

Short communication

Electrochemical characterization of a hydride-forming metal alloy surface-modified with palladium

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Abstract

The effect of surface palladium films on the electrochemical properties of hydride-forming metal alloys used as cathode materials in Ni-metal hydride cells has been studied. The results indicate that the presence of surface Pd improved the discharge capacity and rate capability of the hydride electrodes. The enhancement in performance may be explained on the basis of the electrocatalytic effect of Pd on the kinetics of the hydrogen absorption/desorption (hydriding/dehydriding) reactions.

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1. Introduction

There is currently a renewed interest in the study of hydrogen-storage devices, especially in the preparation of metallic alloys with enhanced hydrogen-storage capabilities in which energy densities comparable to those of cryogenic alloy-stored hydrogen are attained. The use of such alloys as negative electrodes in rechargeable alkaline cells, such as the Ni-metal hydride (Ni-MH) battery, is a major application [1–12]. Ni-MH batteries afford higher energy density and longer cycle life than Ni–Cd cells; in addition, the need for Cd, a highly toxic element, is eliminated.

It has already been demonstrated [2–9,13] that electroplating the alloy electrode with a variety of metals such as Cu, Ni, Pd leads to a vast improvement not only in cycle lifetimes but also in high-rate discharge abilities. In the case of Pd [9,11,12], it has been surmised that the Pd coatings are easily permeable by hydrogen atoms but not by oxygen atoms. Consequently, the Pd-coated metal alloy surface is resistant to oxidation during the charge/discharge cycles.

In this work, electrochemical studies on the kinetics of the hydriding/dehydriding processes at the alloy hydride electrodes as a function of the amount of surface Pd are presented. The Pd-coated alloy electrodes were tested along charge and discharge cycles in alkaline media at 25 °C, and

their discharge capacity and cycle life behavior were evaluated.

2. Experimental

The composition of the alloy investigated was $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$, where Mm (mischmetal) is 43.1% La, 3.5% Ce, 13.3% Pr and 38.9% Nd. The alloy powder particles were coated with Pd by electroless deposition using hypophosphite as the reducing agent [14]. In this procedure, the alloy powder was immersed in an electroless plating bath containing: 2 g/l $PdCl_2$, 3 ml/l HCl (38%), 160 ml/l NH_4OH (with 28% NH_3 content), 27 g/l NH_4Cl , and 10 g/l $NaH_2PO_2 \cdot H_2O$ (55 °C, pH 10). The electroless Pd plating was carried out by using different Pd-to-alloy weight ratios. The amount of deposited Pd was determined by the difference between the Pd concentration in the electrolyte bath before and after the electroless plating procedure. The working electrodes were prepared by mixing 75 mg of the Pd-coated alloy powder with 75 mg of teflonized carbon (Vulcan XC-72 and 33 wt.% PTFE) and pressing the mixture on a current collector made of Ni mesh (1 cm²); in this manner, electrodes with a geometric area of 2 cm² were obtained. The counter electrode was made up of sintered Ni, and the reference electrode was Hg/HgO; all potentials reported are referred to the Hg/HgO reference electrode. In all the experiments, the electrolytic solution contained 6 M KOH at 25 °C. The working electrodes were subjected to

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successive charge/discharge cycles at a current of 10 mA. The charge-cycle duration was 2.2 h and the discharge capacity was measured at a cut-off potential of -0.7 V.

Charge/discharge cycles with amorphous-Pd powder electrodes were also performed in a 6 M KOH at 25 °C. For this purpose, the amorphous-Pd powder was obtained by using the electroless technique described earlier.

3. Results and discussion

The Pd-coated alloy electrodes were activated in 6 M KOH at 25 °C by galvanostatic charge/discharge cycling at 10 mA. After activation, a complete charge/discharge cycle for a Pd-coated electrode showed the typical potential arrest corresponding to the hydrogen desorption process (Fig. 1). Furthermore, a discharge capacity value of 210 mAg^{-1} was attained at the cut-off potential of -0.7 V for the alloy electrode with a 5% Pd content.

