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Effect of electroless coating of Cu, Ni and Pd on $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ alloy used as anodes in Ni-MH batteries

R. Parimala^a, M.V. Ananth^a, S. Ramaprabhu^b, M. Raju^{a,*}

^aCentral Electrochemical Research Institute—Madras Unit, C.S.I.R. Complex, Tarmani, Chennai 600 113, India

^bDepartment of Physics, Indian Institute of Technology, Madras 600 036, India

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Abstract

In order to improve the electrochemical performance, the alloy represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ was microencapsulated with Cu, Ni and Pd. Microencapsulation was done prior to test electrode preparation by electroless plating method. The electrode characteristics such as electrochemical capacity and cycle life were studied for the uncoated and coated alloys. It was found that the coated alloy showed higher discharge capacity and lower activation time in comparison to the uncoated alloy. The phase composition of the alloys was characterized using X-ray diffraction (XRD) and surface morphology was studied using scanning electron microscope (SEM). It was found that the surface microencapsulation of alloy powder was effective in improving the electrode discharge capacity and in reducing the activation time.

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Keywords: Microencapsulation; Ni-MH battery; Alloy; Discharge capacity; Activation

1. Introduction

The development of Ni-MH battery has broadened the application of hydrogen storage alloys in the battery industry. Most recent research in this area has focused on developing and modifying the negative electrode material to increase the electrode capacity and reduce cost. ZrV_2 type alloys have been extensively studied and applied to commercial production of Ni-MH batteries. Microencapsulation of the alloy powder with various kinds of electroless coatings such as Cu, Ni-P, Ni-B, Pd and Co has been shown to be effective on improving the cycle lifetime and the high rate dischargeability [1–6]. Microencapsulation is the process of electroless plating of alloy particles with a thin layer of copper [7], nickel [8,9] or palladium [10].

The coatings lead to superior electrodes, with a constant capacity and longer cycle life compared to those made with bare alloys. Plating these materials results in decreasing the energy density based on the actual weight of the electrode (alloy + coating + binders). In the present work we studied

the effect of electroless plating of Cu, Ni and Pd on the alloy represented by $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$.

2. Experimental

The alloy represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ was prepared by arc melting route. The stoichiometric proportions of the constituent elements were melted together in an arc-furnace under argon atmosphere of 0.5 bar. The sample was remelted several times by turning the buttons upside down after each melting to ensure homogeneity. Weight loss after the final melting was less than 0.8% for the sample. The sample was annealed at 900°C for 72 h in a sealed evacuated quartz tubes (10^{-6} Torr). After the completion of annealing, the sample was slowly cooled to room temperature.

The alloy powder with particle size below 100 mesh was used for electroless coating. Electroless Cu coating was done as follows: Fresh alloy powder represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ was first immersed in 10 g/l SnCl_2 for 5 min and then in 0.5 g/l PdCl_2 aqueous solution for 5 min. The activated powder was

* Corresponding author. Fax: +91-44-2542456.

E-mail address: bnl@vsnl.com (M. Raju).

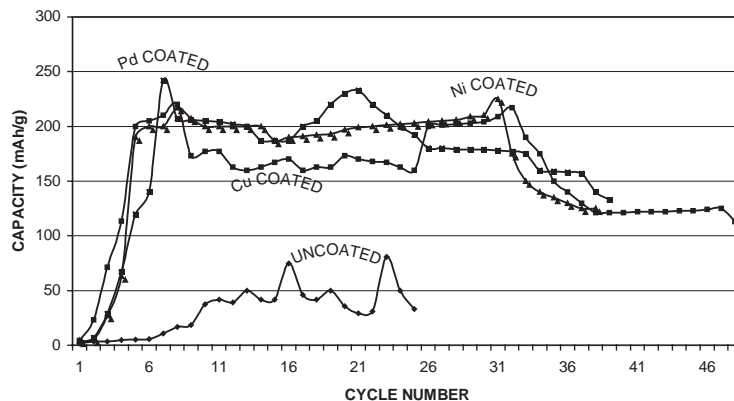


Fig. 1. Performance of $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$.

