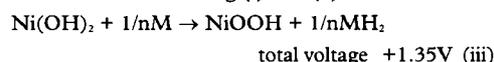
Nickel cadmium (NiCad) batteries are the most common, rugged batteries available, but because they contain cadmium they are being replaced by batteries containing metal hydrides (MH_x), which also have advantageous properties. The recent developments, see Figure 1, in metal hydride battery technology has been driven by the need to replace cadmium as the anode material, due to concerns over its use and environmental effects on its subsequent disposal. Metal hydrides develop a similar voltage to NiCad, use

the same cathode material (nickel(II) hydroxide) but provide a higher energy density. NiMH cells are required to have high capacity, long lifetime, low cost, rapid charging/discharging capabilities and have good resistance to problems caused by over charging/discharging.

The basic electrode reactions in NiMH batteries are shown below as charging reactions (discharge reactions in reverse):



Adding (i) and (ii)



The charging reaction involves the formation of the metal hydride (MH₂) and the nickel hydroxide is converted to the oxyhydroxide. The hydroxide ions and electrons are consumed as water, so there is no net loss of electrolyte.

Fig. 1 Components of the metal hydride electrode; the powder mix of nickel and metal hydride is first machined into an electrode (left, touching the powder); this is then pressed into porous nickel foam to form the finished electrode (right). A discontinuous palladium/ruthenium coating on the metal hydride powders greatly improves the high rate charge and discharge properties of the alloys



Details of the advantages and disadvantages of NiMH over NiCad cells are given in Table I, below (3).

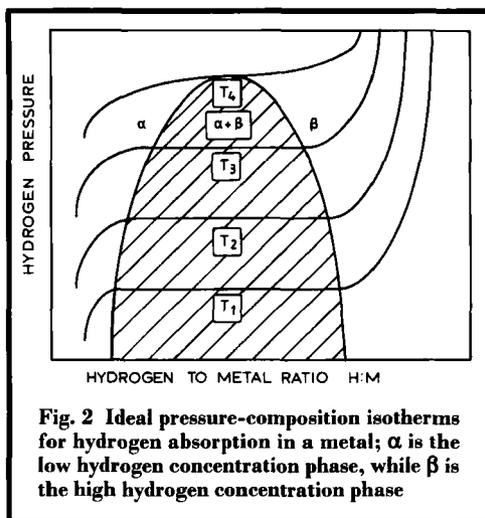
The hydrogen storage properties of the metal hydride anode are, however, quite specific for the battery application. Ideally, a typical metal hydride alloy should have a high capacity, rapid hydrogen absorption/desorption, minimal pressure hysteresis, low cost and a long lifetime (4).

The storage properties of a specific alloy are usually assessed by the measurement of the gaseous hydrogen pressure-composition isotherms. An ideal set of isotherms is shown in Figure 2, which is a representation of how the specific alloy will perform in a battery environment. For battery application, the major

absorption/desorption reactions must occur reversibly at room temperature and at hydrogen pressures of < 0.1 MPa (1 bar). Figure 2 also shows that the effective hydrogen capacity of the alloy decreases with increasing temperature, thus giving a finite operating temperature range (ambient up to 50°C) for these batteries. The hydrogen capacity of the alloy can then be expressed as a 'current (or C) rated capacity'. The current rated capacity is a measure of the amount of charge that an alloy can retain per gram of its mass. Metal hydride storage alloys are of various structures and a typical metal hydride storage alloy, AB₅ (LaNi₅), has a current rated capacity of 250–350 mA h g⁻¹ of alloy.

The first metal hydride to be assessed for battery application was palladium, which has almost ideal storage properties (2). Commercial palladium electrodes were reported in 1967 (5), but due to the cost and the relative mass of the electrodes compared to the conventional material, were not a success. With the discovery of the hydrogen storage properties of LaNi₅, batteries utilising hydride technology became more of a commercial possibility (6). However, poor oxidation resistance limited the cycle life of LaNi₅. In 1984, a breakthrough in metal hydride electrodes was made. Philips Research Laboratories published work that described the systematic alloying of the LaNi₅ alloy with other metals.

