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# Effects of Mm(NiCoAlMn)$_5$ hydrogen storage alloy coated with Ni-Co-P alloy by electroless plating on electrochemical properties of hydride electrodes①

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**Abstract:** The effect of chemical plating with Ni-Co-P alloy on the properties of MH electrodes is investigated. The results show that the efficiency of storage alloy and the activation of MH electrode have been improved by introducing 1.74% cobalt in the Ni-Co-P alloy coating. The initial discharge capacity is 208 mAh/g. The maximum discharge capacity gets to 298.5 mAh/g. At the same time the cycle life of MH electrodes is improved. The discharge capacity of MH electrodes coated with Ni-Co-P is 88% of the maximum discharge capacity after 300 cycles. Whereas the discharge capacity of bare alloy electrodes retains 62% of the maximum capacity after 300 cycles. An increment of discharge capacity is mainly due to the superposition of the oxidation current of Co as well as improved efficiency of microcurrent collection. The effect of Ni-Co-P alloy coating by electroless plating on the kinetic properties of hydride electrode has been systematically investigated by electrochemical techniques. The results indicate that the kinetic properties of MH electrodes, including exchange current density, limiting current density, have been improved markedly. This improvement of kinetic properties leads to the decrease of the overpotential of anodic and cathodic polarization.

**Key words:** rare earths based hydrogen-storage alloys; electroless Ni-Co-P alloy plating; MH-Ni battery
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## 1 INTRODUCTION

Nickel-metal hydride (MH-Ni) rechargeable batteries with hydrogen storage alloys as the negative electrode material have attracted increasing attentions because of several inherent advantages[1-6]. So far, many multi-component, mischmetal-based, hydrogen-storage alloys have been developed to meet the requirement of high cycling life; these include substitution of the nickel by Mn, Co and Al[7]. The composition of the alloy is important, and the effects of surface composition and morphology are also significant. Micro-encapsulation of the alloy powder particles with an electroless plating of copper or nickel has been confirmed to be effective in improving the performance of hydride negative electrodes. The effects of electroless coating of Co-P alloy on the performance of hydride electrodes is the most obvious, but the cost is also higher[8]. In this paper, a study is made of the effects of Ni-Co-P alloy coating by electroless plating on the properties of Mm(NiCoAlMn)$_5$ rare earths based hydride electrodes. To compare with the Ni-Co-P alloy coating, we also give the effects of other metal coating by electroless plating on the properties of hydride electrodes.

## 2 EXPERIMENTAL

### 2.1 Surface modification of alloy powder and electrode preparation

The powder was activated by 0.1 mol/L HCl before electroless plating. Then the activated powder was chemically coated with Ni-Co-P alloy. The optimal chemical composition and operating conditions of the baths are given in Ref.[9]. The bath was continuously stirred at 85±1 ℃ during the plating process. After plating, the powder was washed thoroughly with de-ionized water and then alcohol. The powder was finally filtered under reduced pressure. The alloy particles and 10% nickel powder were mixed with 2% polyvinyalcohol (PVA) into a paste, which was applied to a porous foamed substrate nickel dried in vacuum, and finally pressed at a pressure of 500 MPa.

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### 2.2 Electrochemical measurements

A three-compartment glass cell separated with sintered glass was employed for electrochemical measurements. The MH electrode was placed in the central compartment and the two positive electrodes in compartment on each side. The positive electrodes had sufficiently larger electrochemical capacities than that of MH electrode. An Hg/HgO (6 mol/L KOH) electrode was employed as the reference electrode. The electrolyte was 6 mol/L KOH + 0.63 mol/L LiOH solution. Galvanostatic charge-discharge cycling tests were performed at room temperature. The MH electrode was charged for 7 h and discharged to − 0.60 V (vs Hg/HgO) after a rest period of 20 min, both at a constant current density of 60 mA/g.