plated using the following solutions: 12 g/l CuSO_4 , 55 g/l Rochelle salt, 15 g/l NaOH and finally at 35 ml/l HCHO [pH = 11.5–12]. Electroless Ni coating was done as follows: Fresh alloy powder represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ was first immersed in 10 g/l SnCl_2 for 5 min and then in 0.5 g/l PdCl_2 aqueous solution for 5 min. The activated powder was plated using the following solutions: 60 g/l NiCl_2 , 80 g/l sodium citrate, 20 g/l NH_4Cl and finally at 20 g/l sodium hypophosphite [80–95°C, pH = 4–6]. Electroless Pd coating was done as follows: Fresh alloy powder represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ was first immersed in 0.5 g/l PdCl_2 aqueous solution for 5 min. The activated powder was plated using the following solutions: 350 g/l NH_4OH , 33.6 g/l disodium salt of EDTA and finally at 0.3 g/l hydrazine [80°C, pH = 9–10].

2.1. Charge–discharge characteristics

For electrochemical studies the electrode with bare alloy and coated alloy powders were used as battery active material. The composition of the negative electrode was: 1 g MH powder, 25 wt% acetylene black and 10 wt% PTFE dispersion. The slurry of MH powder, additive and PTFE dispersion was covered on two sides of a nickel mesh with the geometric area 6 cm^2 and pressed at 800 kg cm^{-2} to obtain a sheet. It was then dried at 150°C for 1 h. The thickness of the negative plate is 1.5 mm. A sintered nickel hydroxide [$\text{Ni}(\text{OH})_2/\text{NiOOH}$] plates with thickness 1 mm were used as the positive electrodes of the Ni-MH cell. A polyamide non-woven cloth was used as a separator. The negative electrode was sand-witched between the two positive electrodes. The battery characteristics were examined at room temperature by an automatic galvanostatic charge–discharge unit at a constant current of 40 mA g^{-1} . The discharging cut-off potential was set to -0.600 V with respect to the reference Hg/HgO electrode. The resting time between charge and discharge was 10 min.

2.2. XRD studies

Powder X-ray diffractogram of the uncoated and coated alloys were carried out using JEOL model JDX-8030 with 2θ scan mode at an operating rate of 40 kV, 20 mA with CuK_α radiation (Ni filter). The ‘peak search’ to tabulate the XRD data and ‘Search Match’ software for the comparison of observed data with the standards were used.

2.3. SEM studies

Scanning Electron Microscopy was used for the study of surface topography of the uncoated as well as coated alloy powder. SEM imaging was done using JEOL JAMP Auger-Scanning Microscope.

3. Results and discussion

3.1. Charge–discharge characteristics

The discharge capacity of the uncoated and coated alloy as a function of cycle number is shown in Fig. 1. It can be noticed that the coated alloys needed less number of charge–discharge cycles to get activated. In the case of the electrodes prepared using coated alloys with Cu, Ni or Pd, the maximum capacity was achieved within 3 cycles of charge–discharge process. The electrode prepared with uncoated, bare alloy was not activated at all even after 25 charge–discharge cycles. This observation can be explained as follows: Coating the alloy powder with Cu, Ni and Pd makes the alloy surface an excellent hydride forming material with other elements, which may contribute to the hydrogen storage capacity. The uncoated alloy powder was easily oxidized on the surface layer, which resulted in long activation time. When the alloy powder was covered by Cu, Ni or Pd, hydrogen atoms would easily penetrate the surface layer but oxygen atoms would find it difficult to penetrate this layer.

It can be noted from Fig. 1, that the discharge capacity of the electrode prepared using coated alloys increased during cycling. The specific capacity of the uncoated alloy electrode remained constant at a very low value of around 45 mA h g^{-1} for nearly 25 charge–discharge cycles. But for the coated alloy electrodes the specific capacity increased during cycling. The maximum capacity obtained with Cu coated alloy is 211 mA h g^{-1} , Ni coated alloy is 214 mA h g^{-1} and that of Pd coated alloy was 242 mA h g^{-1} . From Fig. 1, it is clear that the coated alloy showed better cycle life and higher discharge capacity. The coating of Cu, Ni or Pd on the alloy powder increased the electron conductivity and then improved the electrochemical performance. The sequence of the discharge capacity of the alloy, as can be observed from Fig. 1 is Pd coated $>$ Ni coated \geq Cu coated $>$ uncoated. This is believed to have resulted from the different catalysis effect of the above metal coatings on the hydrogen evolution reaction.

