Effect of alloys modified by an alkaline solution containing potassium borohydride on the kinetic properties of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydride electrode

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Abstract

This paper describes the effects of treating the alloy powder of an electrode with 6 M KOH solution containing y M KBH_4 (y = 0.0, 0.005, 0.01, 0.02 and 0.03) on the kinetic properties of the electrode, including high rate dischargeablilty HRD, exchange current density I_0, symmetry factor β, limiting current density I_L, diffusion coefficient of hydrogen in the α-phase D_α, and electrochemical polarization η_e and concentration polarization η_c. The results show that the kinetic parameters HRD, I_0, I_L and D_α increase markedly with the increase in the concentration of KBH_4, the η_e and η_c decrease rapidly with increasing concentration of KBH_4, but the symmetry factor β does not change. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

In recent years, nickel–metalhydride (Ni–MH) batteries, where metal hydrides were used as negative electrodes, have been extensively produced because of their high energy density, high charge and high dischargeability, long charge–discharge cycle life and environmental compatibility [1].

$LaNi_5$ alloys combined high absorption and desorption of a large amount of hydrogen with fast electrochemical activation and good charge and discharge kinetics, but the storage capacity of this alloy declined rapidly during charge and discharge cycles, because the alloy decomposed to $La(OH)_3$ and nickel and too high pressure plateau [2]. In order to improve the cycle life of $LaNi_5$ alloys and/or lower the pressure plateau, various substitutions in $LaNi_5$ alloys, (of Co, Mn, Al, Si, Cu, Sn, Fe or Cr [2–9] for Ni, and of Ti, Zr, Nd, Pr or Ce [1, 10–13] for La), were introduced. The benefit of substitution was accompanied by an undesirable decrease in hydrogen absorption and adsorption capacity, long activation and slow kinetics of hydrogen absorption and desorption [7]. Therefore, in order to improve these electrochemical properties, various surface modifications were introduced. Suda et al. [14, 15] treated the hydrogen storage alloys with aqueous fluoride solutions or alkaline solutions containing hydrazine. Ogawa et al. [16] reported treating the alloys with a hot and concentrated alkaline solution. Kuriyama et al. [17] reported modification of the electrodes by an alkaline solution containing $Co(OH)_2$ and Iwakura et al. [18, 19] reported the electrodes modification by an alkaline solution containing hypophosphite or potassium borohydride. Surface modification by an alkaline solution containing potassium borohydride is a very effective method, but research [18, 19] was focused on the effect of treatment on the activation and discharge capacity of hydride electrodes. The present paper describes a systematic investigation of the effects of modifying the alloys by an alkaline solution containing potassium borohydride on the kinetic properties of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydride electrodes, including high rate dischargeability HRD, exchange current density I_0, limiting current density I_L, the symmetry factor

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β and the apparent diffusion coefficient of hydrogen D_α in the α-phase.

2. Experimental

The ingots of hydrogen storage alloy with the composition $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ were prepared by induction melting in an argon atmosphere. The Ml is denoted as lanthanum-rich misch metal, which is composed of 64.6 wt% La, 5.89 wt% Ce, 26 wt% Pr and 2.24 wt% Nd. The purity of the other metals is at least 99.9 wt%. Upon melting, the ingots were mechanically ground into fine powder with an average particle radius of 20 μm.

The alloy powder was pretreated with 6 M KOH solution containing y M KBH_4 (y = 0.0, 0.005, 0.01, 0.02 and 0.03). The ratio of alloy (g) to the solution (cm^3) is 1:5. The treatment temperature was 80°C and the time 5 h. After treatment, the alloy powder were rinsed with distilled water and then dried in a vacuum.

The metal hydride electrode was made by mixing 0.1 g of alloy powder with 0.2 g of copper powder and then the mixture was cold pressed to a pellet with a diameter of 10 mm under a pressure of 20 MPa.