The exchange current density ($i_0$) was measured by linear sweep voltammetry (LSV) at a scan rate of 1 mV/s. The potential of scanning was controlled at ±5 mV nearby the equilibrium potential. In each run, the metal hydride electrode was designed to reach 50% depth of discharge. $i_0$ was calculated from the slope of the polarization curve in the vicinity of the rest potential using Eq. (1)[10]:

$$i_0 = \frac{iRT}{F\eta} \quad (1)$$

The polarization experiments were conducted as above. The cathodic polarization was measured from − 0.9 V to − 1.2 V. The anodic polarization was measured from − 0.9 V to − 0.4 V. The scan rate is 1 mV/.s.

### 2.3 Composition examination

The amount of nickel and cobalt in the Ni-Co-P alloy coating measured by using atom absorption spectrum (Vavian 200).

## 3 RESULTS ND DISCUSSION

### 3.1 Activation property, discharge capacity and cycle-life behaviour

The amount of nickel and cobalt in the Ni-Co-P alloy coating measured by using atom absorption spectrum were 5.1479% and 1.74% (in mass fraction), respectively. The results show that the efficiency of active material of hydrogen storage alloy has been improved by introducing 1.74% cobalt in the Ni-Co-P alloy coating. The effects of electroless coating of Ni-Co-P alloy on the initial discharge capacity and the maximum discharge capacity of MH electrodes are shown in Figs. 1 and 2, respectively. The discharge capacity of the unmodified electrode is only 70 − 80 mAh/g on the first cycle, but the initial capacity of the electrodes coated with Ni-Co-P alloy is 208 mAh/g. This fact indicates that the coating of Ni-Co-P alloy greatly improves the electrocatalytic activity of the MH electrode, so the activation of the electrodes coated with Ni-Co-P alloy is also easier than the unmodified electrodes. The maximum discharge capacity of MH electrodes coated with Ni-Co-P alloy gets to 298.5 mAh/g and higher than the MH electrodes coated with Cu or Ni-P. In the case of MH electrodes coated with Co-P, a potential arrest was clearly observed at − 0.76V (vs Hg/HgO). Consequently, an increment of discharge capacity by Ni-Co-P and Co-P modification was mainly due to superposition of the oxidation current of Co as well as improved efficiency of microcurrent collection and electric conductivity.

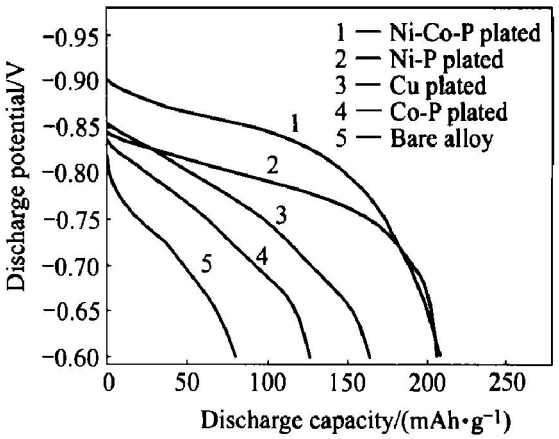


**Fig. 1** Effect of electroless coating on initial discharge curves of MH electrodes

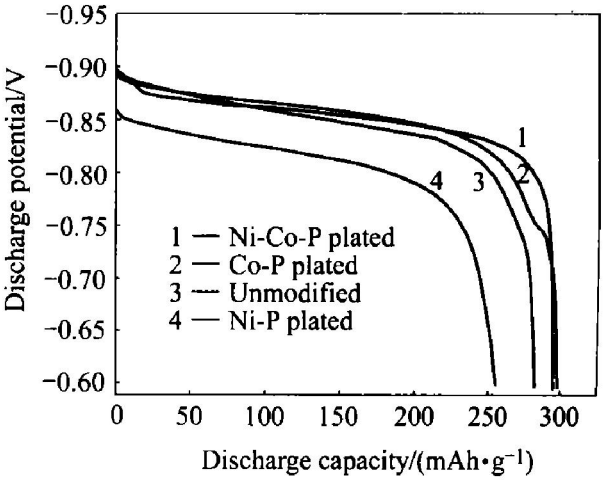


**Fig. 2** Effect of electroless coating on maximum discharge capacity of MH electrodes

The effect of cycling on the discharge capacity of electrodes with Ni-Co-P plating was examined at a constant charge and discharge current of 180 mA/g. From the result shown in Fig. 3, we can see the discharge capacity of MH electrodes coated with Ni-Co-P is 88% of the maximum discharge capacity after 300 cycles. Whereas the discharge capacity of bare alloy electrodes retains 62% of the maximum discharge after 300 cycles.

