



Influence of electroless coatings of Cu, Ni–P and Co–P on MmNi_{3.25}Al_{0.35}Mn_{0.25}Co_{0.66} alloy used as anodes in Ni–MH batteries

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ABSTRACT

Electroless coatings of Ni–P, Co–P and Cu were applied on the surface of non-stoichiometric MmNi_{3.25}Al_{0.35}Mn_{0.25}Co_{0.66} (Mm: misch metal) metal hydride alloy. Elemental analysis was made with Energy Dispersive X-ray Analysis (EDAX). The structural analysis of bare and coated alloys was done by X-ray diffraction (XRD) whereas surface morphology was examined with scanning electron microscope (SEM) and transmission electron microscope (TEM). The electrode characteristics inclusive of electrochemical capacity and cycle life were studied at C/5 rate. Superior performance is obtained with copper coated alloy. Microstructure observations indicate that the observed excellent performance could be attributed to uniform and efficient surface coverage with copper. Also, lanthanum surface enrichment in samples during Cu coating leads to improvement in performance. It is inferred from electro analytical investigations that copper coatings act as microcurrent collectors with alterations in hydrogen transport mechanism and facilitate charge transfer reaction on the alloy surface without altering battery properties. Moreover, supportive first time TEM evidence of existence of such copper nano current collectors (about 8 nm in diameter and length about 20 nm) is reported.

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1. Introduction

Nickel metal hydride (Ni–MH) batteries are presently popular as promising high capacity power sources in various portable electronic devices, electric hand tools and hybrid electric vehicles [1]. Nowadays, many commercial Ni–MH batteries are employing AB₅-type alloys as negative electrode materials [2]. Presently, investigations on the AB₅-type rare-earth-based hydrogen storage alloys are being pursued in order to improve the electrochemical characteristics and reduce the production cost of the alloy. Efforts are also in progress to replace costlier lanthanum with relatively cheaper misch metal. Misch metal is a combination of selected rare-earths. It can be made with different permutations and combinations within the permissible limits, which can vastly alter the electrochemical properties. Amongst the various factors, La/Ce ratio is believed to have significant effect on electrochemical hydrogen storage properties. A detailed investigation on the effect of La/Ce ratio has been reported [3].

Capacity degradation of metal hydride electrodes occurring during cycling is the limiting factor for the development of metal hydride alloys. Surface segregation and decomposition of the alloy

due to oxidation at the surface [4], pulverization and disintegration of the alloy during repeated charge–discharge cycling are the causes for capacity degradation of metal hydride electrodes. Though segregation and decomposition lead to loss of active materials at a lesser degree in a single charge–discharge cycle, the cumulative effect is significant over extended number of cycles. The capacity retention of metal hydride electrode is mainly determined by the bulk properties of the inter-metallics, namely crystal orientation and electronic band structure while the kinetics strongly depend on the surface characteristics. Further, characteristics such as self-discharge rate and cycle life of metal hydride electrodes depend on conductivity and electrocatalytic activity of metal hydride alloy. Hence, it is essential to increase the alloy's conductivity and the electrocatalytic activity so as to improve its performance. Various types of surface modifications [5–9] have been reported to improve the electrocatalytic nature of metal hydride electrodes. Surface modifications of metal hydride alloy particles by electroless plating with Cu, Ni–P, Ni–B, Pd and Co have shown improvement in cycle life and high rate capability [10–13,7].

Remarkable improvement in performance has been noticed with metal hydride electrodes coated with thin silver film of 0.1 μm thick using vacuum evaporation technique [14]. Of late, Wei et al. [10] reported that the effect of electroless Cu coating on AB₅-type metal hydride alloy improves its activation capability. They also observed a decrease in charge transfer resistance and an

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Table 1
Bath composition and process of electroless deposition for microencapsulation

Composition	Content		
	Ni–P	Cu	Co–P
Nickel chloride (g l^{-1})	30	–	–
Copper (II) sulfate (g l^{-1})	–	30	–
Cobalt sulfate (g l^{-1})	–	–	32
Sodium hypophosphite (g l^{-1})	10	–	20
Sodium potassium tartrate (g l^{-1})	–	100	–
Sodium citrate (g l^{-1})	84	–	84
Sodium hydroxide (g l^{-1})	–	50	–
Sodium carbonate (g l^{-1})	–	32	–
Ammonium chloride (g l^{-1})	50	–	50
Formaldehyde (ml l^{-1})	–	29	–
pH	8–10	–	9–10
Temperature ($^{\circ}\text{C}$)	90	25	95

increase in electrochemical activity. Deng et al. [11] have noticed an improvement in electrochemical performance by Cu coating over the uncoated alloy. However, elaborate studies pertaining to different formulations of metal hydride alloys have not appeared in the literature. Hence, in the present work, we have made an extensive study on the effect of electroless plating of Cu, Ni–P and Co–P over the non-stoichiometric $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy for further improvement.

2. Experimental

2.1. Metal hydride alloy preparation and electroless coating

Lanthanum-rich non-stoichiometric $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ hydrogen storage alloy (produced by arc melting at DMRL in collaboration with CECRI) was used for this study. The purity of the constituent elements was above 99 wt.%. The constituent elements were melted together in a button arc-furnace under argon atmosphere (0.5 bar). The samples were re-melted several times by spinning the buttons upside down after each melting to ensure homogeneity. Weight loss after the final melting was less than 0.8%. The sample was annealed at 900°C for 72 h in an evacuated and sealed quartz tube maintained at 10^{-6} Torr. The chunk of the metal hydride alloy was ground for several hours to obtain fine powder.

