

Short communication

Rapid activation of $MmNi_{5-x}M_x$ based MH alloy through Pd nanoparticle impregnation

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Abstract

Faster activation of a multi-component AB_5 based alloy metal hydride electrode through Pd nanoparticle (NP) impregnation is demonstrated. Pd nanoparticle impregnated $MmNi_{5-x}M_x$ based alloy was prepared and characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and elemental mapping techniques. Electro-catalytic activity of laminar metal hydride electrodes containing Pd nanoparticles and micrometer size Ni particles was studied. Hydrogen absorption efficiency of the nanocomposite electrodes was compared with the metal hydride electrodes without Pd nanoparticles. The incorporation of nanostructured materials in the metal hydride alloy increased its hydrogen absorption capacity at the initial stage and activated much faster, indicating its good prospect for energy storage applications.

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1. Introduction

AB_5 type metal-hydride (MH) alloys have been traditionally used for the hydrogen storage in electrochemical systems. These alloys along with $LaNi_5$ based materials have mostly been used as the negative electrode in commercial Ni-metal hydride batteries as well as solid state hydrogen containers due to their high reversible energy storage capacity, good charge-discharge kinetics, and long-term cycling stability (for more than 300 charge-discharge cycles). However, these alloys present some limitations for the use in electrical vehicles, mainly due to their low energy storage densities.

At the end of the last century, carbon nanotubes (CNTs) were considered to be the good materials for hydrogen absorption in solid-gas systems due to their extraordinary superficial properties [1–5]. Recently, better hydro-

gen absorption performance in electrochemical system was reported for MHs when some metal nanostructures or CNTs were incorporated in them [6–11]. There after, the use of low-dimensional materials in electrochemical systems for hydrogen storage has become a tradition. Generally, the additives like Ni and Cu powders of micrometer grain size were mixed at the 1:1 weight ratio with the hydrogen absorbing alloys to induce or increase their electro-catalytic activities. However, in terms of storage energy density, they are not so effective. The use of nanomaterials with enhanced electro-catalytic activities may help to increase the amount of hydrogen stored in AB_5 alloys further due to their selective catalytic properties and improvement of specific energy density by utilization of very small amount.

The stability of the metal hydrides is normally affected by cycling because of their structural changes occurring in the charge/discharge process. These structural changes contribute to a lower value in the specific capacity of the alloys [12] apart from the generation of surface stress

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affecting the electrical contact between the particles, diminishing the electrocatalytic activity of the additives and the performance of the complete hydrogen absorbing system. Several strategies have been reported to improve the performance of the AB₅ type of alloys for absorbing hydrogen by electrochemical methods. One of the mostly followed strategies is the micro-encapsulation of active alloy through electroless or electrodeposition of metal or metal alloys. Materials with good electrical conduction, electrocatalytic or anticorrosive properties like Cu, Ni–P, Ni–B, Pd and Ni–Pd have been used to improve the stability of the alloys [13–16]. However, there are some inherent problems associated with the use of micro-encapsulation process: (a) it is necessary to control the thickness of the coatings to have reproducible characteristics of the micro-encapsulated alloy; (b) the activation is slower than non encapsulated alloys (more charge/discharge cycles are needed to activate completely the alloys); (c) increase of total weight after encapsulation affecting the specific energy density of the alloys.

The use of nanomaterials with electro-catalytic properties can be used to improve the hydrogen absorbing characteristics of the alloys in electrochemical systems. The nanomaterials can be designed with selective properties related to hydrogen reaction like catalytic activity to evolve, adsorb or absorb hydrogen content, as well as anticorrosive or very good electronic conduction characteristics.

In this work, preparation, characterization and hydrogen absorption characteristics of Pd nanostructure incorporated MmNi_{5-x}M_x related alloys are presented. Pd nanoparticles are considered as good material for promoting the initial stage of the hydrogen absorption on the surface of the metal hydride alloy. Utilization of catalytic Pd nanoparticles instead of micro-encapsulation by metal or metal alloys for the efficient absorption of hydrogen in MmNi_{5-x}M_x related alloys are demonstrated.

2. Experimental

The multi-component MmNi_{5-x}M_x material (La_{0.55}Ce_{0.3}Nd_{0.11}Pr_{0.04}) (Co_{0.14}Al_{0.08}Mn_{0.06}Ni_{0.71})_{5.02} from Rhodia Inc. was used in this work as the active metal hydride alloy. The details of alloy preparation was discussed elsewhere [17]. The average particle size of the metal hydride alloy powder was around 32 μm and purity was higher than 99.6%.