### 3.2 High-rate dischargeability and exchange current density

High-rate dischargeability was determined from

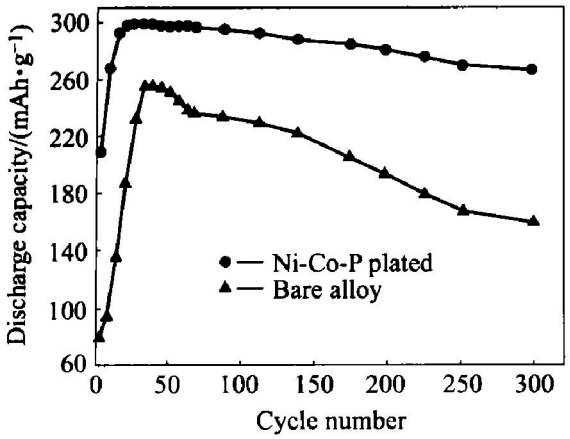


**Fig. 3** Relationship between discharge capacity and cycle number

the ratio of discharge capacity at a given high discharge current density to the discharge capacity at a current density of 60 mA/g. As shown in Fig. 4, the Ni-Co-P alloy coating markedly improves the high-rate dischargeability. It is thought that the high-rate dischargeability is determined by the electrochemical kinetics on the surface and the diffusion rate of hydrogen in the lattice. The surface of the MH electrodes coated with Ni-Co-P alloy has higher electrocatalytic activity as well as higher diffusion coefficient of hydrogen[11]. So they have lower resistance to the diffusion of hydrogen and thus noticeably improving the high-rate dischargeability of MH electrodes.

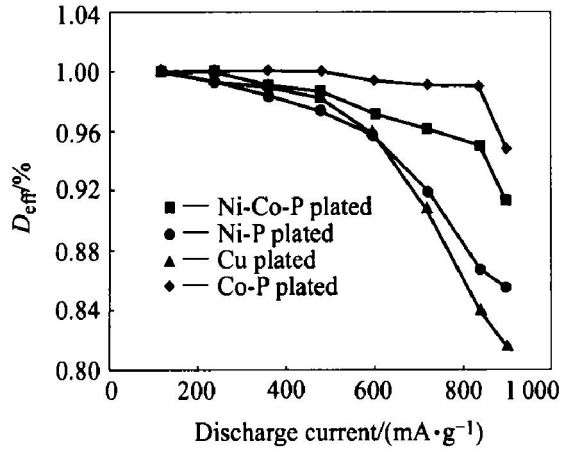


**Fig. 4** Effect of alloy modified by electroless plating on high-rate dischargeability of MH electrodes

To determine the exchange current density, linear polarization curves were obtained for MH electrodes. Typical linear polarization curves are presented in Fig. 5. The exchange current densities were calculated from the curves using Eq. (1). Similar results were obtained for other metal coating[11], the exchange current densities of the coated and unmodified MH electrode are shown in Table 1. As shown in Table 1, the coating of Ni-Co-P alloy greatly improves electrocatalytic activity of the MH electrode,

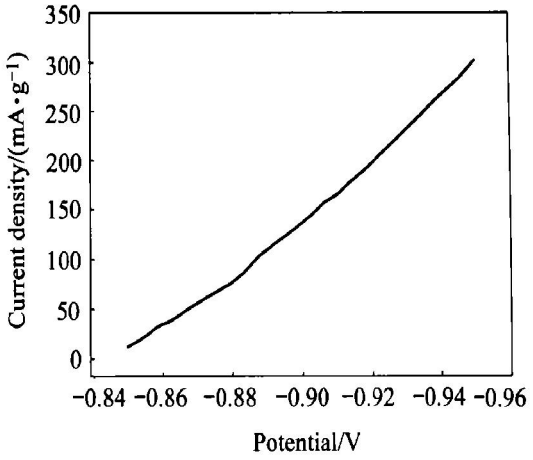


**Fig. 5** Linear polarization of MH electrode of alloy powder modified by electroless plating of Ni-Co-P alloy

so the activation of electrodes coated with Ni-Co-P alloy is easier than the unmodified electrodes.

