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Cyclic voltammetry and electrochemical impedance of $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ alloy electrode before and after treatment with a hot alkaline solution containing reducing agent

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Abstract

The hydrogen storage alloy ($MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$, Mm = Ce-rich mischmetal) electrodes were treated in an alkaline solution containing a reducing agent (KBH_4 or NaH_2PO_2). Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were applied to characterize the electrochemical properties of the alloy electrodes before and after surface treatment. The results show that the charging efficiency and electrochemical reaction activity of metal hydride (MH) electrode were markedly improved by the treating. The reaction of the untreated MH electrode was chiefly controlled by the charge transfer process at the interface of electrode/electrolyte, or by the mixture of the charge transfer and hydrogen diffusion processes, but the reaction of the treated electrode was mainly controlled by hydrogen atom's diffusion in the alloy bulk. The results of EIS measurements indicate that the charge transfer resistance of MH electrode was reduced and its specific surface area augmented after treatment. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen storage alloy electrode; Surface treatment; Cyclic voltammetry; Electrochemical impedance spectra

1. Introduction

Nickel–metal hydride (Ni/MH) batteries have higher specific energy and capacity density, higher charge–discharge rate capability and environmental advantage compared with Ni–Cd batteries. Many multicomponent mischmetal-based hydrogen storage alloys [1–3] have been employed for commercialized cells because of their better activation property, high-rate dischargeability and lower cost compared to AB_2 type alloy. However, the surface of mischmetal-based hydrogen storage alloy is easy to be oxidized. The oxide layer on the alloy surface would affect its electrochemical performance [4]. The electrochemical performance of the MH electrodes is influenced not only by the bulk composition but also by their surface composition and morphology. The surface properties of alloys play an important role especially in electrochemical application. Various surface modifications of the alloy or electrodes have been introduced to improve their electrochemical

characteristics [4–7]. Matsuoka et al. [4] proposed that the surface modification of MH electrode by immersing in a hot alkaline solution containing KBH_4 improved the activation, high-rate dischargeability and discharge capacity, and the effects of KBH_4 concentration and treating time and temperature were discussed. Yan and Suda [5] claimed that the activation rate and high-rate dischargeability of the $LaNi_{4.7}Al_{0.3}$ alloy electrode were enhanced by treating with hot alkaline solution containing hydrazine. Iwakura et al. [6] and Matsuoka et al. [7] investigated the effects of the surface modifications of MH electrode by electroless coating Ni–P and hot alkaline containing hypophosphite on its charge/discharge performance. In the previous paper [8,9], we have demonstrated that the surface treatment of the alloy electrodes in an alkaline solution containing reducing agent effectively improved the activation property, high-rate dischargeability and electrocatalytic activity.

The authors of Refs. [4–7] investigated the effects of the surface modification on the electrochemical performance chiefly by the charging/discharging cycle and surface analysis. Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) are the effective techniques

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for evaluating the electrochemical properties of MH electrodes. In the present paper, CV and EIS were applied to evaluate the effects of surface modification of MH electrodes in hot alkaline solution using KBH_4 or NaH_2PO_2 as reducing agent on its electrochemical characteristics.

2. Experimental details

2.1. Preparation and surface modifications of MH electrodes

The hydrogen storage alloy $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ (Mm = Ce-rich mischmetal, La: 28.3%; Ce: 50.5%; Pr: 5.4%; Nd: 15.9%; other rare earth: 0.3%) powder (200–300 mesh, about 0.7 g) and 10 wt.% nickel powder were mixed well with a small amount of 2% polyvinylalcohol solution, the mixture was scrubbed into a porous foamed nickel substrates with area of 2 cm^2, then dried in vacuum and finally pressed at a pressure of 5000 kg cm^{-2} to form a test electrode. The MH electrode was modified by immersing in 6 mol l^{-1} KOH + 0.05 mol l^{-1} KBH_4 solution or 6 mol l^{-1} KOH + 0.2 mol l^{-1} NaH_2PO_2 at about 70°C for 2–8 h. In order to evaluate the influences of the treatments on the surface compositions of the alloy, the alloy powder was treated. Surface composition of the alloys before and after treating were characterized with aid of X-ray photoelectron spectroscopic analysis (XPS) (Perkin Elmer PHI5300 ESCA System). The contents of elements in the treating solution dissolved from the surface of alloys during treating were analyzed by inductively coupled plasma spectrometry (ICP) analysis.