The cell for electrochemical measurement consisted of the working electrode (metal hydride electrode), the counter-electrode ($NiOOH/Ni(OH)_2$) and the reference electrode (Hg/HgO electrode). The Hg/HgO electrode was equipped with a Luggin tube in order to reduce the IR drop during polarization and electrochemical impedance spectroscopy measurements. The electrolyte was a 6 M KOH solution and the temperature was controlled at 25 ± 1°C. The discharge capacity of the electrode was determined by the galvanostatic method. The cut-off voltage for discharge was fixed at −600 mV with respect to the Hg/HgO electrode. Before polarization and electrochemical impedance spectroscopy measurements, the hydrogen storage alloy electrode was activated completely (10 cycles). In order to investigate high rate dischargeability HRD and to calculate the apparent diffusion coefficient D_α of hydrogen in the α-phase, the discharge capacity at different discharge current densities was measured and the average particle size of the alloys of the hydride electrode was determined by scanning electron microscopy (SEM) after activation.

3. Results and discussion

The hydrogen desorption process during discharge is composed of several partial steps in the alkaline solution [20, 21].

1. Nucleation and growth of α-phase from β-phase.

2. Diffusion of hydrogen from α-phase through the oxide film to the near-surface region of the particle.
3. Transfer of the hydrogen from the absorbed site in the near surface to the adsorbed site on the electrode surface.

$$MH_{abs} \Leftrightarrow^{k_2}_{k_{-2}} MH_{ads}. \tag{1}$$

4. Electrochemical oxidation of hydrogen, namely, the charge transfer reaction at the electrode surfaces.

$$MH_{ads} + OH^- \Leftrightarrow^{k_3}_{k_{-3}} M + H_2O + e. \tag{2}$$
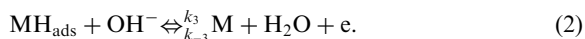
Therefore, after activation, the kinetic properties of hydride electrodes were determined by the exchange current density I_0, diffusion coefficient of hydrogen in the α-phase D_α and the geometric parameter r_0.

3.1. Effect of surface modification on the high rate dischargeability

One of the key parameters characterizing the practical application of hydride electrodes is the rate capacity or high rate dischargeability (HRD) which can be defined as the ratio of the discharge capacity Q_i at cutoff voltage −0.6 V at the discharge current density I_d to the maximum discharge capacity Q_{max}.

$$HRD = (Q_i/Q_{max}) \times 100\%. \tag{3}$$

Fig. 1 shows the high rate dischargeability HRD dependence of concentration of KBH_4. It can be seen that the higher the concentration of the potassium borohydride, the better the HRD. Taking the discharge current density I_d = 1500 mA/g as example, the HRD of untreated electrode is 8.6%, after treated with the 6 M KOH solution (y = 0.0), the HRD is 20.3%, after treated with the 6 M KOH + 0.005 M KBH_4 solution, the HRD is 34%, which is 4 times compared to that of
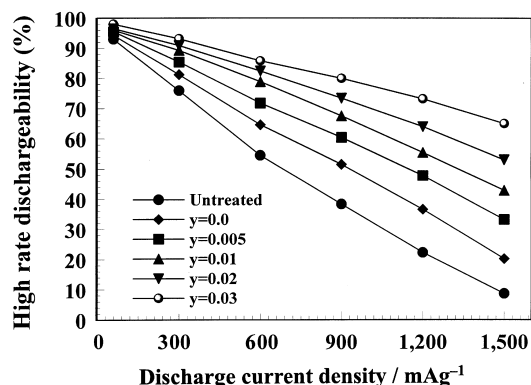

Fig. 1. Effect of the alloy powder treated with the 6 M KOH + y M KBH_4 (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the high rate dischargeability HRD of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydride electrode.
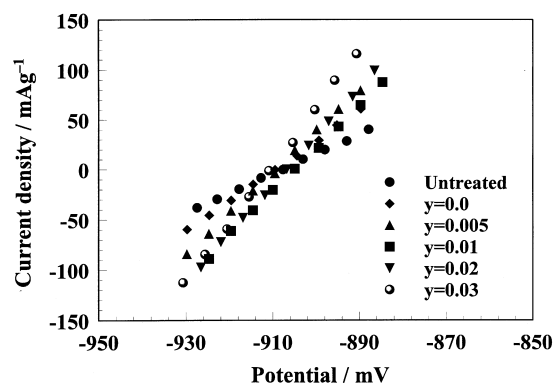
Fig. 2. Effect of the alloy powder treated with the 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the linear polarization of MlNi$_{3.7}$Co$_{0.6}$Mn$_{0.4}$Al$_{0.3}$ hydride electrode.

untreated powder and after treated with the KOH + 0.03 M KBH$_4$ solution, the HRD is 65%, which is 7.5 times higher compared to that of untreated powder.

