INFLUENCE OF METAL COATINGS ON CHARGING/DISCHARGING PROCESSES AT HYDROGEN-ABSORBING ALLOY ELECTRODES

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Abstract

The electrochemical behavior of uncoated and Pd-coated AB$_5$-type alloy electrodes in alkaline solution was evaluated. Results show that metal-coated alloys with a low Pd content <10 wt% exhibit fast activation under charge/discharge cycling and present higher discharge capacities and rate capabilities than the uncoated alloy. The exchange currents per unit of mass for different Pd-coated alloy electrodes were obtained from the slopes of linear polarization curves. For coated alloys with a low Pd content the exchange currents are significantly higher than that for the uncoated alloy. The faster kinetics of hydrogen absorption/desorption processes at Pd-coated alloy electrodes is related to the electrocatalytic effect of Pd on the charge transfer process at the electrode/electrolyte interface, which controls the overall reaction rate.

Resumen

Se evaluó el comportamiento electroquímico de aleaciones metálicas tipo AB$_5$ recubiertas con Pd y sin recubrimiento en solución alcalina. Las aleaciones recubiertas con bajas cantidades de Pd, menores del 10 % en peso, se activan rápidamente bajo ciclado galvanostático y mejoran notablemente las propiedades de carga y descarga respecto a la aleación sin recubrimiento. Las corrientes de intercambio, calculadas a partir de medidas de polarización lineal, son también más altas para las aleaciones recubiertas con bajas cantidades de Pd. La mejoría en la cinética de los procesos de absorción/desorción de hidrógeno en las aleaciones recubiertas se atribuye al efecto electrocatalítico del Pd sobre la reacción de transferencia de carga en la interfase electrodo/electrolito, que determina la velocidad del proceso global.

Introduction

The AB$_5$ intermetallic compounds, typified by LaNi$_5$, are attractive materials for metal hydride electrodes because of their relatively large hydrogen content (6 H atoms per formula unit) and fast absorption/desorption at room temperature [1,2]. However, the use of the LaNi$_5$ alloy is precluded because of the fast capacity loss caused by cyclic charging-discharging in alkaline electrolytes. The use of AB$_5$-type substituted alloys showing a smaller increase in the unit cell volume than the initial alloy, as result of

hydrogen absorption, causes a decrease in the rate of capacity loss during cyclic operation and an increase in the rate capability of the alloy electrode at high currents.

Substitution of La in the $LaNi_5$ alloy by low cost mischmetal (Mm) with a La content within 40 % causes a significant increase in the equilibrium pressure corresponding to the absorption plateau (15 atm at room temperature) and consequently an overpotential increase, which leads to a considerable reduction in charging efficiency. In order to decrease the equilibrium pressure to the desired range (from 0.1 to 2 atm) partial substitution of Ni by Co, Al and Mn is employed [2].

Alloys of composition $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$ exhibit a good performance, since a significant pressure decrease in the absorption plateau occurs with a simultaneous retention of a relatively high hydrogen storage capacity and a slight electrode capacity drop during cyclic operation. Coating of the powdered alloy with a thin layer of Cu or Ni, called microencapsulation, diminishes alloy pulverization during cyclic operation, thus increasing the cycle life of the alloy electrode [3,4].

The activation of the alloy plays a key role in the hydrogen absorption process, since it defines the reaction rate of hydrogen with the metal and the incorporation to its structure. During activation, different processes can occur [2,5], such as: i) the reduction of metal surface oxides that interfere with hydrogen; ii) reduction in particle size due to cracks produced by the increase in volume; iii) changes in the chemical composition and/or surface structure of the metal. It has been found that Ni, Pd, and Pt coatings increase the rate of activation of mischmetal–based alloy electrodes during charging/discharging, which has been attributed to the improved electrocatalytic activity for hydrogen electrode reaction [6-9]. It has also been pointed out that the surface catalytic properties of the metal coating play a crucial role in the charge/discharge kinetics [7,9,10].