2.2. CV and electrochemical impedance measurement of MH electrode

Electrochemical measurements were performed using a three compartments glass cell separated with a sintered glass. The MH electrode was positioned in the central compartment and two counter nickel hydroxide electrodes with a larger electrochemical capacity were placed in compartments on each side. The reference electrode was a Hg/HgO (6 mol l^{-1} KOH) electrode. The electrolyte was a 6 mol l^{-1} KOH solution. CV for the unmodified and modified MH electrodes were carried out in the potential region between −0.3 and −1.3 V vs. Hg/HgO at different sweep rates using an electrochemical testing system. The EIS measurements were carried out under open-circuit conditions by using a Solartron 1250 frequency response analyzer and a Solartron 1286 potentiastat. EIS of the electrodes were recorded from 10 000 to 0.002 Hz by ±5 mV perturbation. For the electrode after charge/discharge cycle, its depth of discharge was adjusted to 50% by discharging at a current density of 100 mA g^{-1}. The EIS were analyzed with the nonlinear least squares fitting (NLLSF) program EQUIVCRT [10].

3. Results and discussion

3.1. Effect of surface modification on CV characteristics of MH electrode

The cyclic voltammograms (CVs) of both unmodified and modified MH electrodes are illustrated in Fig. 1. In anodic branch of the CVs, the anodic peak is observed near by −0.60 V vs. Hg/HgO, which is attributed to the oxidation of absorbed hydrogen atom on the surface. The anodic peak current increases and its potential slightly shifts to the positive direction with increasing scan rate. In
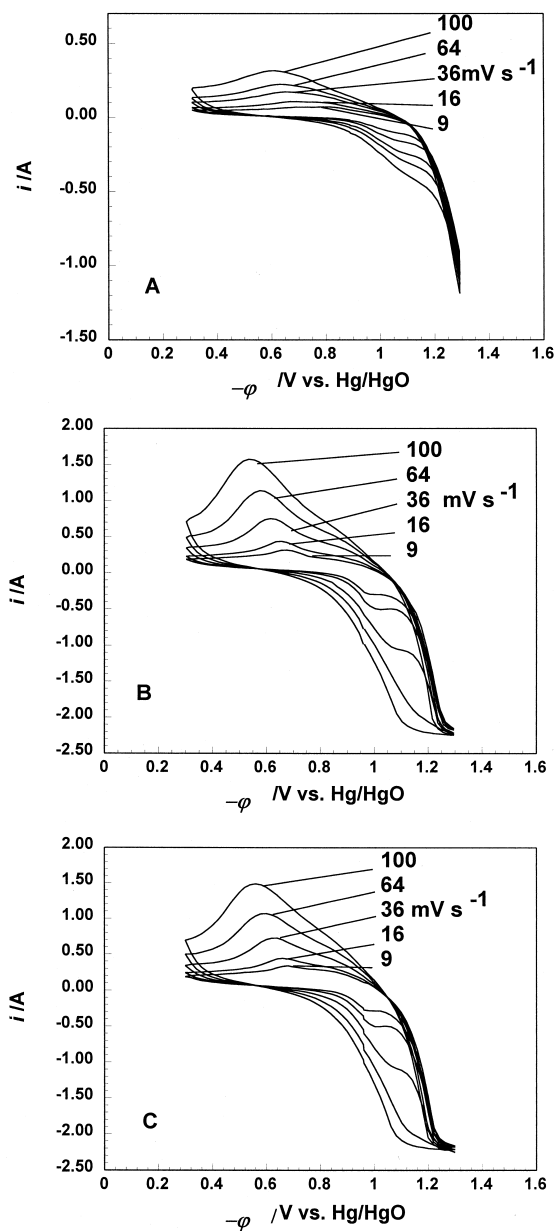