Fig. 2 shows the changes in the discharge capacity of metal hydride electrodes that contained varying amounts of surface Pd during the initial charge/discharge cycles. The number of cycles needed to activate the electrodes and to attain full capacity decreased upon increasing the Pd content. Moreover, for the alloy with a 6% Pd content, the full capacity was obtained after only a few cycles. Plots of the discharge-rate capabilities as a function of Pd content are shown in Fig. 3; in these experiments, the electrodes were first charged at 10 mA for 2.2 h and then discharged at a different rate C , where C denotes the current that would completely discharge the fully charged electrode in 1 h. Electrodes with Pd content of 5 and 10% exhibited high capacities at both low and high discharge rates; in comparison, the uncoated alloy electrodes displayed rapid decay at high discharge rates. This difference may be attributed to the electrocatalytic effect of Pd on the charge-transfer process at the electrode surface.

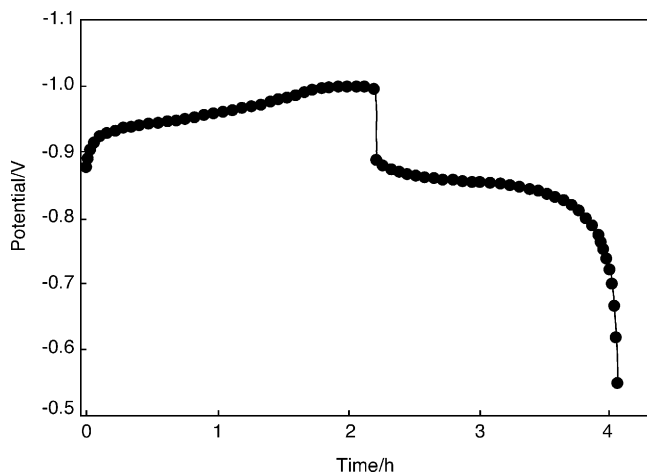


Fig. 1. The potential variation during the 12th galvanostatic charge/discharge cycle of a Pd-coated electrode with a 5% Pd content. Charge/discharge current: 10 mA. Electrolyte: 6 M KOH at 25 °C.

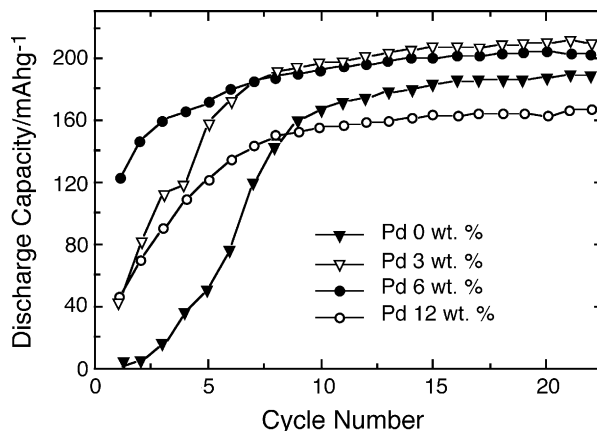


Fig. 2. Discharge capacity as a function of the number of charge/discharge cycles for alloy electrodes coated with varying amounts of Pd. Charge/discharge current: 10 mA. Experimental conditions were as in Fig. 1.

The increase in capacity for Pd-coated alloy electrodes has been thought to result from the formation of a hydride at the amorphous-Pd film [10]. However, experiments with amorphous-Pd powder indicated the absence of appreciable hydrogen absorption. In this study, the amorphous-Pd powder electrodes were cycled using charging/discharging currents of 5 mA. The potential versus time curves obtained under these conditions (Fig. 4) indicate the absence of any significant potential arrest, which is characteristic of the hydrogen desorption process. Furthermore, for the amorphous-Pd electrodes discharge capacities as low as 7 and 13 mAg^{-1} (Fig. 5) were attained at cut-off potentials of -0.7 and -0.4 V, respectively, as compared to the higher discharge capacities (180 – 220 mAg^{-1}) obtained for the Pd-coated alloy electrodes.

