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Article

The Effect of Palladium Coating on Hydrogen Storage Alloy Electrodes for Nickel/Metal Hydride Batteries

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Este trabalho apresenta estudos de carga/descarga realizados sobre ligas metálicas multi componentes ("misch metal alloys") recobertas com Paládio e que podem ser utilizadas como eletrodos em baterias de níquel/hidreto metálico. Foi determinado o efeito do recobrimento nas características voltamétricas, no ciclos de vida e na capacidade sob diversos regimes de descarga para os eletrodos de liga metálica. O número de ciclos necessários para ativar os eletrodos de liga metálica diminui quando o conteúdo de Pd aumenta. Os resultados mostram também que as ligas recobertas com Pd apresentam uma maior capacidade de carga e um desempenho melhor que aquelas sem o Pd. Essas melhores características podem ser atribuídas ao efeito catalítico do Pd sobre a reação de hidrogênio.

Charge / discharge studies carried out on Pd - coated misch metal - based alloys for use in nickel-metal hydride batteries are presented. The effect of Pd coating on the voltammetric characteristics, life cycle behavior, and rate capability of the alloy electrodes was determined. The number of cycles required to activate the alloy electrodes decreases with an increase in the Pd content. The results also show that Pd - coated alloys exhibit higher storage capacities and better performance than bare alloys.This improved performance can be attributed to the catalytic effect of Pd on the hydrogen electrode reaction.

Keywords: *metal hydride electrodes, hydrogen storage capacity, palladium coating*

Introduction

At present there is a renewed interest in research on hydrogen reversible storage resulting from the recognition of the many potential advantages of such a system for use in electrochemical energy storage devices. For example, in power sources that utilize hydrogen as a fuel, the chemical storage of hydrogen as a metal hydride may lead to a considerable reduction in operating pressures and volume. Volumetric energy densities comparable to those of cryogenic hydrogen can be attained for applications where the weight is less important, such as in the terrestrial storage of solar-electrolytic hydrogen, and when the bi-functional hydrogen electrode is employed in alkaline batteries. When fully developed, Ni-MH batteries, for example, will adequately replace the existing Ni-Cd batteries for several stationary (reserve and emergency power sources, emergency lighting in public buildings such as schools, hospitals, etc.) and portable (video cameras, cellular telephones, lap-top computers, etc.) applications. The advantages of Ni-MH batteries over the Ni-Cd system are: (i) a higher cell energy density, and (ii) the elimination of toxic cadmium thereby preventing environmental damage. Furthermore, the development of Ni-MH batteries will make them potential candidates for transportation applications, such as in electric vehicles, with large benefits in the reduction of environmental pollution[1].

In the selection of appropriate intermetallic compounds for hydrogen storage, stability is obviously one of the most important factors, and thus the choices of candidate materials are discussed mainly based on their affinity for hydrogen. The empirical model formulated by Miedema[2,3], and commonly referred to as "the rule of reversed stability", is generally used as a guide for the prediction of the heat of formation of intermetallic compounds and alloys. Accordingly, since the stability of a ternary hydride, AB_xH_y, increases with the increasing stability of the intermetallic compound, AB_x, the plateau pressure of a candidate hydrogen storage alloy can be adjusted by an appropriate choice of its modifiers. In addition, the hypothesis that an intermetallic compound will more readily accommodate hydrogen atoms (*i.e.*, its free energy of formation will become more negative, as the volume of their interstitial sites increases) can be used as a complementary tool in selecting candidate hydriding alloys. For example, starting with a lanthanum-based hydriding intermetallic alloy, a substitution of cerium, for example for lanthanum, will make the intermetallic compound less stable and thus increase the plateau pressure. Furthermore, modifiers are selected according to their properties as hydrogen absorbers, catalytic effects for enhanced hydrogen absorption kinetics, sintering inhibition, and resistance to oxidation and attack from the corrosive electrolyte environment[4-12].

In this research, the effect of Pd coating on the intermetallic compound $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$, where Mm (misch metal): 43.1 wt% La, 3.5 wt% Ce, 13.3 wt% Pr, and 38.9 wt% Nd was studied in order to improve both the kinetics of hydrogen absorption in the alloy and its life cycle characteristics.