Table I Advantages/Disadvantages of Nickel Metal Hydride Batteries over NiCad	
Advantages	
Higher capacity than NiCad	
Low maintenance	
More environmentally friendly	
Rapid recharge	
Low memory effect	
Reasonable cycle life	
Disadvantages	
High rate performance lower than NiCad	
Poor charge retention	



This dramatically improved cell lifetimes, with only a small reduction in the storage capacity of the alloy (7). The elements introduced into the alloy were mainly cobalt and aluminium. The effect of cobalt was to reduce the rate of fragmentation of the alloy during prolonged hydrogen cycling, and this reduced the rate of oxidation of the alloy and prolonged the cell lifetime. The effect of aluminium was thought to induce a passive surface oxide layer, which prevented the oxidation of the alloy.

By 1990, when the first NiMH battery was commercially produced in Japan, the metal hydride alloy comprised many additional elements which improved lifetime while still maintaining the high storage capacity of the alloy (8–11).

However, the metal hydride alloy was still found to have a small cycle life compared to NiCad batteries, therefore further improvements to the metal hydride electrode were attempted. The 'microencapsulation' technique, involving electroplating the metal hydride particles with up to 10 weight per cent of copper or nickel, provided a continuous coating to the hydride alloy, that protected the active alloy from contact with the electrolyte, and thus prevented oxidation. However, this barrier between the alloy and the electrolyte introduced a rate limiting step to charge/discharge, and added 10 per cent

to the weight of the electrode, without adding to the energy storage capacity (12–13).

Another attempted improvement was a fluorination treatment of the metal hydride particles. This was found to be beneficial to the cell lifetime of electrodes. In this treatment, the metal hydride alloys, which have a rare-earth component were placed in a fluorine-containing environment, and rare-earth fluorides were formed at the surface of the alloy in preference to surface oxides/hydroxides. This surface coating was found to be more chemically stable in the cell environment, and thus extended the cell lifetime. However, the safety issues involved with fluorine make this alternative undesirable (14).

Other coating processes, that have been described in the literature, relate to the deposition of other metals and metal oxides on the surface of the alloy.

Electrochemically coating the alloys with cobalt and palladium, for instance, was found to enhance the cell lifetimes of the alloys (15), and this result was also observed when a nickel-palladium surface coating was applied (16). Cobalt(II) and ruthenium(IV) oxides surface coatings also enhanced the lifetime of the alloy in the cell (17).

Although the cell lifetime of the metal hydride alloys can be dramatically improved by these various techniques, the poor electrochemical activity of the cell still prevented rapid charging/discharging of the alloys. A possible solution was identified by Philips (18–19). It was found that by manipulation of the stoichiometry of the base alloy, highly electrocatalytic intermetallic compounds could be precipitated at the grain boundaries. These compounds were found to enhance the charge/discharge processes within the alloy. The elements found to produce this effect were molybdenum, which formed the MoNi, intermetallic, and aluminium which formed AlNi. From this brief review, it is clear that NiMH batteries are a strong competitor to NiCad, however, electrodes of low cost, rapid charging/discharging characteristics and with oxidation-resistant properties still need to be developed.

Recently, Johnson Matthey has patented new

technology that has resulted in a commercially viable process which allows efficient high rates of charge/discharge in a battery (20). In addition, it may provide protection against overcharge/discharge operations which shorten the lifetimes of the cells (21).

The process involves the discontinuous deposition of platinum group metals onto the surface of the metal hydride alloy. The presence of the platinum group metals enables hydrogen to pass rapidly through the surface of the alloy to the bulk, while still maintaining the hydrogenation activity even after extensive exposure to an oxidising environment. The hydrogen storage alloy used in this investigation was a rare-earth rich pseudo mischmetal with the stoichiometry: $\text{La}_{0.9}\text{Pr}_{0.05}\text{Nd}_{0.05}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.65}\text{Ni}_{1.5}$. This alloy has a two-phase structure of AB_5 -type material, together with a minor A_2B_7 -type phase, and has been found to have the hydrogen capacity AB_5H_x where x is ~ 4.8 . It is also completely deactivated after exposure to air. After examination on a high resolution scanning electron microscope (HRSEM), it was found that the surface of the alloy was discontinuously decorated with platinum group metals, in the range 0.16 to a maximum of 8 weight per cent (of the total weight of the alloy). The coated alloys were found to be extremely resistant to deactivation, while exhibiting very rapid hydrogenation kinetics.