The alloy powder with a particle size of $75\text{ }\mu\text{m}$ was used for electroless coating. Prior to coating, the alloy was sensitized by immersing in acidified SnCl_2 (10 g l^{-1}) for 10 min. Electroless deposition of nickel was carried out with moderate stirring in an alkaline hypophosphite bath at $80\text{--}90^{\circ}\text{C}$ for 30 min. The pH was monitored continuously and maintained between 8 and 10 by periodic addition of NH_4OH . After deposition, the alloy powder was rinsed with deionized water, filtered and dried. Cobalt encapsulation was done with moderate stirring in an alkaline hypophosphite bath at $90\text{--}95^{\circ}\text{C}$ for 30 min. The pH was maintained between 9 and 10. Copper electroless deposition was carried out in sulphate–tartrate bath at room temperature for 30 min. The details of bath composition and process variables are listed in Table 1.

2.2. Physical characterization

SEM analysis was performed to examine the surface morphology of the bare as well as coated alloy powders using HITACHI model S-3000H microscope. TEM studies have been performed to investigate the textural orientation of electroless deposit using Tecnai-20-G² microscope. Qualitative surface elemental analysis was done with Energy Dispersive Analysis by X-rays (EDAX). Specific surface areas of the bare and coated alloys were obtained using the BET surface area analyzer. Powder X-ray diffraction data of the bare and microencapsulated alloys were collected using a PANalytical X'per PRO model diffractometer with $\text{Cu K}\alpha$ (2.2 kW maximum) radiation. The XRD data were analyzed by a 'Crysfire' indexing package.

2.3. Charge–discharge experiments

Metal hydride electrodes for bare and coated alloys were prepared with 1.0 g of alloy powder. Slurry of the alloy powder with appropriate amounts of conducting material (KS 44) and binder (polytetrafluoroethylene) was applied on both sides of nickel mesh substrate and had a geometrical area of $3\text{ cm} \times 2\text{ cm}$. The electrode was pressed under 75 MPa and heat treated at 408 K for an hour. The thickness of the electrode after compaction was 1.0 mm. A sintered nickel hydroxide $[\text{Ni}(\text{OH})_2/\text{NiOOH}]$ electrode of thickness 1.0 mm was used as the positive electrode. A polyamide non-woven cloth was used as the separator. The negative electrode was sand-witched between two positive electrodes. 6M KOH was used as electrolyte. Galvanostatic

charge–discharge cycling was performed at a current density of 60 mA g^{-1} in a Bitrode LCN cycle life tester. Charging was done for 7 h and discharging was done till the potential of the metal hydride alloy electrode reached -0.700 V with respect to the Hg/HgO reference electrode. Life cycling experiments were done with an overcharge factor of 20% after a 10 min pause after full charge.

2.4. Electrochemical investigations

Electrochemical studies were performed using the Autolab Potentiostat/Galvanostat Model 30. Electrochemical impedance spectroscopy experiments were carried out in the frequency range of 100 kHz to 10 mHz after activation of metal hydride electrode at 50% state of charge. The amplitude of perturbation was 10 mV. Cyclic voltammograms of metal hydride electrodes were also recorded between -1.2 and -0.2 V at different scan rates viz., 2, 5 and 10 mV s^{-1} .

3. Results and discussion

3.1. SEM, TEM and EDAX analyses

The observed surface morphology of bare and electroless coated (Ni–P; Cu; Co–P) alloys are illustrated in Fig. 1(a)–(d). It can be noticed that the coverage of metal encapsulation is uniform on the alloy particles. TEM images of bare as well as electroless copper coated metal hydride alloy are presented in Fig. 2(a) and (b), respectively. The surface of the uncoated metal hydride alloy particles (Fig. 2(a)) appears rather smooth while TEM image of the electroless copper coated one (Fig. 2(b)) lucidly depicts the needle like superstructure over the alloy particles. It is obvious that the protruded needle like morphology facilitates a larger surface area for electrochemical hydrogen storage as it can act as microcurrent collectors. To the authors' best of knowledge, such an observation is first of its kind to be reported in the literature so far. The selected area electron diffraction patterns of bare as well as electroless copper coated metal hydride alloy are displayed in Fig. 3(a) and (b), respectively. Significant changes were noted in the selected area electron diffraction patterns on copper microencapsulated metal alloy particles.

The results of EDAX analysis illustrated in Table 2 shows the weight percentage of coated elements on the metal hydride alloy particles (Ni, 12.76%; Cu, 6.59%; Co, 67.13%). In the case of nickel and cobalt coatings, phosphorus content is enhanced and this could be attributed to the presence of sodium hypophosphate solution in the bath. Also, lanthanum enrichment is noticed in the case of Cu plating.

3.2. Surface area analysis

BET surface area analysis revealed the specific surface area of bare, Ni–P coated, Cu coated and Co–P coated particles as 1.0372, 1.5668, 1.9180 and $2.1151\text{ m}^2\text{ g}^{-1}$, respectively. Co–P coated particles show the highest surface area values among the investigated samples.