2.1. Preparation of Pd nanoparticles

Colloidal Pd nanoparticles were prepared by chemical reduction of a palladium salt in inert atmosphere. Methanol solution of PdCl₂ (0.033 mmol in 25 ml) was prepared by dissolving the salt (99.0%, Alfa Aesar) in methanol under rigorous stirring for 24 h at room temperature. After the solution was prepared, 25 ml methanol solution of poly(*N*-vinyl-2-pyrrolidone) (150 mg PVP, 10,000 MW) was added to the solution. An extra 50 ml of methanol was added to the mixture to make 100 ml in total. The solution was de-aired by bubbling argon for 1 h at 50 °C under stirring. Then 6 ml of 0.044 M NaBH₄ aqueous solution was added to the solution at 25 °C. The color of the reaction mixture changed gradually on addition of NaBH₄ solution indicating the formation of Pd nanoparticles. PVP used for the synthesis process acted as a protecting agent for the Pd nanoparticles. Formation of Pd nanoparticles of about 2.2 nm average size with narrow size distribution can be seen from the transmission electron micrograph (TEM, Philips Tecnai 200 operated at 200 keV) micrograph shown in Fig. 1.

2.2. Impregnation procedure

Metal hydride alloy powder based on (La_{0.55}Ce_{0.3}Nd_{0.11}Pr_{0.04}) (Co_{0.14}Al_{0.08}Mn_{0.06}Ni_{0.71})_{5.02} was impregnated by Pd nanoparticles. 0.01 g of metal hydride powder was

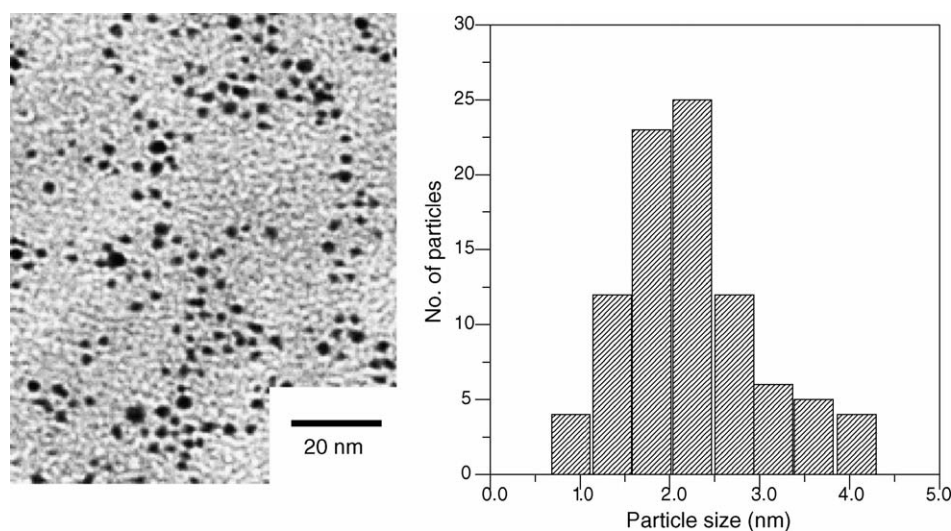


Fig. 1. Typical TEM micrograph of the colloidal Pd nanoparticles (left) and their size distribution histogram (right).

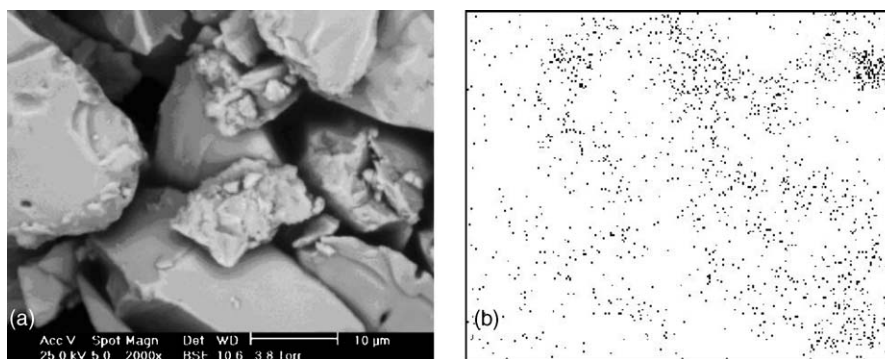


Fig. 2. Typical SEM image of the Pd nanoparticle impregnated MH alloy (a) and Pd mapping on the same area (b).

immersed in 1 ml colloidal solution containing Pd nanoparticles. The mixture was heated at 40 °C for 8 h under magnetic stirring (60 rpm) to evaporate the solvents completely. A chemical bath treatment by a strong alkaline solution was used for activating the surface of the metal hydride alloy before the impregnation process [17].