Solid-Gas Work and Electrochemical Data

The solid-gas hydrogenation properties of the coated alloys were assessed gravimetrically, and hydrogen uptake was measured as a function of mass change on a microgram scale. The readings were taken under constant pressure atmospheres.

Having measured the solid-gas characteristics, sealed NiMH button cells were then constructed for electrochemical assessment, see Figure 1. The cells were prepared by intimately mixing the coated alloy with 30 wt.% nickel powder of average particle size $15 \mu\text{m}$ and 99.9 per cent purity, and electrodes of diameter 26 mm were formed by pressing. The electrodes were then

pressed into nickel foam baskets of 99.9 per cent purity having 110 PPI (pores per inch). The separator material was non-woven nylon 66 polymer. Additional sets of alloys coated with platinum group metals, to a total concentration of 0.16 wt.%, were also prepared for the electrochemical studies.

Coatings and Absorption/Desorption

The coated alloys were examined by transmission electron microscopy. Figure 3 shows a palladium coated particle. It is observed on the selected face that the bright field image shows a degree of continuity, therefore it is likely that although the coating is overall discontinuous, certain faces of the particle are more active than others during the coating process. In Figure 4, the bright field image of a particle coated with



Fig. 3 TEM Bright field image of a palladium coated particle; 1 cm represents $0.08 \mu\text{m}$
A are the palladium particles coated continuously on this face and B is the base alloy substrate



Fig. 4 TEM Bright field image of ruthenium coated particles; 1 cm represents $0.08 \mu\text{m}$
C are ruthenium particles discontinuously coated on the base alloy surface B

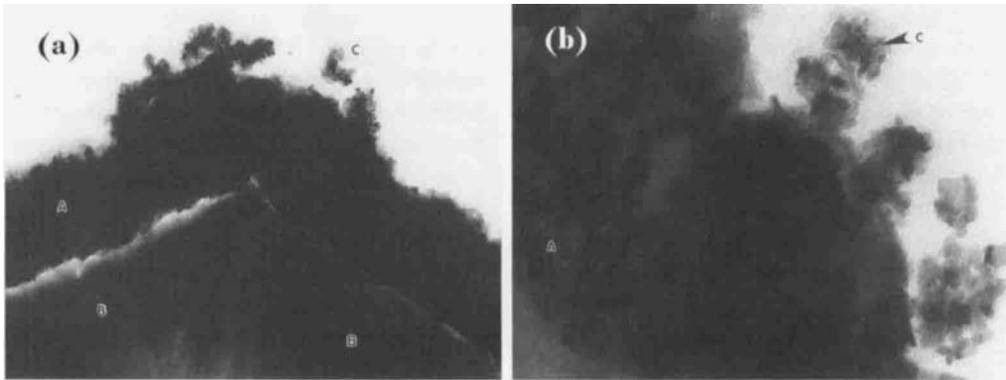


Fig. 5 TEM Bright field image of the combination palladium/ruthenium coated storage alloy
 (a) B is the base alloy; A is the palladium and C is a ruthenium particle 1 cm represents 0.08 μm
 (b) The discontinuous combination palladium/ruthenium coating 1 cm represents 0.036 μm

ruthenium shows a definite discontinuous coating. These observations confirm previous HRSEM work, where the ruthenium coating was discontinuously dispersed over the whole particle, while the palladium coating was more agglomerated on certain faces of each particle. Figure 5 shows an alloy particle coated with the palladium/ruthenium combination, where both facets of the two coating processes can be seen. The overall characteristics of the coating are more localised here due to the palladium deposition, but overall the coating is still discontinuous.

The solid-gas hydrogen absorption and desorption characteristics of the uncoated alloy at room temperature and 1 bar hydrogen pres-

sure are shown in Figures 6 and 7, respectively. It is observed that both the absorption and desorption kinetics are relatively slow, with the alloy reaching a hydrogen:metal ratio of ~ 0.75 after 20 hours exposure under hydrogen, Figure 6. The effects of exposure of the alloy to air are also illustrated, with the alloy no longer able to absorb any hydrogen.