Experimental

The working electrodes were prepared by mixing 130 mg of sieved (< 120 μm) $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$ alloy powder, previously coated by Pd - electroless deposited by the technique described elsewhere[13], with 370 mg of copper powder which was used as the binding material. The mixed powders were then cold pressed to 150 kg/cm^2 onto a 1 cm^2 current collector constructed from a porous nickel mesh. The addition of copper powder reduces the formation of cracks upon electrode cycling, which affects the mechanical integrity of the electrode[14]. The geometric area of the Pd - coated alloy working electrode was about 2 cm^2. The counter electrode (sintered NiOOH) had a much larger geometric area than that of the working electrode. The electrolyte, 1 M KOH, was prepared from reagent grade KOH and deionized water. A Hg/HgO electrode containing the same electrolyte was used as a reference electrode. All experiments were made at 25 °C. Electrochemical hydrogen storage capabilities of the Pd - coated alloy electrodes were monitored by measuring the charge / discharge response of the electrode to currents delivered by a battery cycler made in our laboratory. The working electrodes were previously activated for hydride formation by continuous galvanostatic cycling until a constant value of the hydrogen storage capacity was obtained. In all electrochemical tests, the discharge cut-off potential was -0.6 V *vs.* Hg/HgO reference electrode. The electrochemical measurements also included the determination of the life cycle and rate capability of the Pd -coated alloy electrodes.

The charging-discharging process of the metal hydride electrode is described by the overall reaction:

$$M + x\,H_2O + x\,e^- = MH_x + x\,OH^- \qquad (1)$$

and the electrochemical storage capacity is proportional to the hydrogen content of the metal hydride.

Accordingly, the specific discharge capacity, C_d, was calculated from the amount of electricity, Q, discharged from the electrode, defined per unit weight of the alloy electrode,W, according to:

$$C_d = \frac{Q}{W} \qquad (2)$$

where C_d is expressed in mAh/g.

Results and Discussion

Voltammetric studies

Pd - coated alloy electrodes were cycled at 1 mV/s between -0.4 V and -1.3 V (Fig. 1). The first potential cycle shows electroreduction current peaks due to the presence of copper oxides present in freshly prepared working electrodes. As copper oxides cannot be reformed during the forward scanning in the positive potential direction under

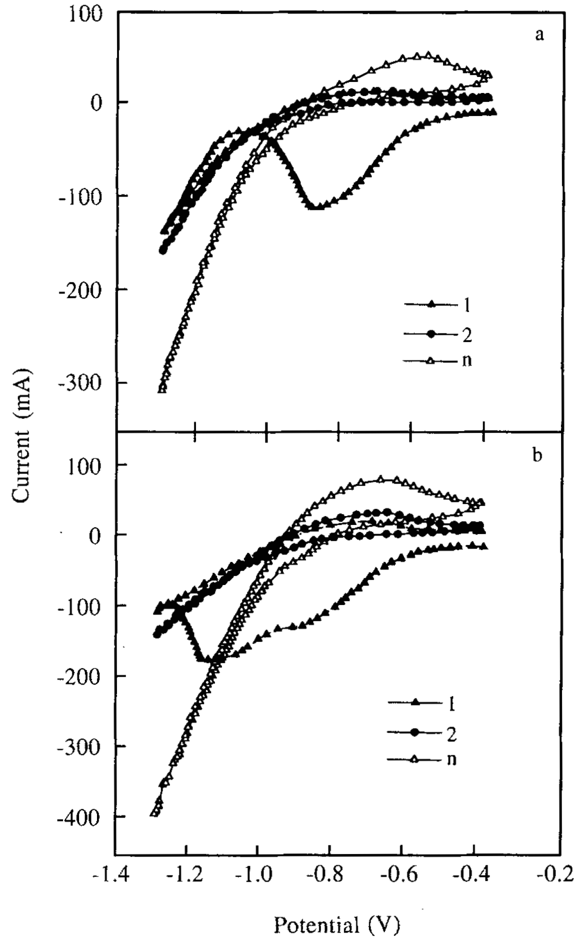

Figure 1. Cyclic voltammograms at 1 mV/s for Pd - coated alloy electrodes with different Pd content: (a) 3%; (b) 6%. The cycle number is indicated in the figure.

the experimental conditions used in this work[15], the electroreduction current peaks were no longer observed in the subsequent cycles, where only the current peaks related to the hydrogen electrode reaction could be detected. Furthermore, during the reverse scanning, the current increased rapidly when the potential decreased below -0.9 V (*vs.* Hg/HgO), due to the contribution of the hydrogen evolution reaction. During the forward scan, a broad anodic current peak related to the electro-oxidation of absorbed hydrogen was observed[4,16]. As the number of reduction - oxidation cycles increases, hydrogen electroformation occurs earlier, and correspondingly the hydrogen electro-oxidation current peak also increases. These processes, as can be inferred from the voltammograms in Fig. 1, are further favored when the Pd content increases from 3% to 6%. The activation effect by potential cycling can be attributed to the reduction of metal surface oxides which increases the reaction surface area. Otherwise, the reaction surface area also increases during the activation procedure due to the continuous expansion and contraction of the metal alloy surface produced by the formation of the hydride phase and the subsequent dehydriding process.