2.3. Metal hydride electrode preparation

Metal hydride electrodes were developed for investigating their electrochemical characteristics for absorbing/desorbing hydrogen. First, INCO T-210 nickel powders were added as additive to the un-impregnated and Pd NP impregnated MH alloys at 1:1 weight ratio. The particle size of the Ni additive was about $1 \pm 0.5 \mu\text{m}$. Here after, we will call the MH alloy with Ni additive as MH–Ni and Pd nanoparticle impregnated MH alloy with Ni additive as MH–Ni–Pd. Laminar electrodes were prepared by cold pressing (using 500 MPa cm^{-2} mechanical pressure) Pd free nickel foams (as substrate) and MH–Ni or MH–Ni–Pd alloys. Previous studies with this kind of preparation technique for obtaining MH electrodes was described elsewhere [18].

The electrochemical characterizations were performed in a three compartment open cell using 6 M KOH aqueous solution as electrolyte, metal hydride electrode as working electrode, a Hg/HgO electrode as reference electrode, and a $(\text{Ni}(\text{OH})_2/\text{NiOOH})$ electrode as counter-electrode. An automatized solartron potentiostat/galvanostat (SI 1287) with impedance analyzer (SI 1260) driven by Corrware software, used to perform electrochemical measurements.

3. Results and discussion

In Fig. 2(a), a typical scanning electron microscope (SEM, JEOL JSM 5600 LV) micrograph of the metal hydride alloy impregnated with Pd nanoparticles is shown. We can observe the crystallites of different sizes ranging from 2 to $30 \mu\text{m}$ with irregular forms in the micrograph. Existence of Pd nanoparticles or their clusters in the samples could not be detected from the SEM micrographs. However, the existence and position

of the nanoparticles in the alloy could be detected by elemental mapping through the SEM microscope. In Fig. 2(b), the distribution of Pd particles (elemental mapping) is presented for the same alloy surface presented in Fig. 2(a). More or less homogeneous distribution of Pd nanoparticles with no preferential Pd cluster formation can be observed. Similar Pd distribution was observed in all the impregnated metal hydride samples, confirming a homogeneous distribution of Pd nanoparticles in them. The chemical composition of the impregnated metal hydride alloy was investigated by EDS attached to SEM. In Fig. 3, the EDS spectra of the MH with and without Pd impregnation are presented. Quantitative estimation of elemental composition for the Pd impregnated and un-impregnated samples obtained from EDS study is presented in Table 1. The presence of Pd (2.07 at.%), along with other constituents of the alloy like Ni, Co, Mn, Nd, Pr, Ce, La and Al could be identified in the impregnated alloy. Appearance of oxygen peak in the EDS spectra of the MH-alloy was mainly due to the surface activation of the alloy by alkali solution and partly from the synthesized alloy. Higher oxygen content (about three times higher) in the Pd impregnated MH alloy than in the un-impregnated metal hydride might be related to the experimental conditions in preparing the Pd nanoparticles. As the EDS spectra of the Pd impregnated and un-impregnated samples reveal not much difference except the presence of Pd in the former (Fig. 3(b)), all the differences in their electrochemical response could be associated to the incorporation of Pd nanoparticles.

Table 1
Quantitative elemental composition of the MH alloy and Pd impregnated MH alloy as determined from EDS

Element	MH alloy (at.%)	Pd impregnated MH alloy (at.%)
O	11.72	39.45
Al	12.84	8.63
Pd	–	2.07
La	8.36	5.08
Ce	6.12	3.00
Pr	1.27	0.50
Nd	2.34	1.28
Mn	4.43	2.51
Co	7.44	6.22
Ni	45.46	31.26