The scanning electron microscope (SEM) images of Pd-coated alloy powders showed that the Pd film possessed a granular structure that is expected to favor hydrogen diffusion into the alloy. SEM-energy-dispersive X-ray (EDX) analysis of the cross section of post-cycled Pd-coated electrodes revealed that electrodes with a 5% Pd content are characterized by non-uniform granular Pd deposits; a

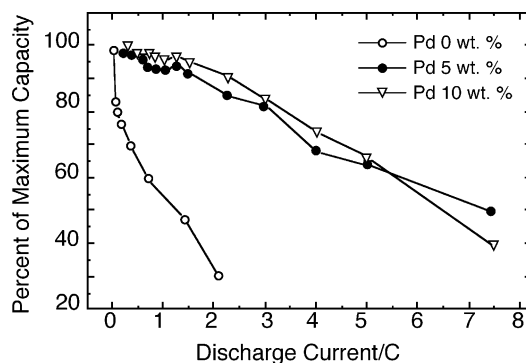


Fig. 3. Discharge-rate capabilities for alloy electrodes coated with varying amounts of Pd. Charge current: 10 mA. Experimental conditions were as in Fig. 1.

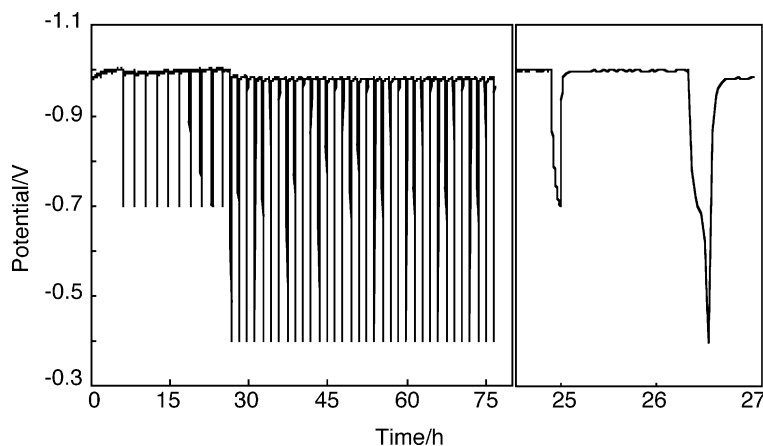


Fig. 4. Electrode potential vs. time plots for an amorphous-Pd powder electrode. Charge/discharge current: 5 mA. Experimental conditions were as in Fig. 1.

considerable increase in the film thickness was observed when the amount of Pd was increased. The SEM images of the cycled electrodes also indicated that the generation of new particles occurred via crack-formation that accompanied the hydriding/dehydriding processes.

The electrocatalytic effect of the surface Pd on the hydriding/dehydriding process was studied by means of cyclic voltammetry and linear polarization measurements. Voltammograms for the alloy electrodes coated with varying amounts of Pd content were obtained between -0.4 and -1.3 V at a sweep rate of 1 mV/s; the results are shown in Fig. 6, where a shift (from -0.65 to -0.74 V) in the potential of the anodic peak can be noted when the Pd content was increased from 5 to 10%. Furthermore, for the uncoated alloy electrode the anodic current peak appears at ca. -0.63 V. The anodic peak corresponds to the hydrogen desorption reaction,



which is the rate-determining step in the overall dehydriding process. Since the potential of the peak is a measure of

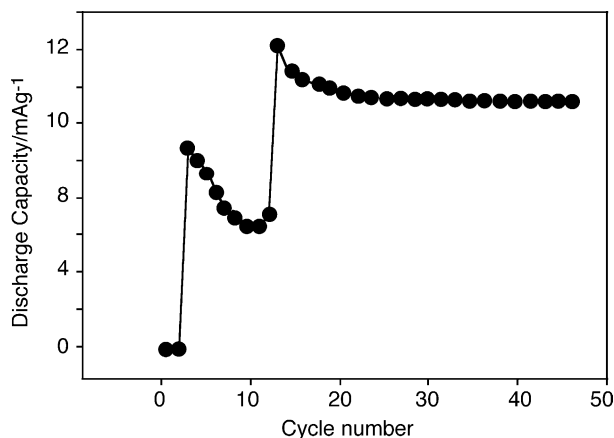


Fig. 5. Discharge capacity vs. cycle number plot for an amorphous-Pd powder electrode. Charge/discharge current: 5 mA. Experimental conditions were as in Fig. 1.