Figures 8 and 9 show the analogous absorption/desorption plots, respectively, for alloys coated with platinum group metals. All the coated alloys show improved absorption/desorption rates, and the ruthenium containing alloys show prolonged resistance to deactivation, even after exposure to air. However, the combination-coated alloy has faster responses.

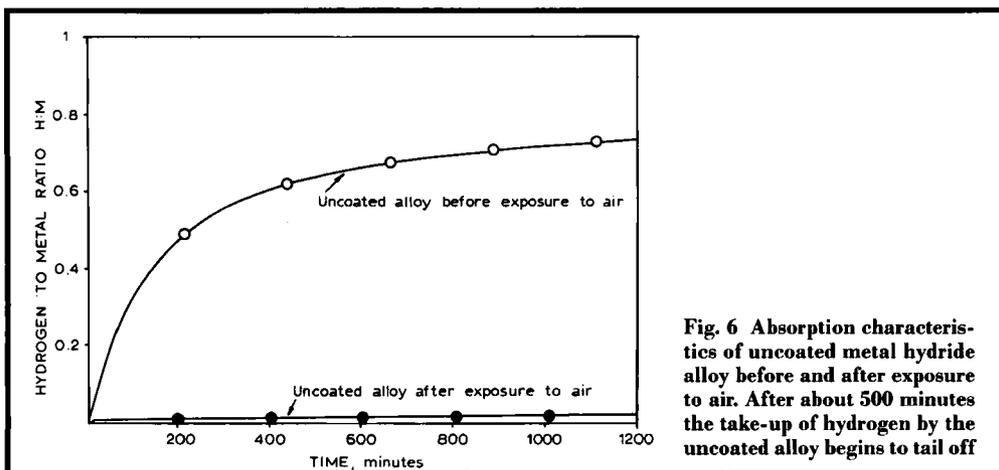


Fig. 6 Absorption characteristics of uncoated metal hydride alloy before and after exposure to air. After about 500 minutes the take-up of hydrogen by the uncoated alloy begins to tail off

Fig. 7 Desorption characteristics of uncoated metal hydride alloy before and after exposure to air. The uncoated alloy clearly retains considerable quantities of hydrogen, even after 50 hours

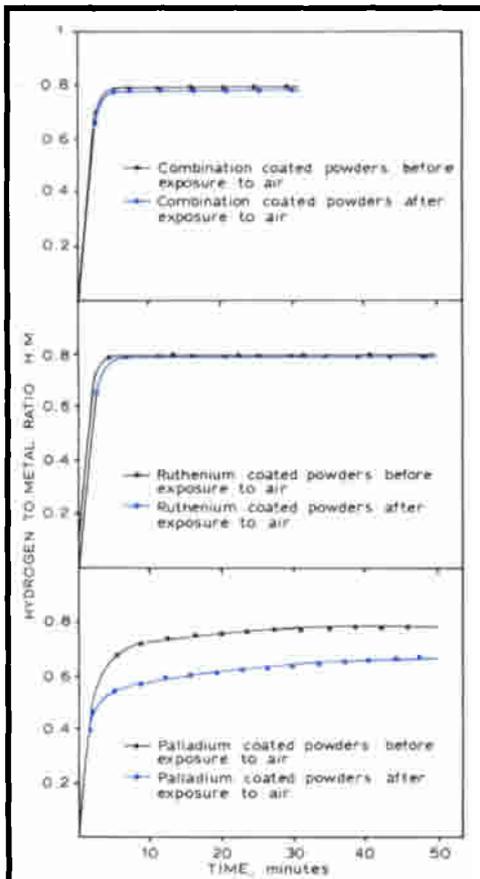
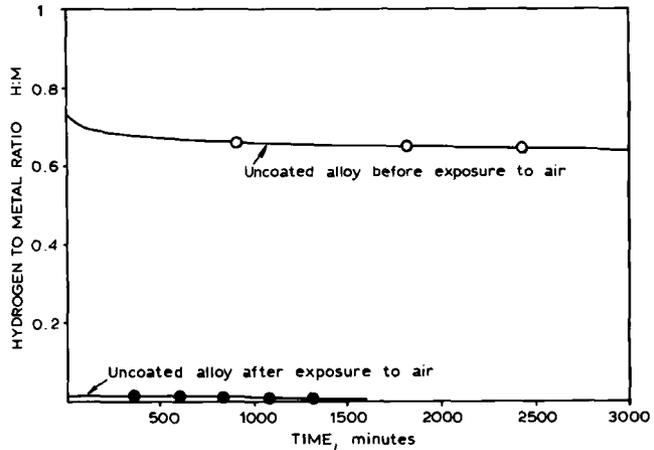