In this work, the electrochemical behavior of uncoated and Pd-coated alloy powder electrodes in 6 M KOH at 25° C was investigated in order to determine their possible application as the negative electrode in nickel/metal hydride rechargeable batteries. The discharge capacities and discharge rate capabilities of metal-coated electrodes with different Pd content were evaluated. From linear polarization measurements, the dependence of the exchange current associated with the charge–transfer process at the electrode/electrolyte interface upon the Pd content in the alloy was also determined.

Experimental

The alloy investigated was $MnNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$, where Mn is 43.1 wt % La, 3.5 wt % Ce, 13.3 wt % Pr and 38.9 wt % Nd. The alloy powder with a particle size of less than 100 μm was coated with Pd by electroless deposition using hypophosphite as the reducing agent [11]. The electroless Pd plating was performed by using different Pd-to-alloy weight ratios. 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 cm^2).The geometric area of the working electrodes was about 2 cm^2. 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 the electrochemical tests, the electrolytic solution contained 6 *M* KOH at 25°C. The working electrodes were subjected to 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.

The linear polarization measurements were performed under potentiodynamic conditions at 1 mV/s after fully charging the alloy electrodes and the open circuit potential had been stabilized. From the polarization curve slopes for Pd-coated alloy electrodes with a different Pd content, the corresponding exchange currents per unit of mass of alloy were evaluated.

Results and discussion
Discharge characteristics

The metal-coated alloy electrodes with different Pd contents were subjected to an activation treatment comprising their charge/discharge cycling in 6 M KOH at a constant current of 10 mA. The electrode potential versus discharge capacity plots corresponding to the first cycles (Figure 1a), at which the activation process takes place, show that the discharge capacity increases upon increasing the Pd content from 0.5 wt % to 20 wt %. As the number of charge/discharge cycles increases the overpotentials decrease and higher discharge capacities are attained (Figure 1b). Furthermore, the number of cycles to activate the alloy electrodes and attain full capacity also decreases on increasing the Pd content (Figure 2). Thus, full capacity was obtained after only a few cycles for the alloy with a 6 wt % Pd content. After full activation, metal-coated electrodes with 5 wt % Pd exhibit the highest discharge capacities, whereas for alloy electrodes with a Pd content higher than ca. 10 wt %, the discharge capacities decrease on increasing the Pd content. This decrease in discharge capacity has been attributed to limitations to the hydrogen atom diffusion process arising when the Pd coating thickness exceeds a certain critical value [12].

Discharge-rate capability

The discharge-rate capabilities of the metal-coated alloy electrodes are also strongly dependant on the Pd content (Figure 3). For these runs, the alloy electrodes were 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. Metal-coated alloy electrodes with Pd contents of 5 wt % and 10 wt % exhibit high capacities at both low and high discharge rates, whereas the uncoated alloy electrodes display a rapid capacity decay at high discharge rates. As discussed below, the improved performance of Pd-coated electrodes is related to the electrocatalytic effect of Pd on the charge-transfer process at the electrode/electrolyte interface.

SEM-EDX analysis

The scanning electron microscope (SEM) image of Pd-coated alloy powder is shown in Figure 4. As can be seen, the amorphous-Pd film[8,14] exhibits a granular structure that is expected to favor hydrogen diffusion into the alloy. No appreciable changes in morphology and roughness of the metal coatings for Pd contents between 0.5 wt% and 20 wt% can be observed. SEM-energy-dispersive X-ray (EDX) analysis of the

cross section of post-cycled Pd-coated alloy electrodes reveals that electrodes are characterized by nonuniform Pd deposits (Figure 5). Then, no direct relationship between the average Pd coating thickness of the alloy particles and the Pd/ alloy weight ratio can be obtained. However, a considerable increase in the Pd film thickness is observed when the content of Pd is increased from 5 wt% to 20 wt%. The SEM images of the post-cycled electrodes also indicate that the generation of new alloy particles occurs via crack-formation that accompanies the hydriding/dehydriding processes.
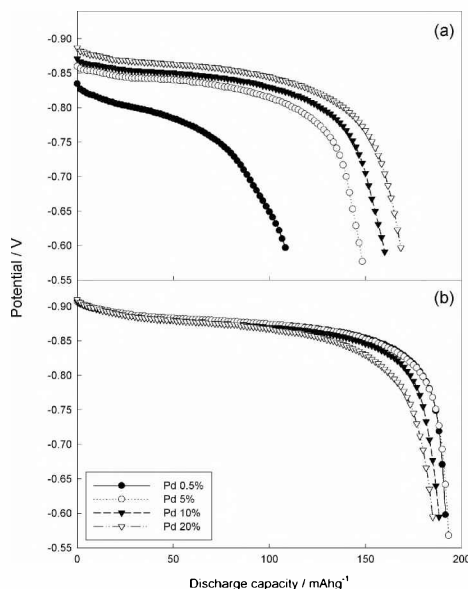
Figure 1*: Electrode potential versus discharge capacity plots for Pd-coated alloy electrodes with different Pd contents. Charge/discharge current: 10 mA. (a) 5th cycle; (b) 20th cycle.*