The position of the broad anodic current peak corresponding to the dehydriding reaction:

$$H_{ab} + OH^- \longrightarrow H_2O + e^- \qquad (3)$$

reflects the overpotential for this reaction and provides information about the effect of Pd on the reaction kinetics. Thus, the voltammograms in Fig. 1 show that the anodic current peak potential shifts from ca. -0.60 V to ca. -0.68 V on increasing the Pd content from 3% to 6%. Furthermore, for the alloy electrode without Pd coating, the anodic current peak appears at ca.-0.57 V. As the diffusion coefficient of hydrogen reported for the La-based AB_5 alloy is around 10^{-7} cm^2 s^{-1} [17], and taking into account that this value is large enough and on the order of that of Pd[18], it is reasonable to assume that Pd plating has a catalytic effect on the charge transfer step on the surface of the electrode,

$$H_{ad} + OH^- \longrightarrow H_2O + e^- \qquad (4)$$

which controls the overall electro-oxidation process of absorbed hydrogen[4].

The influence of the activation treatment on the electrochemical behavior of Pd-coated alloy electrodes

Pd-coated alloy electrodes with different Pd contents were subjected to an activation treatment comprised of cycling the electrodes in 1M KOH using a constant current at C/10 for 14 h in the charge, and at C/4 in the discharge, up to the cut - off potential, where C/x denotes the current that would completely discharge the fully charged electrode in x h. The corresponding electrode potential *vs.* discharge capacity plots (Fig. 2) show that after the first cycles the alloy electrode without Pd coating exhibits both high overpotential and low discharge capacity. As the number of charge-discharge cycles increases, the overpotential decreases and higher discharge capacities are attained as a consequence of the above-described activation effect. On the other hand, Pd - coated electrodes present low overpotentials, and high discharge capacities are obtained after a few cycles.

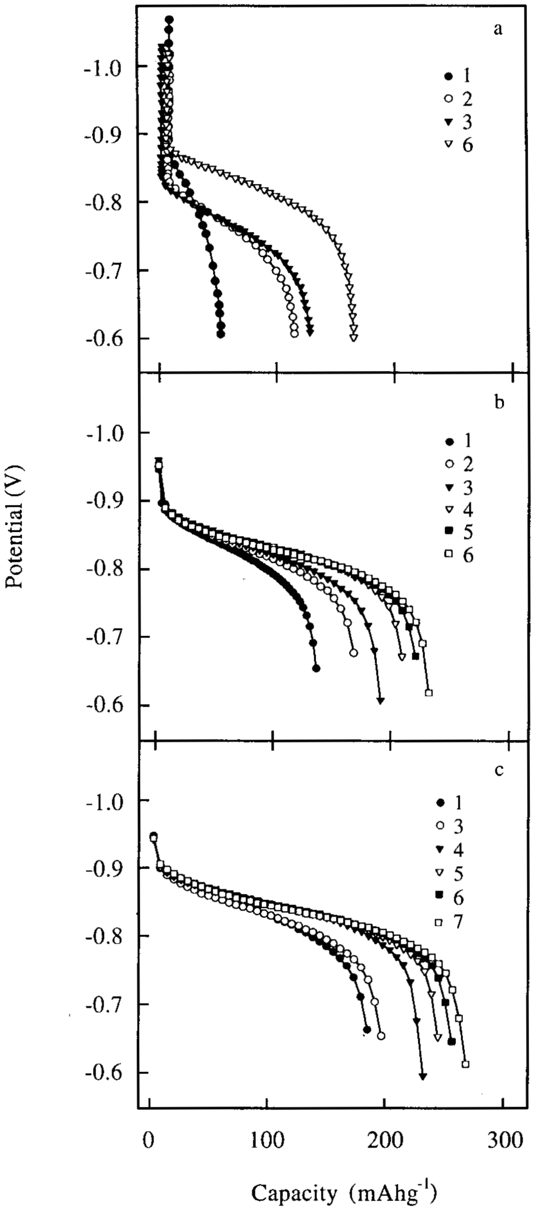

Figure 2. Plots of electrode potential *vs.* discharge capacity for Pd - coated alloy electrodes with different Pd content : (a) 0%; (b) 3%; (c) 6%. The cycle number is indicated in the figure.

Life cycle behavior of Pd-coated alloy electrodes with different Pd contents

The Pd-coated alloys were subjected to charge-discharge cycling at C/2 rates. The corresponding discharge capacities were determined at -0.6 V. The number of cycles to activate the alloy electrodes and to attain full capacity decreased with an increase in the Pd content (Fig. 3). Full capacity was obtained after 6-10 cycles for Pd-coated alloy electrodes with a Pd content ≥ 6%. Furthermore, the Pd-coated alloy electrode with 6% Pd presented the highest discharge capacity, which was on the order of 285 mAh/g (Fig. 4). It should be noted that after prolonged cycling, *e.g.*, more than 40-50 cycles, the alloy electrode undergoes some mechanical deterioration due to the consecutive expansion and contraction of the binder lattice during cycling.