Fig. 8 Absorption characteristics of a substrate metal hydride alloy surface powder-coated with platinum group metals, before and after exposure to air. The palladium/ruthenium combination-coated alloy displays stability in air

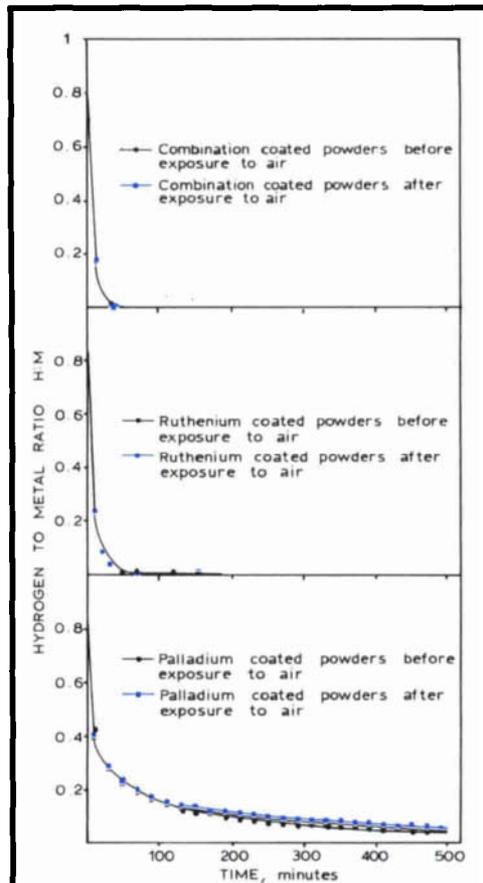
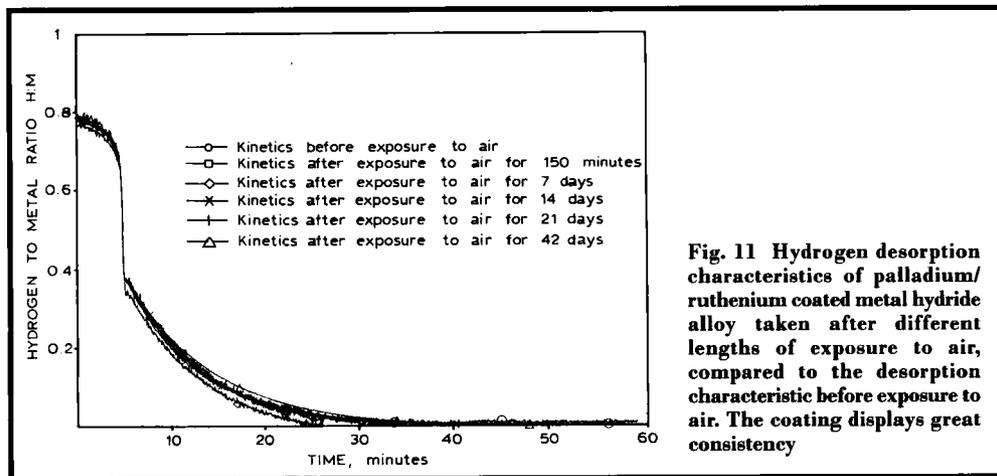
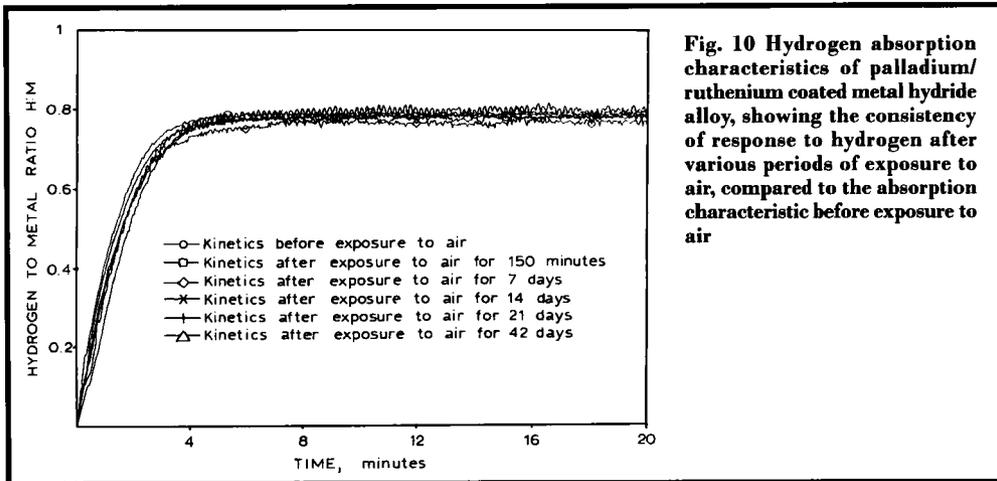