**Table 1** Exchange current density $i_0$, limiting current density $i_L$, symmetry factor $\beta$ and diffusion coefficient of hydrogen $D_{\alpha(H)}$ of MH electrodes modified by electroless plating[11]

| Alloy | $i_0$/(mA·g$^{-1}$) | $i_L$/(A·m$^{-2}$) | $\beta$ | $D_H$/(cm$^2$·s$^{-1}$) |
|---|---|---|---|---|
| Ni-P | 231.1 | 1 710 | 0.551 | $2.771\times10^{-7}$ |
| Co-P | 288.9 | 2 136 | 0.543 | $2.121\times10^{-6}$ |
| Ni-Co-P | 252.1 | 1 894 | 0.571 | $7.322\times10^{-7}$ |
| Bare alloy | 24.39 | 581 | 0.526 | $2.114\times10^{-9}$ |

### 3.3 Cathodic and anodic polarization of MH electrodes modified by electroless plating

Fig. 6 shows the cathodic polarization of the MH electrodes coated with Ni-Co-P alloy, Ni-P, Co-P and unmodified. It can be found that the MH electrode coated with Co-P has the smallest overpotential followed by the Ni-Co-P alloy, the Ni-P and finally the unmodified. Fig. 7 shows the transient anodic current in response to overpotential of the MH electrodes coated with Ni-Co-P alloy, Ni-P, Co-P and unmodified. The anodic current, in general, increases as the overpotential increases, but when strongly polarized, a limiting current ($i_L$) can be observed. Fig. 7 illustrates the relationship between anodic current and transient polarization response of the MH electrodes coated with Ni-Co-P alloy, Ni-P, Co-P and unmodified. When the electrodes were polarized, the absolute values of $i_L$ for the MH electrodes coated with Co-P, Ni-Co-P alloy, Ni-P and unmodified are 2 136, 1 894, 1 710 and 581 A/m$^2$, respectively. The dischargeability is controlled by two processes: one a kinetic process, the other a diffusion process.

When the MH electrodes are discharged with high-rate current density, the diffusion of hydrogen atom in the bulk of alloy becomes the rate-determining step. Because the Co-P and Ni-Co-P alloy coating significantly reduces the rate of hydrogen desorption at the surface of the alloy, the diffusion coefficient of hydrogen in the hydrogen storage alloy rises, as shown in Table 1.