After activation, the high rate dischargeability HRD can be expressed as [20]

$$HRD = 1 - \left(1\frac{3FD_\alpha C_{\alpha\beta}}{I_d\rho r_0^2}\left[1 - \frac{I_d}{I_0}\right.\right.$$
$$\left.\left.\times \exp\left(-\frac{0.332\beta F}{RT}\right)\right] + 1\right)^3 \qquad (4)$$

where F is Faraday constant, D_α is the apparent diffusion coefficient of hydrogen in α-phase including hydrogen diffusion through the oxide film on surface and transfer from the absorbed sites to adsorbed sites, $C_{\alpha\beta}$ is the hydrogen concentration of the α-phase at interface between α- and β-phase, I_d is the discharge current density, I_0 is the exchange current density, r_0 is the average radius of the particle, β is the symmetry factor and ρ is the density.

It is obvious that, supposing the treatment do not affect the thermodynamic properties of powder such as $C_{\alpha\beta}$, the HRD is mainly determined by kinetic proper-

ties, such as exchange current density I_0, the apparent diffusion coefficient of hydrogen in the α-phase (including hydrogen diffusion through the oxidation film on the surface of particles) D_α or the limiting current density I_L. The effect of treatment on the I_0, D_α and the I_L are discussed in the following sections.

3.2. Effect of treatment on the exchange current density I_0

Fig. 2 shows the linear polarization of the alloys treated at different conditions when SOD is 50% and scanning rate is 10 mV/s. It is obvious that the reaction resistance decrease with the increase of the concentration of KBH$_4$. The exchange current density I_0 can be calculated according to following expression [22]:

$$I_0 = \frac{I_d RT}{F\eta} \qquad (5)$$

where R is the gas constant, T the temperature and η the total overpotential.

The exchange current densities I_0, calculated by Eq. (5) are listed in Table 1. The exchange current density I_0 increases from 50.0 mA/g for untreated powder to 142.1 mA/g for y = 0.03, respectively. The I_0 at y = 0.03 is almost three times compared with the untreated powder. It also can be found that, the exchange current density I_0 of the powder treated with KBH$_4$ is much larger than that treated with the pure alkaline solution (y = 0.0), for example, the I_0 is 75.8 mA/g for powder treated with the pure alkaline solution, but after treated with 0.005 M KBH$_4$, the I_0 increases up to 106.1 mA/g, which is 40% greater than that of treated with the pure alkaline solution (6 M KOH).

3.3. Effect of treatment on the diffusion coefficient of hydrogen D_α

During galvanostatic discharge, the apparent diffusion coefficient of hydrogen in α-phase (including

Table 1
Effect of the alloy powder treated with the 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the exchange current density I_0, limiting current density I_L, symmetry β and the apparent diffusion coefficient of hydrogen D_α of the powder

y	I_0 (mAg^{-1})	I_L (mAg^{-1})	β	D_α (cm^2 s^{-1})
Untreated	50.0	1034.0	0.34	3.7×10^{-10}
0.0	75.8	1125.3	0.34	4.2×10^{-10}
0.005	104.1	1309.7	0.35	4.8×10^{-10}
0.01	118.3	1440.3	0.34	5.4×10^{-10}
0.02	130.6	1595.5	0.35	5.8×10^{-10}
0.03	142.1	1805.1	0.36	6.7×10^{-10}

hydrogen diffusion through the oxide film on the surface of particles) can be calculated [23]

$$D_\alpha = \frac{r_0^2 I_d}{15(Q_0 - \tau I_d)} \qquad (6)$$

where Q_0, I_d, τ and r_0 are the initial specific capacity, the discharge current density, transition time, i.e. the time when the hydrogen surface concentration is zero and the average particle radius, respectively.