Table 2
Elemental analysis of bare and electroless coated $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy by EDAX

Sl. no.	Elements (wt.%)	Bare	Ni–P	Cu	Co–P
1	La	18.20	15.95	19.48	12.43
2	Ce	12.50	10.04	9.92	7.24
3	Pr	0.87	0.79	–	–
4	Nd	4.07	3.40	2.85	1.73
5	Ni	48.49	55.57	45.55	43.93
6	Mn	3.50	3.84	4.33	3.11
7	Co	9.93	7.43	9.02	30.21
8	Al	2.45	1.66	2.26	0.97
9	Cu	–	–	6.59	–
10	P	–	1.12	–	0.37

Table 3Cell parameters of bare and coated $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy

Alloy	Cell parameters		Cell volume (V) ($\text{\AA}^3$)
	a ($\text{\AA}$)	c ($\text{\AA}$)	
Bare	5.0107	4.0780	88.6696
Ni–P coated	4.9949	4.0703	87.9449
Cu coated	4.9992	4.0773	88.2479
Co–P coated	5.0068	4.0747	88.4600

3.3. XRD studies

The crystal structure of bare and coated alloys were studied using the technique of X-ray powder diffraction in order to understand any microstructural features that could correlate with electrochemical performance. The obtained diffraction patterns are shown in Fig. 4. The reflections are assignable to CaCu_5 -type hexagonal symmetry. The peak signatures are indexed and lattice parameters a , c and unit cell volume V are summarized in Table 3. The cell volumes are found to be decreasing with electroless coating and the order of the sequence is: Cu coated < Co–P coated < Ni coated < bare. It is interesting to note that Cu coated samples have undergone appreciable volume reduction and this could be attributed to the associated release of hydrogen caused during the electroless coating thereby leading to a localized reducing atmosphere augmented with the induced stress upon the inner lattice resulting to a reduction in cell volume.

An examination of the patterns of copper coated alloy indicates peaks broadening and thereby confirming the presence of copper

Table 4Activation capability and maximum capacity of bare and coated $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloys

Type of coating	Activation number	Maximum capacity (mAh g^{-1})
Bare	4	235.00
Cu	10	270.00
Ni–P	10	255.00
Co–P	9	242.00

microencapsulation. As the surface of a solid plays a vital role in the electrochemical properties of any redox species, the presence of copper on the surface of this alloy is expected to improve the performance. Copper is softer than the metal hydride alloy, thus providing strong binding, as well as good electrical and thermal conduction.

3.4. Activation capability

The activation capability of metal hydride alloy is characterized by the initial activation number. The initial activation number denoted by n is defined as the number of charge–discharge cycle required for attaining the maximum discharge capacity at a constant current drain. The variation of discharge capacities of the investigated alloy electrodes as a function of cycle number is illustrated in Fig. 5 and the activation numbers are given in Table 4. The activation capabilities of the coated alloys were inferior to the uncoated samples as is evident from the table. This is in contrast to our earlier investigations [15] on ZrV_2 -type $\text{ZrMn}_{0.2}\text{V}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.8}$ alloy wherein surface microencapsulation of alloy powder was