Linear polarization studies

Electrochemical charging of a metal hydride electrode in alkaline aqueous solutions consists of the electrochemical reduction of water at the metal surface, resulting in the formation of adsorbed hydrogen atoms. These hydrogen atoms then diffuse into the bulk of the host metal to form a metal hydride via recrystallization of the condensed phase. Discharging consists of dehydriding, followed by oxidation of the released hydrogen atoms. The electrochemical reactions can therefore be expressed as follows:

$$H_2O + e^- \leftrightarrow H_{ad} + OH^- \tag{1}$$

and

$$H_{ad} \leftrightarrow H_{ab} \tag{2}$$

where H_{ad} and H_{ab} denote the hydrogen atom on the electrode surface and in the bulk of the alloy, respectively. Reaction (1) represents the charge-transfer process, which takes place at the interface between the alloy and the electrolyte, and reaction (2) corresponds to the dissolution and diffusion of hydrogen in the alloy from the electrode surface to the bulk of the alloy.
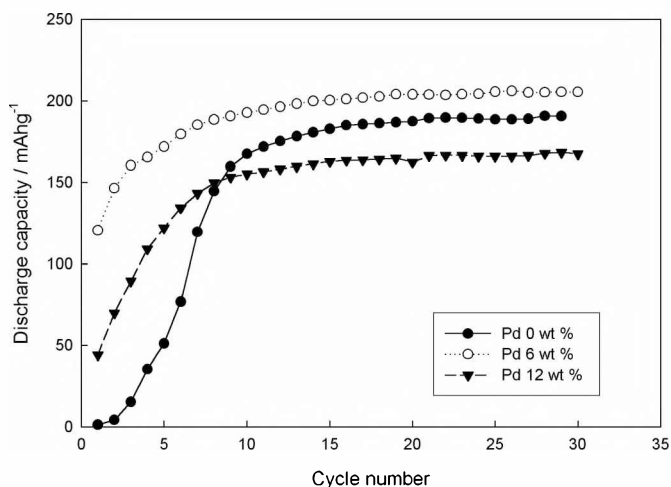
Figure 2: *Discharge capacity versus cycle number plots for Pd-coated alloy electrodes with different Pd contents. Charge/discharge current: 10 mA.*
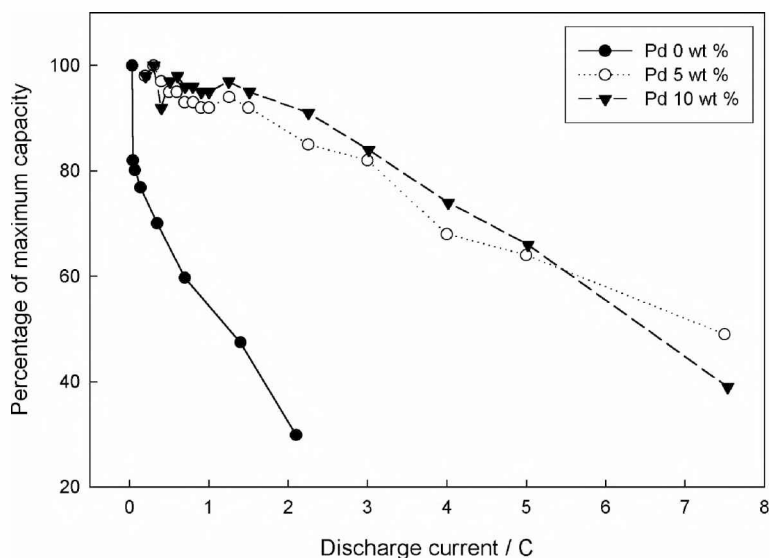