3.2. XRD studies

The XRD patterns of the uncoated and coated alloys were shown in Fig. 2. The main phase of the alloys from XRD pattern showed a C-14 type Laves phase with a hexagonal structure. The occurrence of the hexagonal Laves phase structure was determined by calculating NOE (number of outer electrons) as 6.9 for the $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ alloy. Indexing (hkl) of the uncoated and coated alloy powder are given in Fig. 2. The lattice parameters ‘ a ’, ‘ c ’ and the unit cell volume ‘ V ’ of the uncoated and coated alloy were listed in Table 1. From this, one can observe an increase in cell volume of the coated alloys when compared to the bare alloy powder. This can be explained as follows: when the alloy powder was coated with Cu, Ni or Pd by electroless coating technique, the hydrogen atoms were produced as an intermediate in the final step of coating which involves reduction process. The intermediate hydrogen atoms penetrated the crystal lattice of the alloy, which increased the cell volume. This increase in cell volume helped in the increase of electrochemical absorption and desorption of more amount of hydrogen. This increases the cell performance. Also the sequence of cell volume increase follows the pattern Pd coated $>$ Cu coated \geq Ni coated $>$ uncoated. This indicates that, of the three coatings that were done on the fresh alloy powder represented by $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$, Pd coating was superior to both Ni and Cu coatings. The cell performance of both Ni and Cu coated alloy was found to be more or less equal. But all the coated alloys performed better than the bare alloy.

3.3. SEM studies

The surface morphology of the uncoated and microencapsulated alloy powders and also the cycled electrodes respectively were shown in Figs. 3 and 4. Fig. 3 shows the

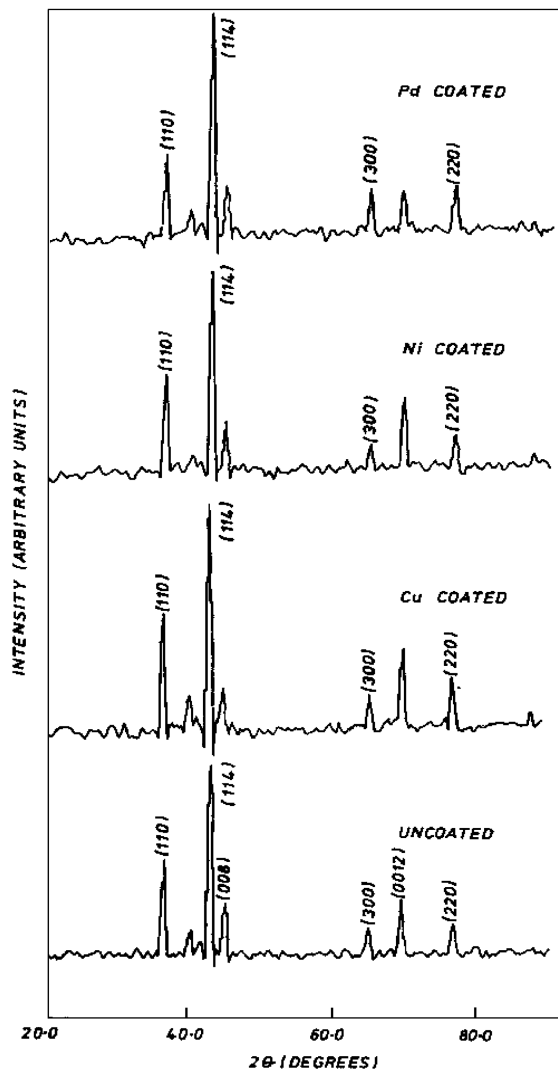


Fig. 2. XRD patterns of uncoated and coated alloys.

Table 1

The lattice parameters and unit cell volume of the uncoated and coated alloy powder

Nature of the alloy powder	a (\AA)	c (\AA)	V (\AA^3)
Uncoated	4.9657	16.1953	345.76
Cu coated	4.9681	16.2248	346.80
Ni coated	4.9661	16.2004	346.00
Pd coated	4.9690	16.2354	347.16

surface morphology of the uncoated, Cu, Ni and Pd coated alloy powder. The covering of Cu, Ni or Pd of the alloy powder leads to a reduced electrochemical polarization resistance when charging/discharging. This indicates that the