Fig. 9 Desorption characteristics of platinum group metals coated metal hydride alloy before and after exposure to air. The combination-coated alloy clearly demonstrates the stability of the coating to air



The palladium/ruthenium combination coating was also assessed for retaining prolonged activity for absorption/desorption of hydrogen, by exposing samples to air for up to six weeks, see Figures 10 and 11. After this length of time there was no appreciable loss of capacity.

ious rates, see Table II. Figure 12 shows a typical 0.2C discharge profile (over a five hour time period) comparing the coated alloy with the uncoated base alloy. It was observed that the platinum group metals coated material has a

Charging/Discharging Studies

Having assessed the capacity of the cells, studies on charging/discharging were performed. Charging of the cells followed the European Standard for NiCad cells (22), that is, charging was performed at a rate of 0.1C, which means that charge was fed into the cell at current of 15 mA. Capacity was calculated to be 150 mA h.

The charged cells were then discharged at var-

Charge rating	Discharge/charging times
3.0C	20 min
2.0C	30 min
1.0C	1 hour
0.5C	2 hours
0.2C	5 hours
0.1C	10 hours

higher discharge voltage and slightly improved discharge efficiencies. The fact that there is little difference between the coated and uncoated alloys is a typical result as button cells are engineered to show high efficiencies at low discharge rates. At a higher discharge rate, the difference between the uncoated and coated alloys becomes more pronounced.

In Figure 13 is shown a typical 0.5C discharge profile. While the uncoated alloy shows a loss of efficiency, the coated alloys still display a discharge efficiency of > 90 per cent. This indicates that only trace amounts of alloy are required to improve substantially the charging/discharging properties.

Figures 14 and 15 show discharge profiles of 1.0 and 3.0C, respectively. It is observed that the uncoated alloy fails (that is, it drops below a designated voltage) fairly quickly. The coated

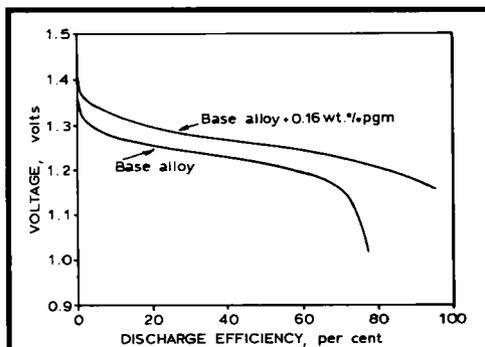


Fig. 12 The discharge characteristics of cells, comparing coated and uncoated alloys. Closed cells: 0.2C discharge