Figure 3: *Discharge-rate capabilities for Pd-coated alloy electrodes with different Pd contents. Charge current: 10 mA.*

The rate of the hydriding/dehydriding processes is determined by the kinetics of one of these steps. If the alloy particles are small, as in this case, the hydrogen diffusion path is rather short, and then the rate-controlling step is the charge-transfer process [13]. However, for large alloy particles, the diffusion of hydrogen inside the alloy particle
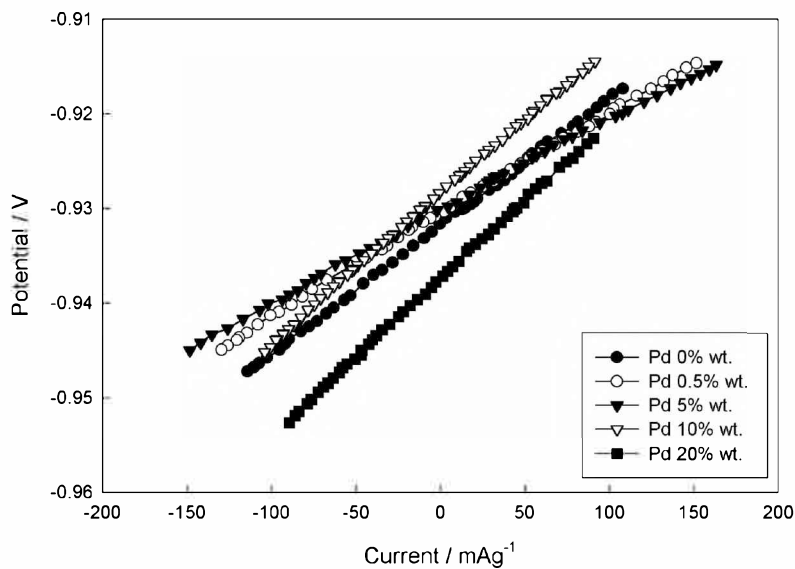
affects the hydriding/dehydriding processes and it may determine the overall reaction rate.
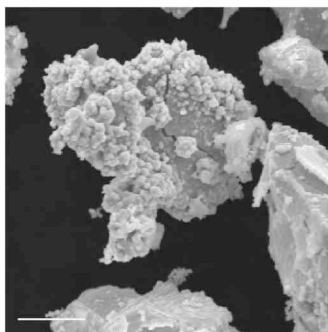
Figure 4: *SEM image of a Pd-coated alloy powder. Scale: 10 μm.*
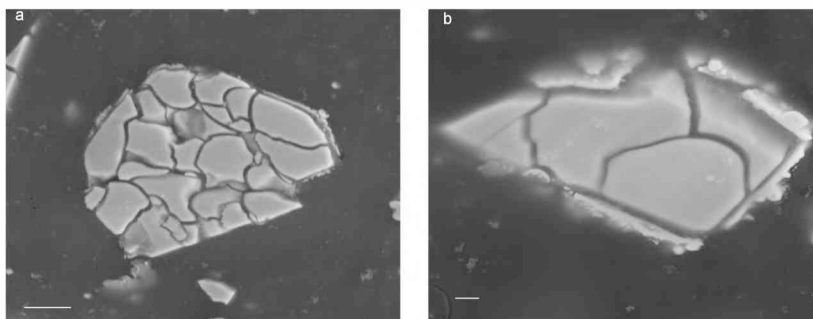

Figure 5: *SEM images of post-cycled alloy electrodes coated with two different Pd contents: (a) 5 wt % Pd; (b) 20 wt % Pd. Scale: 10 μm.*

Figure 6: *Electrode potential versus current plots for Pd-coated alloy electrodes with different Pd contents at 100 % state of charge.*