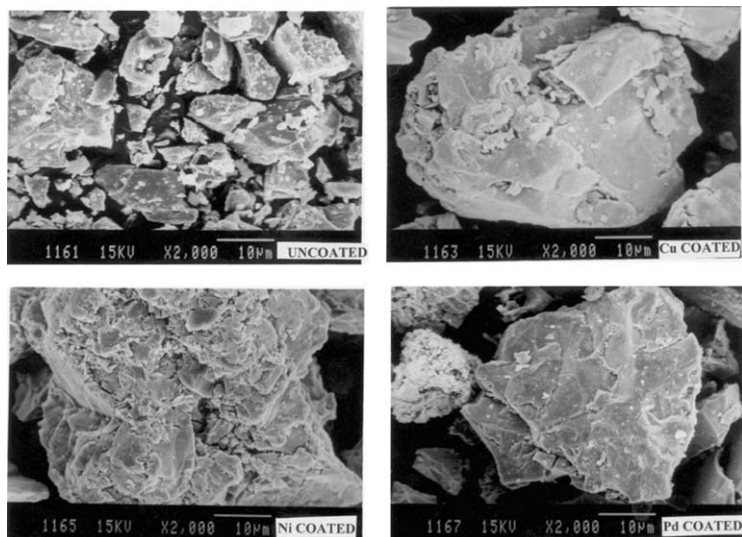


Fig. 3. SEM images of the uncoated and coated alloy powder ($\times 2000$ magnification).

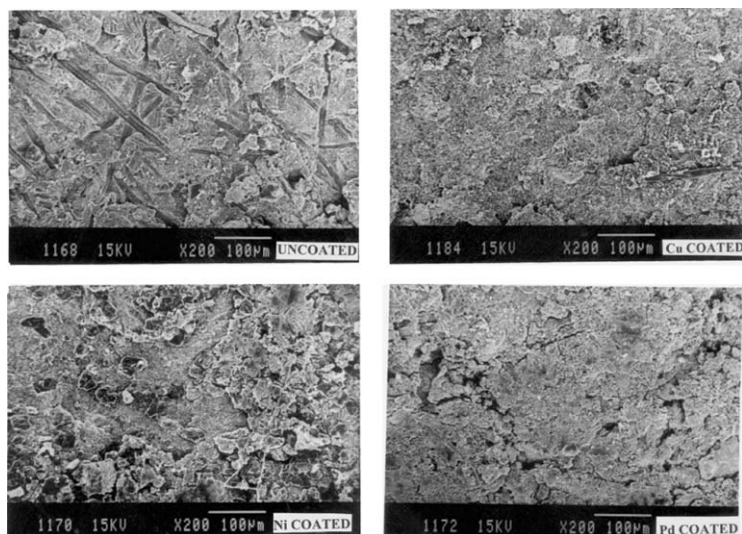


Fig. 4. SEM images of the electrodes prepared using uncoated and coated alloy powders after cycling ($\times 200$ magnification).

coatings on the alloy powder can protect the alloy from oxidation whilst they do not block the hydriding/dehydriding reaction of the electrode in an alkaline solution.

Fig. 4 shows the surface morphology of the electrode prepared using uncoated and coated alloys after 35 charge–discharge cycles at $\times 200$ magnification. From Fig. 4, it can be noted that the surface of the electrode prepared from coated alloys are planar, smooth without any cracks. In the case of the electrodes prepared using uncoated alloy, the surface was found to be rough with cracks. This also indicates that hydrogen diffusivity is more pronounced in the case of electrodes prepared using coated alloy.

4. Conclusion

1. When the alloy powder represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ was coated with Cu, Ni or Pd using an electroless coating technique, it was found that the activation time taken for the alloy to reach the maximum capacity was decreased considerably. This can be attributed to the increase in cell volume and also to the different catalytic effects of the metal coatings on the hydrogen evolution reaction.
2. Electrodes prepared using bare alloy powder showed lower discharge capacity (of around 45 mA h g^{-1} even

after 25 charge–discharge cycles) than that of the electrodes prepared using coated alloy powder. This is believed to be due to the fact that the uncoated alloy needed more number of charge–discharge cycles to get activated.

3. Of all the three metal coatings that were done on the alloy represented by the composition $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$, maximum discharge capacity was achieved for the Pd coated alloy (242 mA h g^{-1}). Both the Ni and Cu coated alloys gave more or less equal discharge capacity (214 mA h g^{-1} for the Ni coated alloy and 211 mA h g^{-1} for the Cu coated alloy). This showed that Pd coating increased the hydriding/dehydriding reaction of the electrode in an alkaline solution better than the Cu and Ni coating.

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