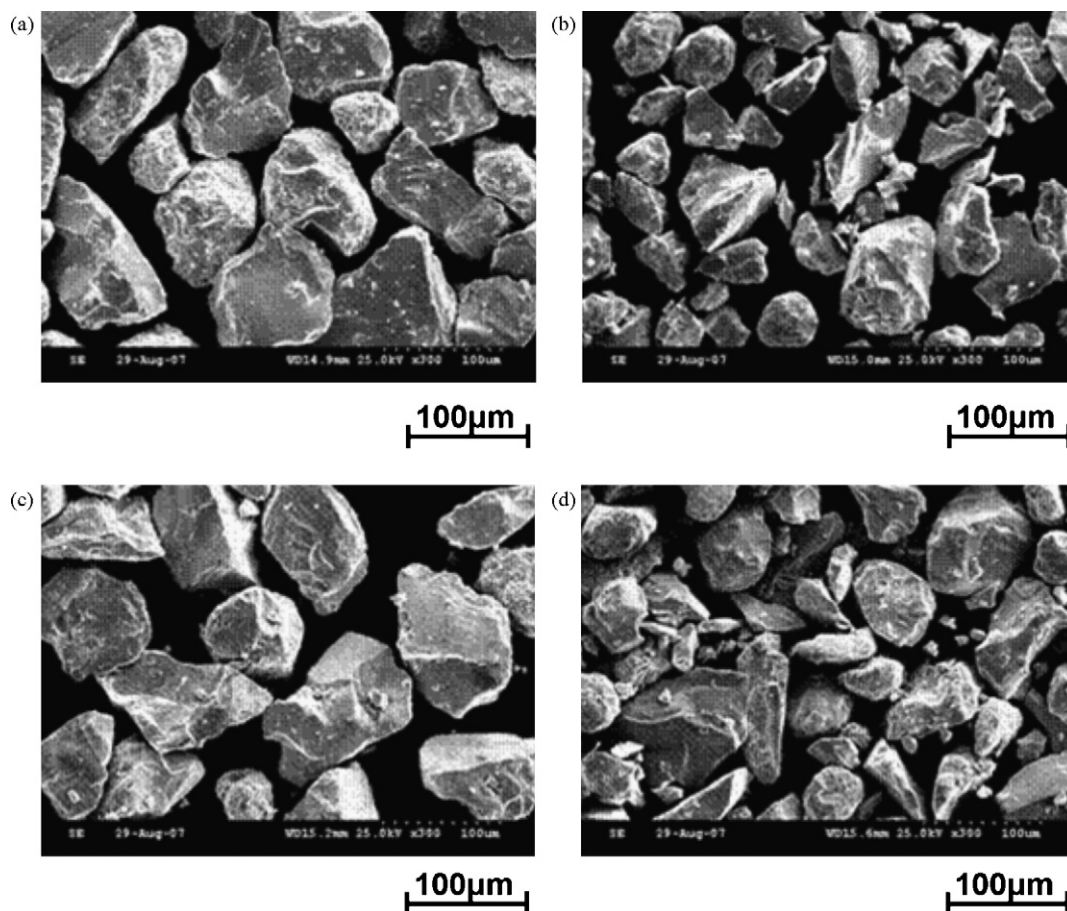


Fig. 1. Morphology of bare and coated $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy. (a) Bare alloy, (b) Ni–P coated alloy, (c) Cu coated alloy and (d) Co–P coated alloy.

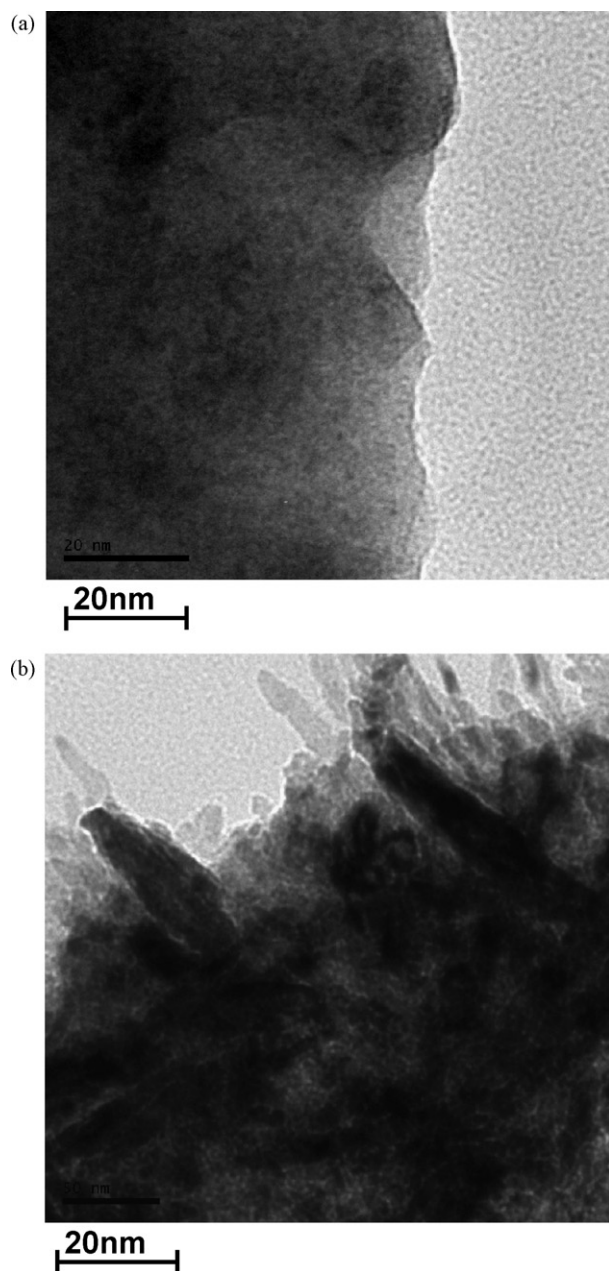


Fig. 2. TEM micrograph of $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy. (a) Bare alloy and (b) copper coated alloy.

effective in reducing the activation time, and other related reports [16]. This is also in contrast to the reported faster activation of classic MH–Ni composite electrodes achieved through Pd nanoparticle impregnation [17]. A very small amount of Pd nanoparticles could activate the MH surface to facilitate the charge transfer process in hydrogen ion reduction. Also some studies [10,18] on effects of Ni and Cu coating of hydride-forming metal alloys on their performance as the cathode material of a Ni–MH cell have indicated that such coatings significantly improve the electrode rate capability and alloy activation time.

The surface modifications lead to actual improvements in the corresponding electrochemical reactions by enhancing the performance and/or the mechanical stability of the electrode material. Despite the fact that known mechanisms of electrocatalysis do not provide a suitable theoretical framework to explain