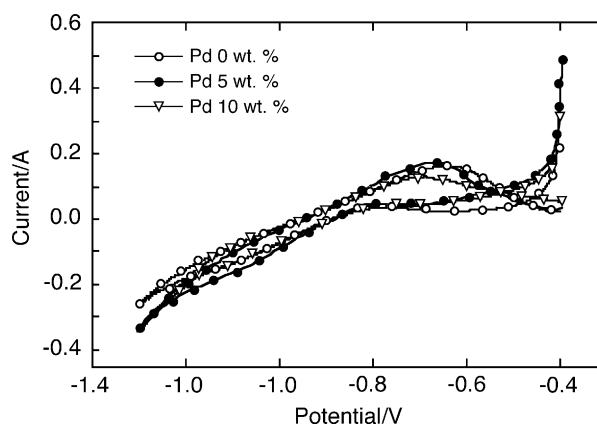


Fig. 6. Cyclic voltammograms in 6M KOH at 25°C , at a sweep rate of 1 mV/s, for the alloy electrodes coated with varying amounts of Pd content.

the overpotential of the dehydriding reaction [8,9], it is reasonable to argue that the surface Pd has a catalytic effect on the charge-transfer reaction that takes place at the electrode surface.

Linear polarization studies were carried out on Pd-coated alloy electrodes with varying amounts of Pd content at

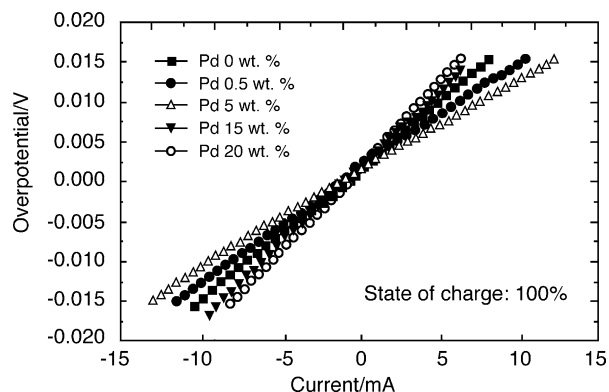


Fig. 7. Overpotential vs. current plots for electrodes coated with varying amounts of Pd at 100% state of charge. Experimental conditions were as in Fig. 1.

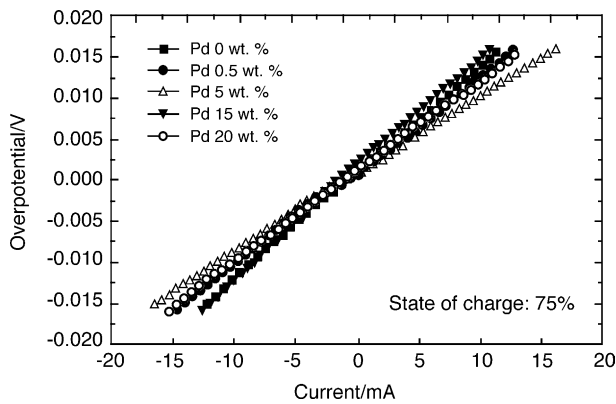


Fig. 8. Overpotential vs. current plots for electrodes coated with varying amounts of Pd at 75% state of charge. Experimental conditions were as in Fig. 1.

different states of charge (hydrogen content of the electrode). Figs. 7 and 8 show the polarization curves measured at low overpotentials (<30 mV) for Pd-coated electrodes at states of charge of 100 and 75%, respectively. Under these conditions, the slope of the linear polarization curve represents the polarization resistance [10,15].