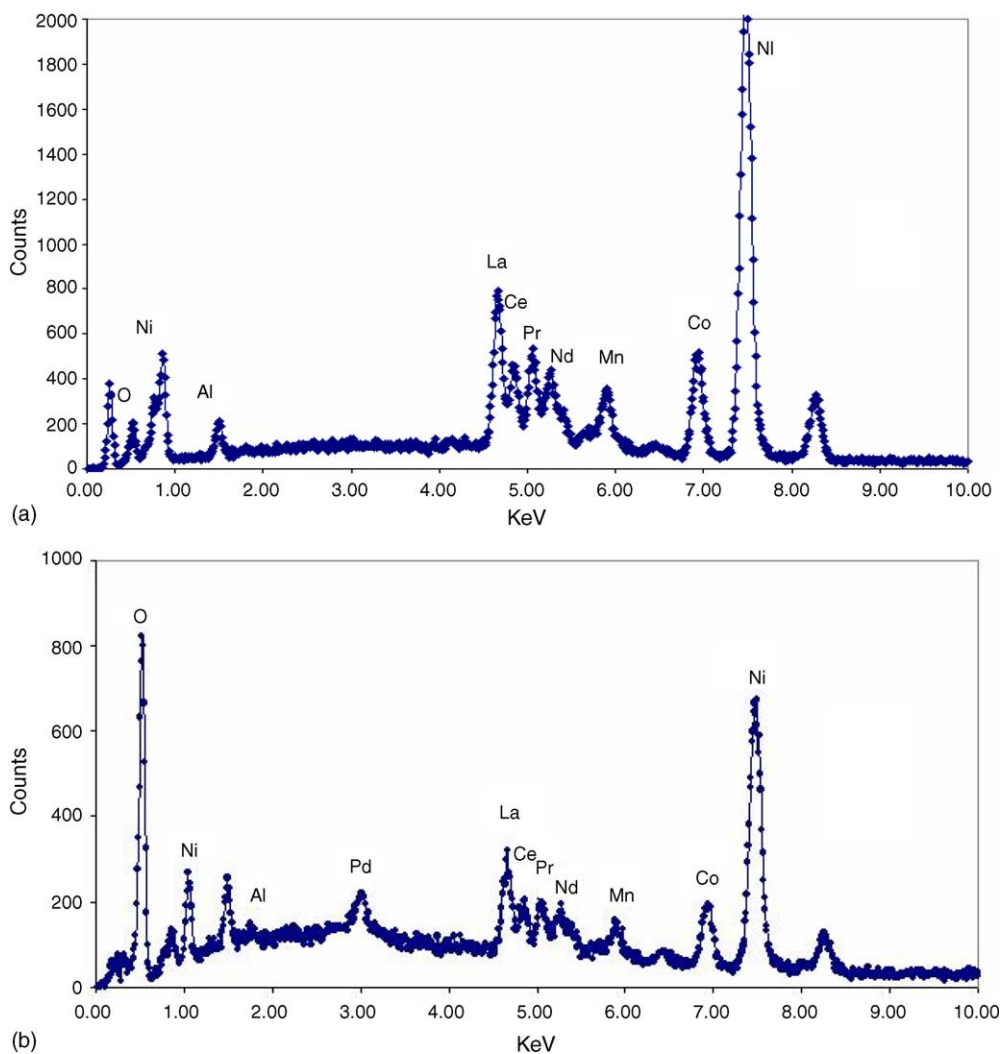


Fig. 3. EDS spectra of the MH before Pd impregnation (a) and after Pd impregnation (b).

The electrochemical investigation of hydrogen absorption of the alloys was based on monitoring their charge/discharge characteristics. For comparison, the laminar electrodes without (MH–Ni) and with Pd nanoparticles (MH–Ni–Pd) prepared with similar experimental conditions were studied at room temperature. For the charging process, the first four charge cycles started at -0.55 V/Hg/HgO on applying a charging current density of 50 mA g^{-1} and took about 3 h to reach a maximum charging potential of -1.020 V/Hg/HgO for both the electrodes before reaching the condition for hydrogen evolution reaction. The increase in anodic potential during charging is due to increase in absorbed hydrogen in the matrix of the MH–Ni electrode. The charging characteristics of both the electrodes (MH–Ni and MH–Ni–Pd) were very similar which might be due to the side HER reaction, preventing an accurate evaluation of the hydrogen charging process. Thus, the contribution of incorporated Pd nanoparticles in the metal hydride was investigated in the discharge process, where the electrochemical performance of the system is mainly determined by

hydrogen concentration in the bulk of the metal hydride composite.