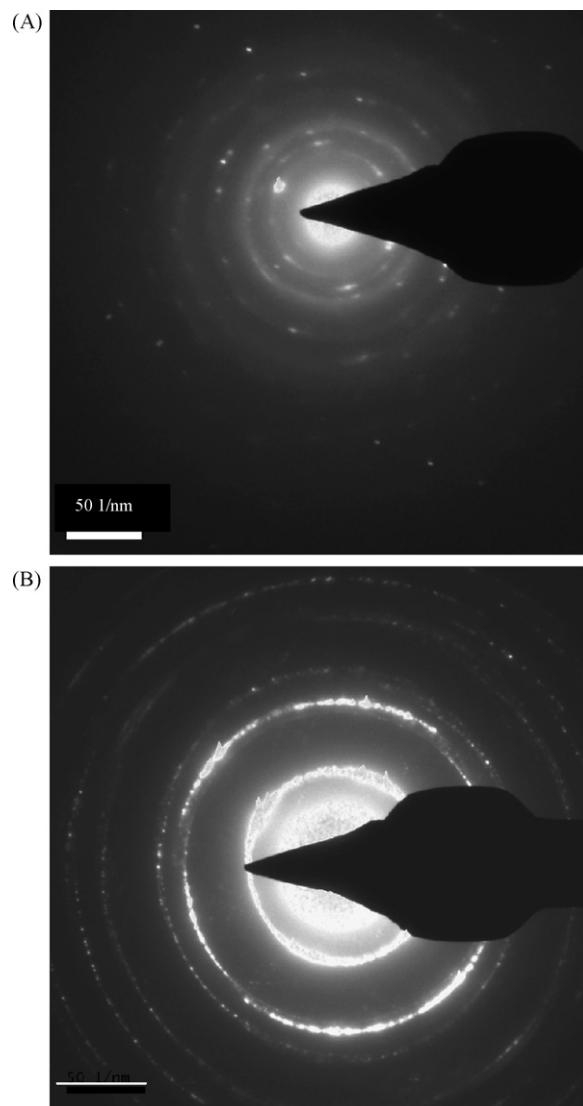


Fig. 3. Electron diffraction pattern of $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy. (A) Bare alloy and (B) copper coated alloy.

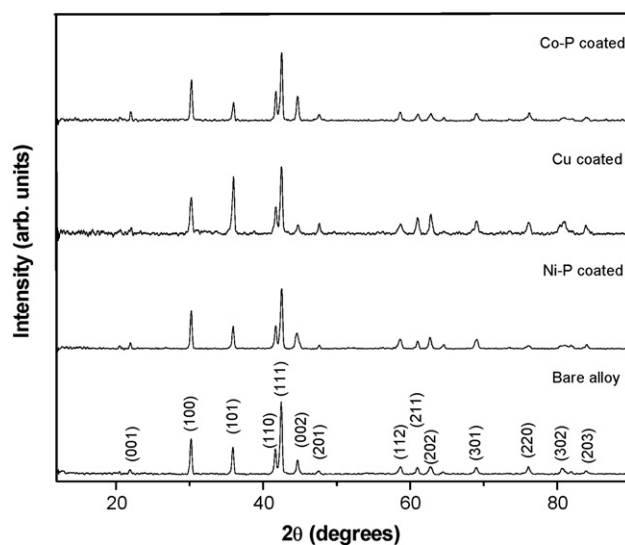


Fig. 4. XRD pattern of $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy.

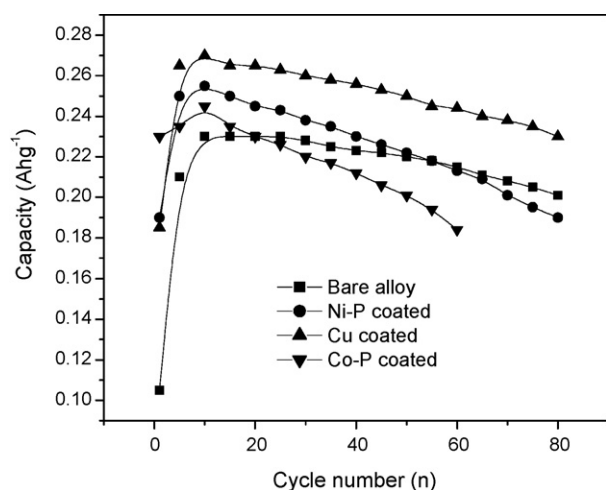


Fig. 5. Cycling behaviour of bare and coated $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride electrodes.

the electrochemical improvements produced by electrode surface modifications, a few valuable contributions towards a better understanding of the electrocatalytic process have been published. In this regard, we must point out the synergistic effect promoted by the hypo–hyper d-electronic combination of elements employed for the hydrogen evolution reaction and the inhibition of the oxidation of the hydrogen storage material enabled by metallic oxide deposition [19]. There is no significant difference between the two apparent activation energies for the electrode reactions for the electrodes with and without the Cu coating at the same hydrogen concentration [20].

3.5. Discharge capacity

The maximum discharge capacities obtained at C/5 rate for the coated and uncoated alloys can be seen in Table 4. These results reveal that the alloys with Cu electroless coating are the best and exhibit 15% improved performance over bare alloy. This is due to the improvement in discharge efficiency of the MH electrode by the faster charge transfer reaction arising from copper's superior electrical and thermal conductivity [21]. The presence of Cu grains not only enhances the effectiveness of current collection but also improves the charge transfer process on the alloy powder and electrolyte interface. It is worth mentioning that microencapsulation of the alloy with a thin Cu layer has already been reported to greatly decrease the self-discharge rate at any temperature [22]. The order of capacity improvement for nickel–phosphorous coated alloy is 8.5% over bare alloy. Nickel coating on the surface can provide both the active sites for the redox reaction of hydrogen and the pathway for the diffusion of hydrogen leading to a slower capacity decay and longer cycle life. However in contrast to the improvement seen in Ni based coatings on $\text{Mg}_{1.9}\text{Y}_{0.1}\text{Ni}_{0.9}\text{Al}_{0.1}$ MH alloy samples [23], we have observed only a moderate improvement.