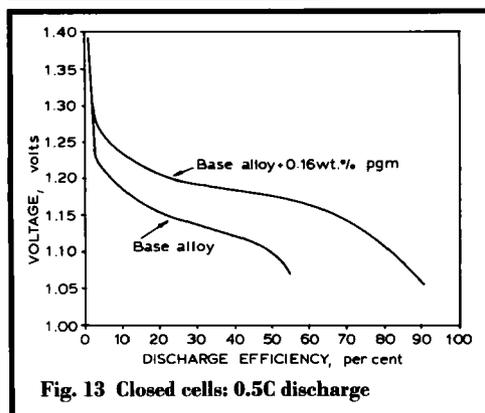


Fig. 13 Closed cells: 0.5C discharge

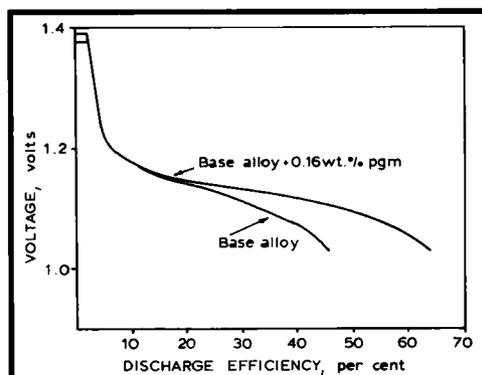


Fig. 14 Closed cells: 1.0C discharge

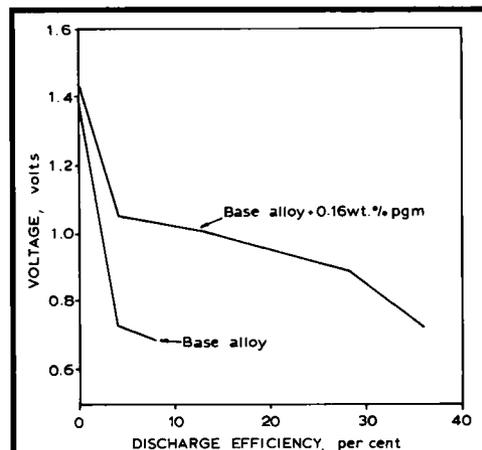
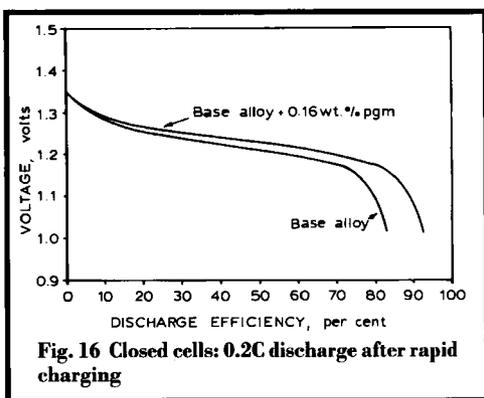


Fig. 15 Closed cells: 3.0C discharge

alloy, however, maintains the voltage for longer than the uncoated materials, showing that the alloy has high discharge rate capability. However, it must be emphasised that the button cell configuration is not designed to withstand high rate discharging. Nevertheless, the difference between the uncoated and coated material is still clear to see.

Rapid charging of the alloys was also attempted. The cells were charged at a normal charge rate, then discharged at 0.2C. This was followed by a 3.0C (20 minute) charge and again discharged at 0.2C.

In Figure 16 the difference in efficiencies between these two charge rates is shown. It is observed that there is only a minimal loss of efficiency when increasing the charge rate by 30



times. It can therefore be concluded that these alloys are likely to be highly efficient at high rates of charge and discharge.

Conclusions

The data presented suggest that the surface deposition of trace amounts of platinum group metals on metal hydride electrode alloy considerably improves the charging/discharging properties of the electrodes. It can be concluded that for alloys of this type, commonly encountered in NiMH cells, the surface provides a barrier to rapid charging and discharging and the platinum metals, deposited on the surface, are thus reducing the potential barrier and allowing the rapid and efficient charging/discharging of the alloy.

A comparison between the power/energy profiles of typical secondary batteries and this technology suggests that the properties observed here are superior to those of the current NiMH cells and are competitive with the NiCad technology, while being more cost effective.

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Platinum Metals Chemistry Conference

The seventh international conference on the Chemistry of the Platinum Group Metals will be held at the University of Nottingham from 25th to 30th July 1999. Developments in research on clusters, nanostructures and their properties, anti-cancer drugs, polymerisations and other catalytic reactions, ligand effects, catalyst screening, syntheses of complexes and their properties, and photochemistry will be discussed, with speakers coming from Europe, Canada, the U.S.A., New Zealand, Hong Kong and Japan. Plenary lectures will be delivered by Professors B. F. G. Johnson, R. H. Grubbs, D. M. P. Mingos, N. P. Farrell, R. A. Van Santen, J.-P. Sauvage and G. van Koten. There will be poster displays with prizes, and a student bursary is available.

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