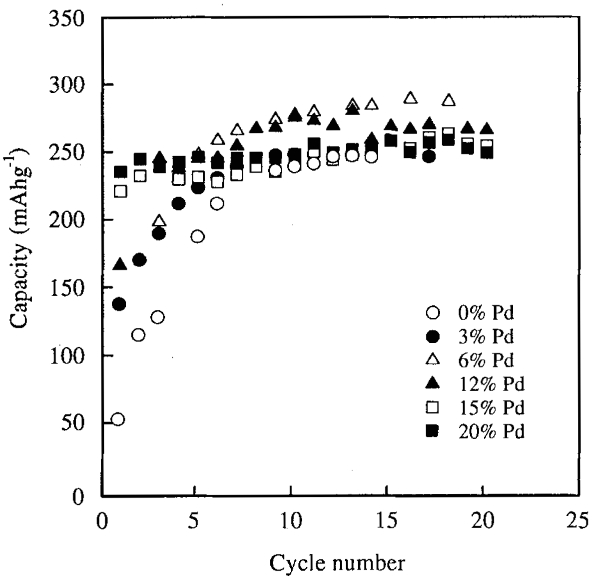

Figure 3. Life cycle behavior of Pd - coated alloy electrodes with different Pd content.

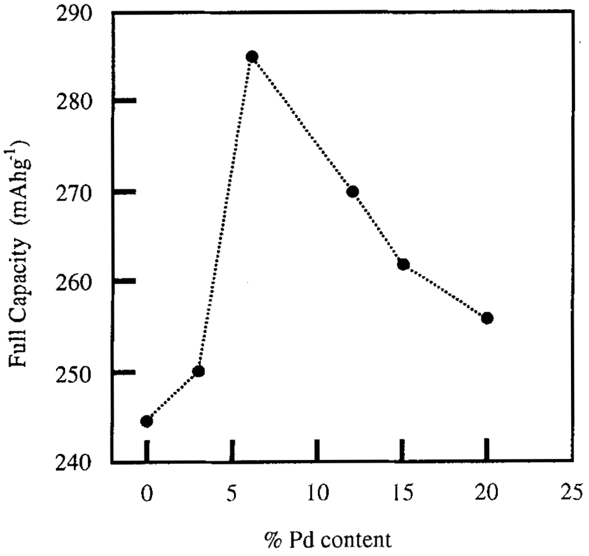

Figure 4. Dependence of the full discharge capacity of Pd - coated alloy electrodes on Pd content.

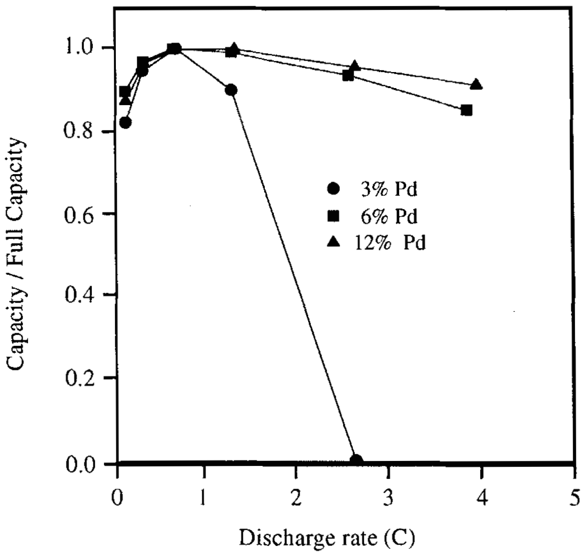

Figure 5. Discharge rate capabilities for Pd - coated alloy electrodes with different Pd content.

The effect of Pd content on the discharge rate capability of Pd-coated alloy electrodes

Plots of the discharge rate capabilities for Pd - coated alloy electrodes with different Pd contents are presented in Fig. 5. The electrodes were first charged at C/2 for 2 h 20 min, and then discharged at different rates. Fig. 5 shows that the Pd - coated alloy electrodes with a Pd content ≥ 6% have high discharge capacities at low discharge rates, and they retain these high capacities even at higher rates of discharge, whereas for a Pd content ≤ 3%, the Pd - coated alloy electrodes exhibit a high decay in their capacities at high discharge rates.

Conclusions

Pd-coated alloy electrodes exhibited excellent hydrogen storage behavior and good performance as metal hydride electrodes in alkaline solution. The Pd coating was very effective for increasing both the discharge capacity and rate capability and decreasing the galvanostatic cycling time for activating the alloy electrodes. The highest discharge capacity was attained after 6-10 charge - discharge cycles for alloy electrodes with a 6% Pd content. The improved performance of Pd-coated electrodes is attributed to the catalytic effect of Pd on the charge transfer step on the electrode surface.

Acknowledgments

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