Co–P coatings are marginally helpful as the improvement is only about 3.2% and the capacity degradation is faster when compared with other coated and bare electrodes. Generally addition of cobalt is expected to increase the capacity and cycle life. But our present studies have portrayed a contrary picture. This may be due to large amount of cobalt coating and the formation of $\text{Co}(\text{OH})_2$ on the surface of alloy particle which impedes the hydrogen absorption–desorption reaction. However it is interesting to note that the capacities of the alloys improve with microencapsulation. Assuming 5.51 hydrogen atoms are

adsorbed by one formula unit of the alloy, the theoretical capacity was calculated to be 353 mAh g^{-1} . The experimental capacity obtained for the bare and copper coated electrodes are 235 and 270 mAh g^{-1} , respectively. Thus at least 78–80% of theoretical capacity has been realised in the case of copper coated alloys. The capacity degradation is estimated to be $0.41 \text{ mAh g}^{-1} \text{ cycle}^{-1}$ for bare electrode; $0.57 \text{ mAh g}^{-1} \text{ cycle}^{-1}$ for copper coated electrode; $0.92 \text{ mAh g}^{-1} \text{ cycle}^{-1}$ for nickel–phosphorous coated electrode and $1.1 \text{ mAh g}^{-1} \text{ cycle}^{-1}$ for cobalt–phosphorous coated electrode.

3.6. Cycle life

The discharge capacities of bare and coated alloy powders are compared in Fig. 5 as a function of cycle number. After 20 charge–discharge cycles the capacity decay of the Cu coated alloy powder is 4.6%, which slightly exceeds the uncoated alloy (1.6%). The capacity decay due to cycling is somewhat better at 13.4% in the case of Ni coated alloy. The present observation is in line with the results reported by Jun and Yunshi [24], wherein the Ni coated MmNi_5 multicomponent hydrogen storage alloy electrode exhibited a higher discharge capacity and longer cycle life than that using the bare alloy. The surface modification of the Mg_2Ni alloy electrode with copper significantly improves its initial performance [25]. However the charge–discharge tests showed that the surface modification by Ni had only negligible effect on the capacity degradation of amorphous MgNi [26] metal hydride alloy. The ball-milled Ti–base alloy electrode using Ni flakes as a surface modifier suffered only 8% of capacity decay even after 180 cycles [27]. The capacity decay due to cycling is more pronounced at 5.9% in the case of Co–P coated alloy. It is evident from Fig. 5 that the cycle life generally gets improved by microencapsulation except in the case of Co–P.

Microencapsulation by copper obviously provides complete coverage of the inter-metallic alloy powder surface which helps to prevent corrosion or oxidation of both the active material ($\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloy) and the catalyst (Ni clusters) [20,28]. The needle like growth of copper during electroless deposition led to decrease in contact resistance. Therefore, it is suggested that the improved electrode characteristics are attributed to the copper layer deposited on the metal hydride alloy particles by the dissolution and precipitation (DP) process [29]. The initial electrochemical performance of metal hydride electrodes, which use copper and nickel electroless plated hydrogen storage alloy particles shows improved performance, but the cycle lives are the same as that of a bare metal hydride electrode. Thus, it is concluded that though these pretreatment methods affect the initial electrochemical performance of the MH electrode, they do not retard the generation of cracks and subsequent formation of oxides in the alloy particles. The cycle lives of these metal hydride electrodes mainly depend on the bulk properties of the alloy particles [30].

3.7. Electrochemical impedance and cyclic voltammetric studies

The Nyquist plots of bare and coated metal hydride alloy electrodes at fully charged state are shown in Fig. 6. They are helpful in the determination of charge transfer resistance and other kinetic parameters. The impedance curve consists of a small semicircle, a large semicircle and a straight line in the high frequency, medium frequency and low frequency region, respectively. The Warburg impedance observed rather subtly (since the frequency is limited to 5 mHz) is due to diffusion of hydrogen into the bulk of alloy. The impedance plot obtained for bare and coated electrodes in the present study was fitted into an equivalent circuit as shown in

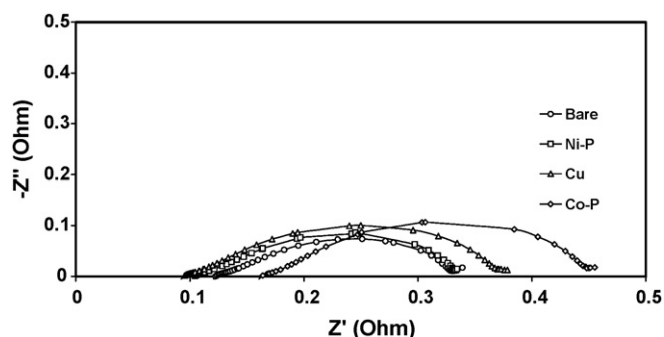


Fig. 6. Electrochemical impedance spectra of $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride electrodes.

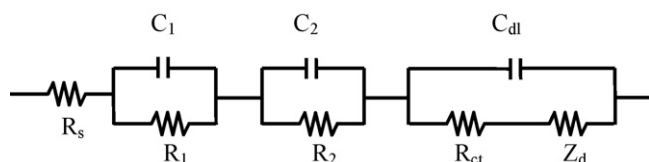


Fig. 7. Equivalent circuit for the Nyquist plot.