Fig. 1. CVs of the hydrogen storage alloy electrodes. (A) Untreated electrode, (B) electrode treated in 6 mol l^{-1} KOH + 0.05 mol l^{-1} KBH_4 solution at about 70°C for 8 h and (C) electrode treated in 6 mol l^{-1} KOH + 0.2 mol l^{-1} NaH_2PO_2 solution at about 70°C for 8 h.

cathodic branch of CVs, there is a plateau attributed to the adsorption of the hydrogen atom on the electrode surface and a peak of the hydrogen evolution. However, it must be noticed that the anodic peak height and area of the modified MH electrodes are much larger than those of the unmodified one. Kitamura et al. [11] compared the CV characteristics of $LaNi_5$-type alloy electrodes with and without Pd-plated layer. They claimed that the anodic area in CVs of $LaNi_5$ alloy electrode was much larger than that of $MmNi_5$ electrode, and it was caused by the fact that the $LaNi_5$ alloy had a higher the hydrogen storage capacity than that of $MmNi_5$ alloy. The anodic peak currents of the electrodes with Pd-plated layer were much higher than those of the corresponding electrodes without Pd-plated layer. It was obvious that the result of the Pd-plated layer markedly improved the electrocatilytic activity of $LaNi_5$-type alloy electrode.

The contents of elements in the solution dissolved from the alloy surface during treating were analyzed by ICP, and the results are listed in Table 1. It can be seen that Al and Mn were preferentially dissolved, and Ni and Co cannot be found in the solution. Fig. 2 shows the atomic relative ratio of $Ni/(La + Ce + Ni)$ of the alloy surface before and after treating by means of XPS analysis. Form Table 1 and Fig. 2, it was found that a Ni-rich surface layer was produced because of the preferential dissolution of Mn and Al. It is believed that a Ni-rich surface layer is of high electrocatalytic activity and good activation [4,6,9]. In addition, the specific surface area was augmented due to etching of the strong base solution and micro-crack and pulverization of the alloy [9]. For this reason, the surface modification considerably improved the discharge capacity and electrocatalytic activity of MH electrode. Therefore, the higher anodic peak current and larger peak area in CVs of modified MH electrodes are mainly caused by the improvement in capacity and electrocatalytic activity of electrodes after surface treating.

Amount of anodic oxidation of hydrogen during anodic sweep of CV would be expressed by means of the quantity (Q) of discharge calculated by following equation,

$$Q = \int_{t_1}^{t_2} i \, dt = \int_{\phi_1}^{\phi_2} \frac{i}{v} \, d\varphi$$

where t_1, t_2 and t are times; and φ_1 φ_2 and φ are potentials; i is anodic current; v is scan rate.
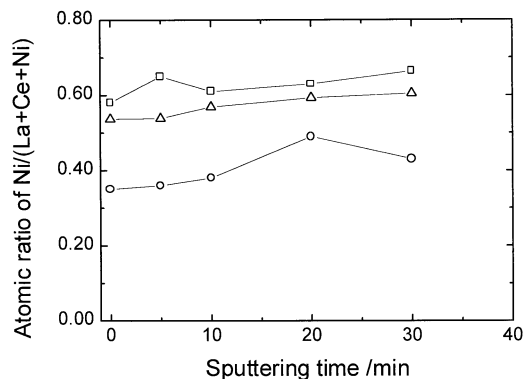

Fig. 2. Atomic ratio of $Ni/(La + Ce + Ni)$ of the alloy surface before and after treating by XPS analysis. ($\bigcirc$) Untreated alloy powder, ($\square$) alloy powder treated in 6 mol l^{-1} KOH + 0.05 mol l^{-1} KBH_4 solution at about 70°C for 8 h and ($\triangle$) alloy powder treated in 6 mol l^{-1} KOH + 0.2 mol l^{-1} NaH_2PO_2 solution at about 70°C for 8 h.