The kinetics of the charge transfer process for metal-coated alloys with different Pd contents was studied by linear polarization methods. Figure 6 shows the linear polarization curves obtained at low overpotentials, near the equilibrium potential, for different Pd-coated electrodes at a state of charge (hydrogen content in the electrode) of 100 %. The slope of the linear polarization curve represents the total electrode resistance, which is composed of the polarization resistance (R_p) and the ohmic resistance (R_Ω). The charge transfer process that takes place at the electrode surface mainly determines the polarization resistance. Since $R_\Omega \ll R_p$, the slope of the linear polarization curve represents the polarization resistance, which can be used to estimate the exchange current per unit of mass (i_0) associated with the charge-transfer process, according to the following equation [10,14,15]:

$$i_0 = \frac{RT}{FR_p} \tag{3}$$
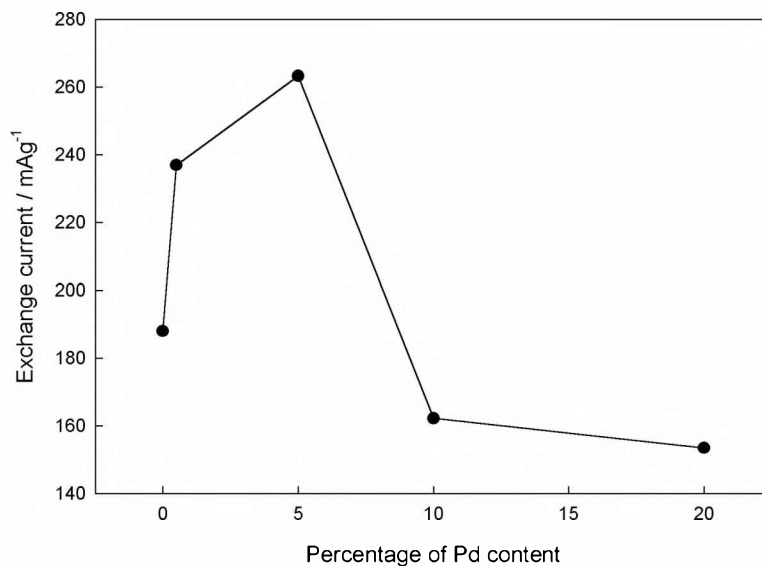
Figure 7: *Exchange current for Pd-coated alloy electrodes at 100 % state of charge as a function of Pd content.*

The exchange currents for Pd-coated alloy electrodes at 100 % state of charge are plotted as a function of the Pd content (Figure 7). As can be seen, the exchange current increases on increasing the Pd content from 0 wt% to 5 wt% and then decreases for Pd contents higher than 10 wt%. This decrease in the exchange current, as was explained above, is assigned to the appearance of limitations to hydrogen diffusion inside the alloy particles that affect the overall hydriding/dehydriding processes for alloys covered with thick Pd coatings. The maximum exchange current corresponds to metal-coated alloys with a 5 wt% Pd content. These results are consistent with data derived from the discharge curves and rate capability measurements and correlate well with kinetic parameters obtained from studies on the performance of uncoated and Pd-coated alloys of similar composition [15,16]. Therefore, the faster kinetics of the

hydriding/dehydriding processes at metal-coated alloy electrodes with a low Pd content should be attributed to the electrocatalytic effect of Pd on the charge-transfer process at the electrode/electrolyte interface (reaction 1), which determines the overall reaction rate.

Conclusions

The study of the electrochemical behavior of uncoated and Pd-coated alloy electrodes in alkaline solution reveals that metal coatings with a low Pd content < 10 wt % considerably improve the charging/discharging properties of the alloy electrodes. The exchange currents per unit of mass obtained from the slopes of linear polarization curves for metal-coated alloy electrodes with low Pd contents are significantly higher than that corresponding to the uncoated alloy electrode at the same state of charge. The maximum exchange current corresponds to metal-coated alloy with a 5 wt% Pd content. Correspondingly, the improvement in the charging/discharging characteristics of Pd-coated alloy electrodes should be assigned to the electrocatalytic effect of Pd on the charge-transfer process at the electrode/electrolyte interface, which is the rate-controlling step in the overall hydriding/dehydriding processes.

Acknowledgements

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