Fig. 7 [26] using non-linear least square fitting (NLLS) to obtain the electrode kinetic parameters. The intercept at high frequency region is directly related to electrolyte resistance (R_s). It can be observed that the electrolyte resistance varies in all the experiments that are because of the accumulation or non-uniform distribution of charge transfer species at the electrode–electrolyte interface. The semicircle at high frequency region represents contact resistance (R_1) and contact capacitance (C_1) between current collector and the active material. R_2 and C_2 represent the contact impedance between the alloy particles. R_{ct} denotes the charge transfer resistance at the electrode electrolyte interface [31]. The capacitance C_{dl} is usually represented as Q_{cpe} , which is double layer constant phase element on the electrode surface. Hydrogen diffusion behaviour is represented as a straight line in low frequency region (Z_d). However, in the observed impedance spectrum there is no specific Warburg impedance and it may be concluded that it is due to the porous nature of the electrode [25].

The values of charge transfer resistance obtained from the equivalent circuit for the different alloys are presented in Table 5. It is seen that the charge transfer resistance is the least ($174.51 \text{ m}\Omega \text{ cm}^2$) in the case of copper coated electrode. The present observation is attributed to the presence of copper encapsulated alloy particles on the surface which act as microcurrent collectors. Further, the copper encapsulation provides better connectivity between the alloy particles. Also the copper coated electrode delivers the highest capacity (270 mAh g^{-1}) among the coated electrodes. This may again be due to the needle like growth of copper electroless deposition as is evident from the Fig. 2(b). The charge transfer resistance of the Co–P coated electrode is the highest ($258.87 \text{ m}\Omega \text{ cm}^2$) and this does not favor for hydrogen storage. The cycle life curves also portray a dismal performance for Co–P coating. The important cri-

teria for selection of metal hydride system are the kinetics of the hydrogen absorption–desorption on the alloy electrode–electrolyte interface and within the bulk of the solid phase. This is usually obtained from the value of apparent exchange current density (i_0), since this is a measure of catalytic activity of the alloy. Exchange current density can be obtained from R_{ct} values using the following equation:

$$i_0 = \frac{RT}{nF} \left(\frac{1}{R_{ct}} \right) \quad (1)$$

where F is the Faraday's constant, R is the gas constant, T is the temperature in K and the i_0 calculated for the bare and coated electrodes are also included in Table 5. It is inferred from this table that the Co–P coated alloy electrodes show i_0 values lesser than bare alloy electrode thereby indicating a poor catalytic behaviour. On the other hand, the copper coated and Ni–P coated electrodes exhibit slightly higher values compared to the bare alloy. Thus it is confirmed that the coated alloys possess better electrocatalytic activity. Exchange current density is representative of the oxidation or reduction reaction rate on the electrode under equilibrium potential. An increase in the exchange current density of a metal hydride electrode is indicative of its kinetic properties. In our experiments the maximum exchange current density was obtained for copper coating.

Cyclic voltammograms of bare and copper coated metal hydride alloy electrodes obtained at different scan rate viz., 2, 5 and 10 mV s^{-1} after activation cycles are compared in Fig. 8. It can be seen that both the electrodes exhibit similar anodic and cathodic behaviour. Further, both the electrodes exhibit facile cathodic performance than the anodic side. Thus it is inferred that the overall redox behaviour is anodically controlled. A closer observation on both regions indicate that the cathodic peaks of copper coated electrodes deliver higher cathodic peak currents (181 mA) than that of the uncoated counterpart (117 mA). In contrast, the anodic peak currents for both the electrodes almost remain same. Furthermore, in the case of copper electrodes in the anodic region, a shoulder around -1.10 V is observed and is assignable to higher charge capacity. The absence of this shoulder in the case of uncoated electrodes could be attributed to the poor charging consequently leading to the corresponding low discharge capacity. This fact is supplemented by the better discharge characteristics of copper coated electrodes.

The relationship between peak current and potential scan rate is shown in Fig. 9. From the figure it can be seen that the peak potential of the tested electrodes varies with square root of scan rate and exhibit a linear dependence. From the Fig. 9, it is concluded that the electrodes are not completely reversible and diffusion is the rate determining step. The diffusion coefficient of the uncoated and copper coated electrodes are obtained from the following equation [32]:

$$I_p = 2.99 \times 10^5 n(\alpha n_\alpha)^{1/2} S C v^{1/2} D^{1/2} \quad (2)$$

where I_p is the peak current in A, n is the charge transfer number, n_α is the number of electrons transferred upto and including the rate determining step, α is the transfer coefficient, S is the surface area of the electrode in cm^2 , C is the concentration of the diffusion species in mol cm^{-3} , and v is the scan rate in V/s . The obtained dif-

Table 5

Charge transfer resistance and exchange current density values of bare and coated $\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride electrodes

Property	$\text{MmNi}_{3.25}\text{Al}_{0.35}\text{Mn}_{0.25}\text{Co}_{0.66}$ metal hydride alloy			
	Bare	Ni–P coated	Cu coated	Co–P coated
Charge transfer resistance ($\text{m}\Omega \text{ cm}^2$)	247.89	191.53	174.51	258.87
Exchange current density (mA g^{-1})	123.90	160.36	176.00	118.65