Since reaction (1) is the rate-determining step of the overall dehydrogenating process, the polarization resistance is mainly determined by the charge-transfer process at the surface of the electrode. In Figs. 9 and 10, the polarization resistance for the different states of charge of Pd-coated alloy electrodes is plotted as a function of the Pd content; in both cases, the polarization resistance exhibited a minimum for metal alloys that contained only 5% Pd, which is reflected in the faster kinetics of the charge-transfer reaction at the electrode surface.

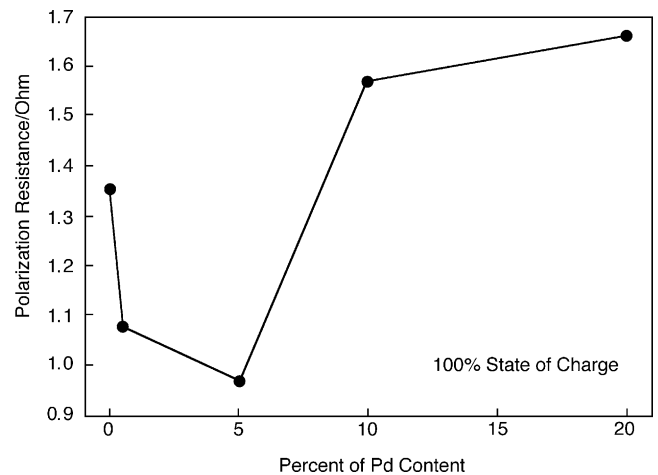


Fig. 9. Polarization resistance for the alloy electrodes at 100% state of charge as a function of Pd content. Experimental conditions were as in Fig. 1.

4. Conclusions

The Pd-coated alloy electrodes exhibited higher discharge capacities and increased rate capabilities than for the uncoated electrodes. SEM images of the Pd-coated alloy powders indicated Pd deposition with a granular structure, a condition that would favor hydrogen diffusion into the alloy. The improved performance of the Pd-coated electrodes is mainly related to the catalytic effect of Pd on the kinetics of the charge-transfer process at the electrode surface; under these conditions, the rate of the activation of the metal alloy is also increased. A Pd content between 5 and 10% provided optimum performance of the surface-modified hydride electrodes.

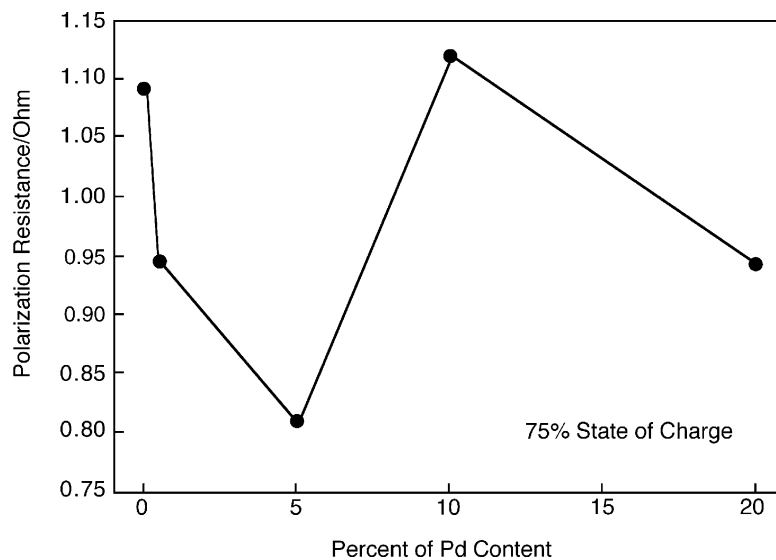


Fig. 10. Polarization resistance for the alloy electrodes at 75% state of charge as a function of Pd content. Experimental conditions were as in Fig. 1.

Acknowledgements

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