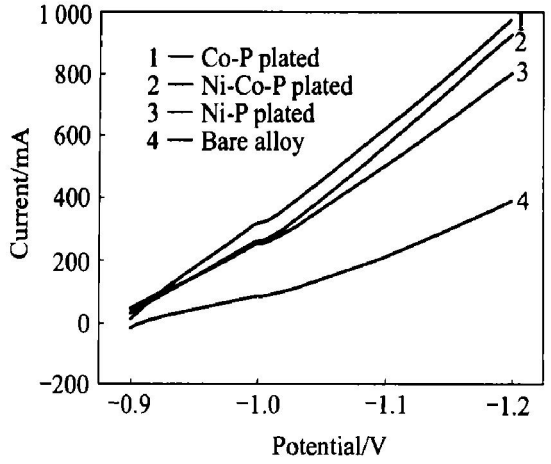


**Fig. 6** Cathodic polarization of MH electrodes modified by electroless plating

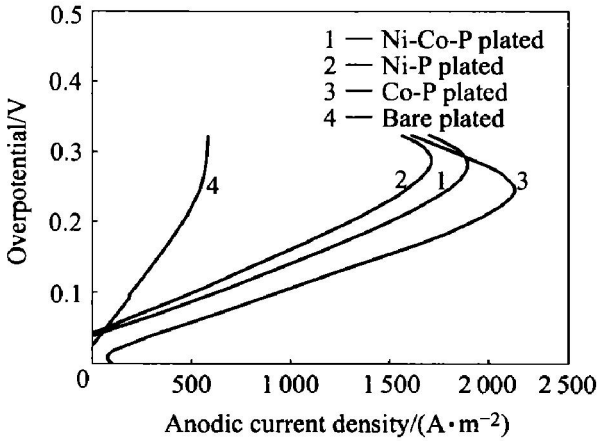


**Fig. 7** Anodic current in response to overpotential of MH electrodes modified by electroless plating

Based on the concept of free energy curves and Fick's law, the anodic overpotential can be expressed as[9, 12, 13]

$$\eta = \frac{RT}{\beta F}\ln\left(\frac{i_L}{i_0}\right) + \frac{RT}{\beta F}\ln\left(\frac{i}{i_L - i}\right) \quad (2)$$

According to Eq. (2), a plot of $\eta$ vs $\ln\left(\frac{i}{i_L - i}\right)$ should produce a straight line with its slope and intercept being $\frac{RT}{\beta F}$ and $\frac{RT}{\beta F}\ln\left(\frac{i_L}{i_0}\right)$. Hence $\beta$ can be calculated from the data of $i_L$ and $T$. Similar results are obtained for other metal coating, and relevant kinetic parameters are calculated and summarized in Table 1.

To differentiate the contribution of charge-transfer and mass-transfer resistance, Eq. (2) was employed to calculate the concentration overpotential ($\eta_c$) and electrochemical overpotential ($\eta_e$) during discharge. Fig. 8 shows the relationship between overpotential and discharge current density for the MH electrode coated with Ni-Co-P alloy. It is apparent that at low discharge current $\eta_e$ is greater than $\eta_c$, whereas at high current $\eta_c$ becomes dominant. This also means that the release of hydrogen in the bulk is the rate-determining step for metal hydride at a high rate discharge.

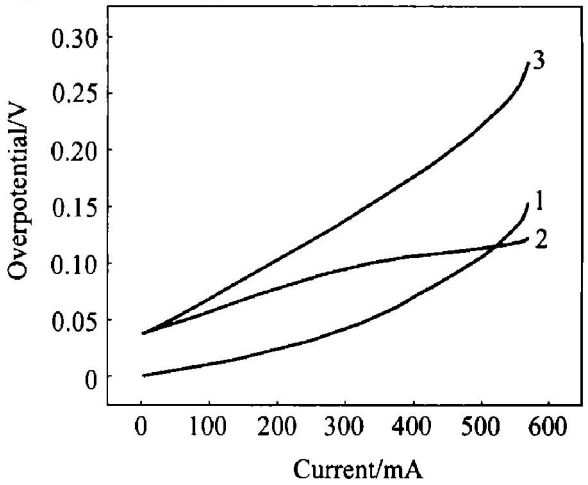


**Fig. 8** Concentration overpotential $\eta_c$(1), electrochemical overpotential $\eta_e$(2) and total electrochemical overpotential $\eta$(3) of MH coated with Ni-Co-P alloy

## 4 CONCLUSIONS

1) Many important performances of the MH electrode, namely, the discharge capacity, cyclic stability, electrocatalytic activity, polarization and high-rate dischargeability, are improved markedly by the coating of Ni-Co-P, Co-P and Ni-P.

2) The electrocatalytic activity of the MH electrodes was found to increase in the order of bare alloy < Ni-P< Ni-Co-P< Co-P coatings. Among the tested modified metals, the Co-P and Ni-Co-P coatings were very effective for increasing the dischargeability as well as accelerating the activation process. Such changes in electrochemical properties were found to be ascribed to improved microcurrent collection and electrocatalytic activity. In the case of Co-P and Ni-Co-P, the oxidation of the Co itself also contributed to the enlargement of discharging capacity.

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