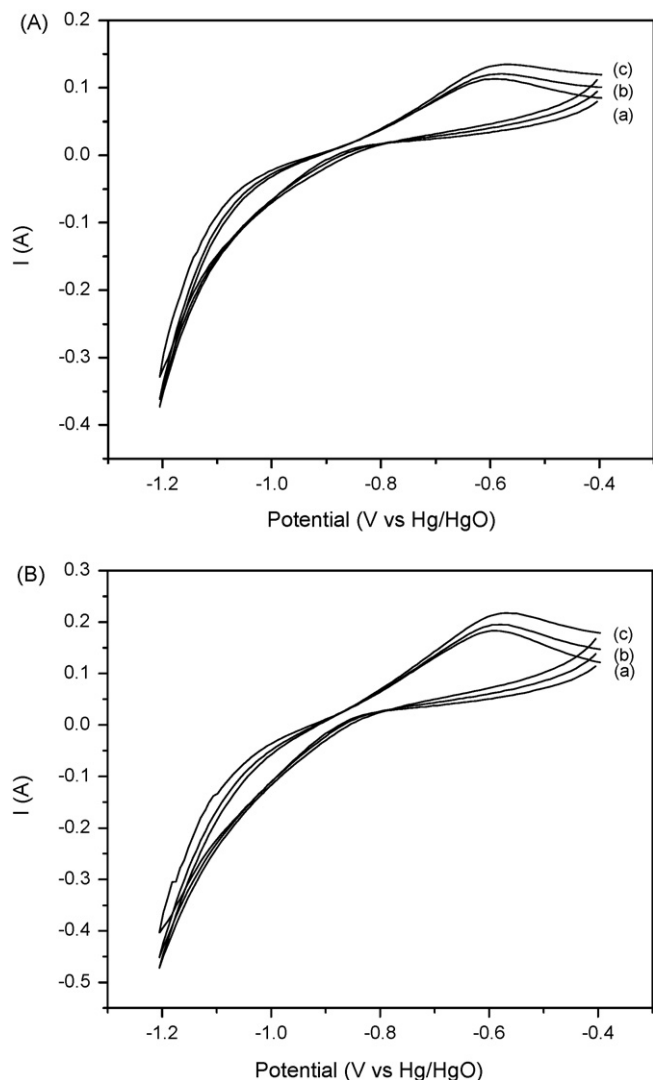


Fig. 8. Cyclic voltammogram of MmNi_{3.25}Al_{0.35}Mn_{0.25}Co_{0.66} metal hydride electrode. (A). Bare electrode and (B) Cu coated electrode. (a) 2 mV/s, (b) 5 mV/s and (c) 10 mV/s.

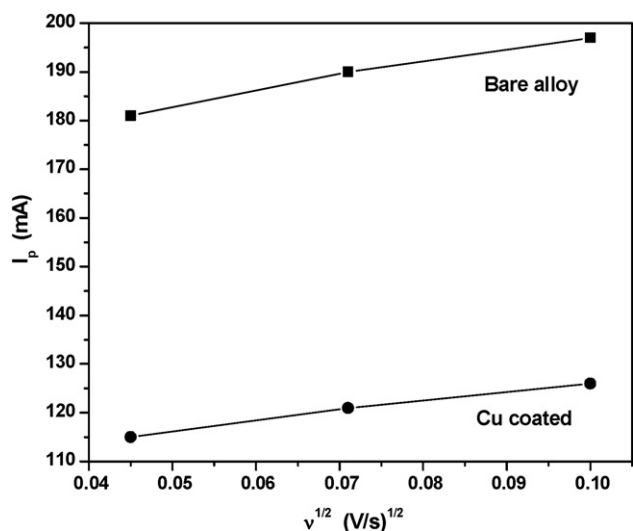


Fig. 9. Peak currents of cyclic voltammograms of MmNi_{3.25}Al_{0.35}Mn_{0.25}Co_{0.66} metal hydride electrode as a function of scan rate for bare and copper coated electrodes.

fusion coefficient for bare electrode is $4.46928 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and that for copper coated electrode is $4.669 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. It has also been noted that the hydrogen transport mechanism is altered with microencapsulation as revealed from changing slopes of the line (in bare alloy it passes through the origin whereas with microencapsulation it does not pass through the origin). It implies that in the copper coated electrode the hydrogen diffusion takes place in a facile manner rather than the bare electrode.

4. Conclusions

Effects of surface microencapsulation on the discharge capacity, cycle life and activation of lanthanum-rich MmNi_{3.25}Al_{0.35}Mn_{0.25}Co_{0.66} alloy electrodes have been investigated. It was found that the microencapsulation with Cu coating greatly improved the electrocatalytic activity for hydrogen evolution reaction and reduced the over potential of charging/discharging, resulting in a remarkable increase in electrode capacity and cycle life. However microencapsulation does not improve activation. The Cu coated alloy delivers the highest electrochemical capacity, whilst the Co-P coated alloy exhibited the least. Basic electro analytical investigations indicate that copper coatings act as microcurrent collectors and facilitate charge transfer reaction on the alloy surface without altering battery characteristics. The existence of copper microcurrent collectors is confirmed from TEM observations.

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