Fig. 4 shows the first four discharge cycles correspond to the initial stage of hydrogen absorption in the MH–Ni electrode and the MH–Ni–Pd electrode. The experimental discharge current used for both the electrodes was 50 mA g^{-1} . While Fig. 4(a) depicts the 1st and 2nd discharge cycles for both the electrodes, Fig. 4(b) depicts their 3rd and 4th discharge cycles. From the first two discharge cycles (Fig. 4(a)), we can see that the activation capacity of the MH–Ni–Pd based electrode is almost two times of the activation capacity of classic MH–Ni based electrode. However, the activation capacity of the two electrodes approaches closer from the 4th cycle (Fig. 4(b)). Though the activation capacity of the MH–Ni–Pd electrode remained slightly higher than that of the MH–Ni electrode even after 18th discharge cycle, we believe the presence of Pd nanoparticles contributed mainly to activate the metal hydride surface to facilitate the charge transfer process through it for hydrogen ion reduction. Though the amount of absorbed hydrogen in the Pd

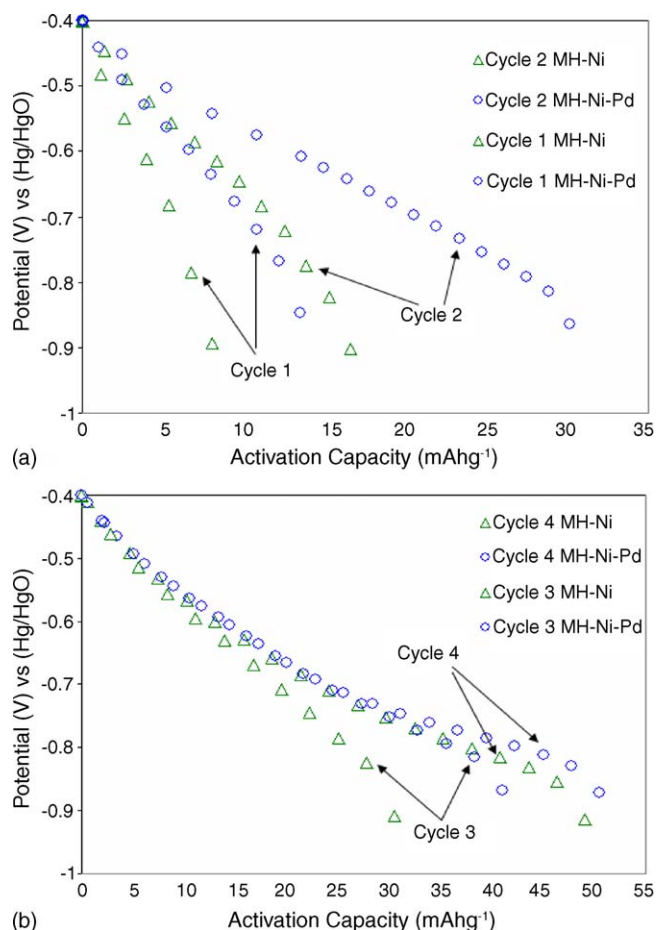


Fig. 4. Comparison of the (a) 1st and 2nd discharge cycles of the MH–Ni and MH–Ni–Pd electrodes and (b) 3rd and 4th discharge cycles of MH–Ni and MH–Ni–Pd electrodes.

nanoparticles could not be quantified by the charge/discharge method used in this work, as the amount of added Pd nanoparticles was very small, the contribution seems to be negligible. From the results we obtained, it is evident that the incorporation of Pd nanoparticles in the MH facilitates the hydrogen absorption process at the initial stage and activates the MH very fast.

4. Conclusions

Faster activation of classic MH–Ni composite electrodes could be achieved through Pd nanoparticle impregnation. The Pd nanoparticles of about 2.2 nm average size could be synthesized through a simple chemical reduction process and could be impregnated in a AB₅ type metal hydride alloys with homogeneous distribution. In electrochemical evaluation, the MH–Ni–Pd system activated rapidly with higher hydrogen

absorption at the initial stage. Our results demonstrate that a very small amount of Pd nanoparticles can activate the MH surface to facilitate the charge transfer process in hydrogen ion reduction. Use of nanostructured Pd not only facilitates the initial hydrogen absorption process in MH or activates the MH electrode rapidly, it also opens up the possibility for hydrogen storage with higher specific energy density.

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