As shown in Fig. 3, the discharge quantity Q of the modified electrode is much larger than that of the unmodified one at the same scan rate. The surface treatment eliminated the oxide layer on the MH electrode and is beneficial to hydrogen diffusion and improves its charge efficiency and capacity. The result is that more amount of hydrogen was absorbed during the cathodic sweep, and then more hydrogen in the alloy diffused from the bulk to the surface to discharge during the anodic sweep. For the same electrode, Q decreases with increasing sweep rate. The diffusion of hydrogen atom from the bulk to the surface could not follow its discharge on the electrode surface at higher scan rate. In general, an oxidation reaction of hydrogen on the MH electrode surface consists usually of two processes, one being the charge transfer at the interface of electrode/electrolyte and the other the
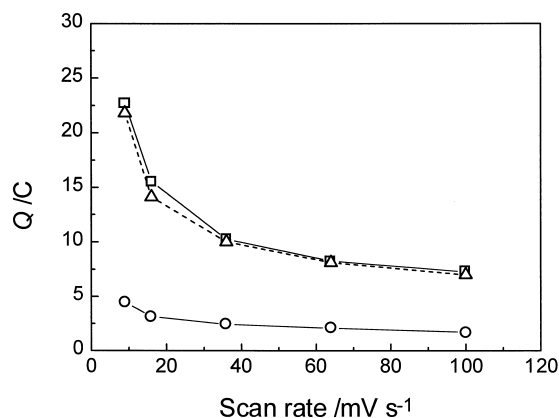

Fig. 3. The charge quantity Q during per anodic sweep as function of scan rate. ($\bigcirc$) Untreated electrode, ($\square$ and solid line) electrode treated in 6 mol l^{-1} KOH + 0.05 mol l^{-1} KBH_4 solution at about 70°C for 8 h and ($\triangle$ and dashed line) electrode treated in 6 mol l^{-1} KOH + 0.2 mol l^{-1} NaH_2PO_2 solution at about 70°C for 8 h.

Table 1
The results of ICP analysis for the contents of the elements in the solution dissolved from the alloys surface during treating (10^{-6} mol l^{-1})

Treatment	La	Ce	Pr	Nd	Ni	Co	Mn	Al
1	0.57	8.2	6.7	7.0	no	no	13.0	432.1
2	0.47	8.1	6.5	6.9	no	no	13.2	395.9

(1) Treated in 6 mol l^{-1} KOH + 0.05 mol l^{-1} KBH_4 at 70°C for 8 h; (2) treated in 6 mol l^{-1} KOH + 0.2 mol l^{-1} NaH_2PO_2 at 70°C for 8 h.

diffusion of hydrogen atom from the alloy bulk to the surface. The reactions are represented as

$$H_2O + e = H_s + OH^- \ (\text{charge transfer process})$$

$$H_s = H_b \ (\text{diffusion process})$$
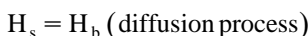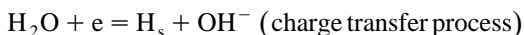
where H_s and H_b denote the hydrogen atoms on the surface and in the bulk of the electrode, respectively. If the rate of charge transfer process was much quicker than that of the hydrogen atom diffusion, i.e., the diffusion was a rate-limited step, Q will rapidly decrease with increasing sweep rate. That Q of the treated electrode sharply decreases with an increase in scan rate, as shown in Fig. 3, indicates that its reaction is mainly controlled by the diffusion. In the case of the untreated electrode, Q decreases slightly with increasing scan rate. The fact is that its reaction is chiefly controlled by the charge transfer process, at least, by mixture of charge transfer and diffusion.

3.2. EIS of MH electrode

The EIS is an effective method for characterizing electrochemical performance of MH electrode. Kuriyama et al. [12–14] discussed the deterioration behavior of AB_5 and AB_2 type alloys electrodes by means of EIS. Yamashita et al. [15] also applied EIS to investigate the influences of conductive binder on electrochemical characteristics of MH electrode. In this work, a typical EIS of MH electrode is shown in Fig. 4. The cole–cole plot consists of two not obvious comparable semicircles and one slope. The semicircle in high-frequency region is attributed to the contact resistance between the alloy particle and the current collector; the other semicircle in low-frequency region is attributed to a charge transfer process on the electrode surface, and the slope is caused by the diffusion of hydrogen in the alloy. The equivalent circuit for EIS of MH electrode is thus expressed in Fig. 5. Kuriyama et al. [14] believed that Y_{30} was relative to the surface area of electrode: the more the Y_{30}, the larger the surface area is. Y_w was relative to the hydrogen diffusion: the less the Y_w, the more difficult hydrogen diffusion is. The parameters of the equivalent circuit of EIS are calculated by the nonlin-

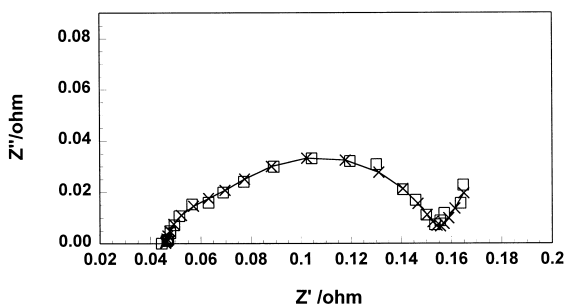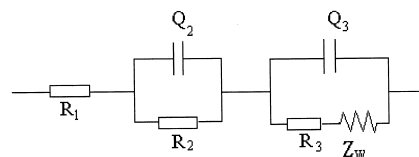Fig. 5. The equivalent circuit of EIS for MH electrode. R_1: resistance of electrolyte. R_2: contact resistance between alloy particles and collector. R_3: charge-transfer resistance at interface of electrode/electrolyte. Q_i: constant phase element $Q_i(\omega) = \{Y_{io}(j\omega)^n\}^{-1}$, $0 < n \leqslant 1$. Z_w: Warburg impedance of hydrogen diffusion, $Z_w(\omega) = \{Y_w(j\omega)^\alpha\}^{-1}$, $0.5 \leqslant \alpha < 1$.

ear least-squares fitting program EQUIVCRT [10]. The results are summarized in Table 2.

The charge transfer resistance R_3 of the untreated electrode at first charge/discharge cycle is larger, and its Y_w is less compared with other electrodes as shown in Table 2. Matsuoka et al. [4] believed that the oxide layer on its surface affected the electrochemical reaction activity but also interfered with the penetration of hydrogen into the crystal lattice. The untreated electrode at first cycle exhibited the lower electrocatalytic activity and hydrogen diffusion capability. With increasing cycle number, the specific surface area increased, and the fresh surface was produced because of the pulverization of the alloy, resulting in improved electrochemical reaction activity and diffusion step by step. Therefore, its charge transfer resistance was reduced, and Y_{30} and Y_w progressively augmented with increasing cycle number. In addition, Table 2 shows that the charge transfer resistances of the treated electrodes are much less than that of the untreated one, and that Y_{30} and Y_w also increase after its treatment. The facts mean that surface modification not only observably improves its electrocatilytic activity and hydrogen atom's diffusion ability but also augments the specific surface area. The surface composition of the treated alloy was analyzed by XPS, and its specific surface area was measured by BET in our previous paper [9] and Ref. [16]. It was confirmed that a nickel-rich layer was produced on the treated alloy surface because of the preferential dissolution of Mn and Al. Machida et al. [17] believed that the nickel-rich layer exists in the form of Ni-cluster or Raney-Ni, which has a high specific surface area and a lower activation energy for the dissociation of water. BET measurement [9,17] showed that the surface modification augmented the specific surface area of the alloy because of its pulverization caused by repeated absorbing/desorbing hydrogen during treating. These are benefit to improve its electrocatalytic activity and hydrogen atom's diffusion. Therefore, the charge transfer resistance R_3 is less than that of the untreated one, and decreases with increasing treating time. At the 10th cycle, the charge transfer resistance of the treated electrode is still less than that of the untreated one. The fact indicated that the surface treatment improved electrochemical reaction activity of MH electrode during charge/discharge cycles. The charge transfer resistance of the KBH_4-treated

Fig. 4. A typical electrochemical impedance spectra of the hydrogen storage alloy electrode. (□) Experimental data and (×) simulated data.

Table 2
The parameters of the equivalent circuit for EIS of MH electrodes

MH electrode	Treating time (h)	Cycle number	R_1 ($\times 10^{-2}$ Ω)	R_2 ($\times 10^{-2}$ Ω)	Y_{20} (S)	n_2	R_3 (Ω)	Y_{30} (S)	n_3	Y_w (S)	α
Untreated	–	1	4.53	1.75	0.423	0.99	1.20	0.615	0.91	5.89	0.62
	–	3	4.60	1.75	0.442	0.98	0.602	1.18	0.85	203	0.68
	–	5	4.47	1.84	0.452	0.98	0.214	1.30	0.85	457	0.66
	–	10	4.59	1.83	0.456	0.91	0.091	1.83	0.78	899	0.68
KBH_4-treated	2	–	4.74	1.67	0.402	0.98	0.421	0.679	0.86	71	0.64
	5	–	4.71	1.61	0.394	1.00	0.131	1.01	0.81	337	0.72
	8	–	4.75	1.74	0.359	0.98	0.079	1.12	0.74	505	0.74
	8	10	4.77	1.54	0.369	0.98	0.041	2.46	0.72	1147	0.71
NaH_2PO_2-treated	2	–	4.12	1.63	0.432	0.98	0.782	0.678	0.92	93.3	0.63
	5	–	4.51	1.67	0.406	1.00	0.367	0.904	0.91	134	0.65
	8	–	4.06	1.54	0.421	0.98	0.209	0.907	0.88	201	0.71
	8	10	4.73	1.64	0.391	0.96	0.052	2.047	0.75	963	0.69

R_1, R_2, Y_{20}, n_2, R_3, Y_{30}, n_3, Y_w and α are defined in Fig. 5.

and NaH_2PO_2-treated electrodes, even before charge/discharge cycling, are less than that of the untreated electrode at 10th and 5th cycle, respectively. It shows that the surface modification has an activation role on the MH electrode. The activation could be explained by the following processes. The electrons and atomic hydrogen are released by the oxidation of the reductant.

$$H_2PO_2^- + OH^- = H_2PO_3^- + H + e$$

$$BH_4^- + 4OH^- = B(OH)_4^- + 4H + 4e$$
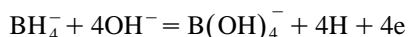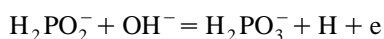
The oxide on the surface of the alloy would be reduced and eliminated and the hydrogen atoms are adsorbed on the surface and then penetrate into the lattice to form hydride. In addition, as shown in Table 2, at the same treating time or cycle, the charge-transfer resistance R_3 of the MH electrode treated in 6 M KOH + 0.05 M KBH_4 is less than that of the MH electrode treated in 6 M KOH + 0.2 M NaH_2PO_2. It means that the surface modification of MH electrode in 6 M KOH + 0.05 M KBH_4 is more effective to improve the activation property and electrocatalytic activity than in 6 M KOH + 0.2 M NaH_2PO_2.

4. Conclusion

The electrochemical characteristics of the untreated and treated MH electrodes were discussed by means of CV and EIS. There are higher anodic peak current and larger peak area in CVs of the modified electrodes compared with the untreated one. The fact indicates that the surface treatment of MH electrode improves its capacity and electrochemical reaction activity. EIS measurements also demonstrate that the surface treatments decrease the charge transfer resistance of the electrode and enhance diffusion of hydrogen atom. The surface modification eliminated the oxide layer on the alloy surface [4,6], augmented its specific surface area [10], and formed a nickel-rich layer with high electrocatalytic activity because of preferential dissolution of Mn and Al.

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