According to SEM results, after activation the radius of the particle is 14.0, 14.0, 13.9, 14.0, 13.8 and 14.1 μm for the powder untreated and treated with 0, 0.005, 0.01, 0.02 and 0.03 M KBH$_4$, respectively. It is apparent that the treatment has no effect on the alloy decrepitation. Substituted these values into Eq. (6), the D_α can be calculated and the results are also presented in Table 1. It can be seen that the apparent diffusion coefficient of hydrogen in the α-phase D_α increases with the increase in concentration of KBH$_4$. It also can be found that the improvement of the D_α is smaller than that of exchange current density I_0 when the powder is treated with same y M KBH$_4$ solution. For example, the D_α of hydrogen when the powder is treated with 0.03 M KBH$_4$ is 81% higher than that of untreated powder, but for I_0, it is 184% higher.

The effect of treatment on the D_α also can be confirmed by the results of electrochemical impedance spectroscopy. Fig. 3 shows the electrochemical impedance spectra for y = 0.0, 0.005, 0.01, 0.02 and 0.03. The low frequency semicircle in the electrochemical impedance spectra is attributed to the hydrogen diffusion in the α-phase according to Wang's mathematical model [24]. The radius of this semicircle decrease with

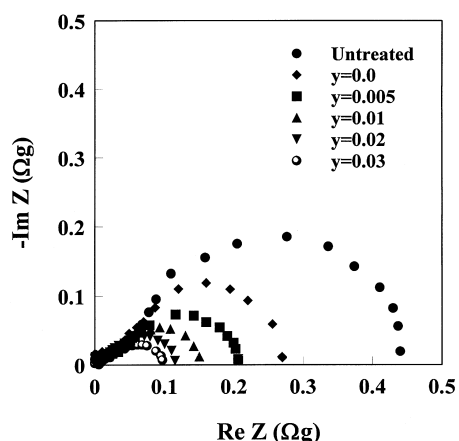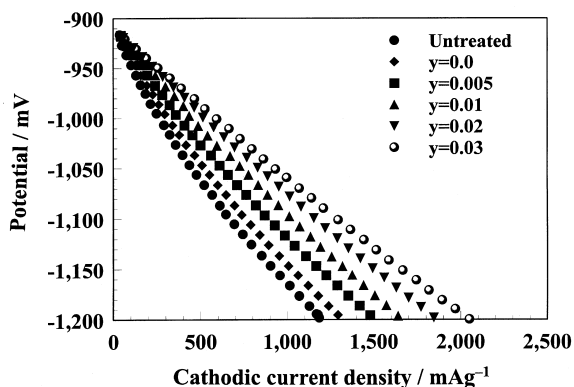Fig. 4. Effect of the alloy powder treated with the 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the cathodic polarization.

increasing concentration of KBH$_4$ means that the apparent diffusion coefficient of hydrogen in α-phase D_α increases with the increase in concentration.

3.4. Effect of treatment on the polarization

The effect of the powder treated with the different concentrations of KBH$_4$ on the cathodic and anodic polarization, where the state of discharge is 50% and the scanning rate of 10 mV/s, are shown in Figs. 4 and 5, respectively. The cathodic and anodic polarization decreases with the increase in concentration of KBH$_4$. The limiting current density I_L of anodic polarization according to Fig. 5 are also listed in Table 1. The limiting current density I_L of anodic polarization are 20%, 39%, 53%, 69% and 92% at y = 0.0, 0.005, 0.01, 0.02 and 0.03 greater than that of untreated powder, respectively.
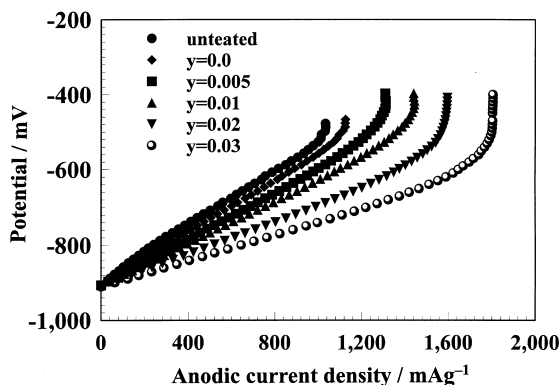

Fig. 3. Effect of the alloy powder treated with the 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the electrochemical impedance spectra of MlNi$_{3.7}$Co$_{0.6}$Mn$_{0.4}$Al$_{0.3}$ hydride electrode.

Fig. 5. Effect of the alloy powder treated with the 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the anodic polarization.
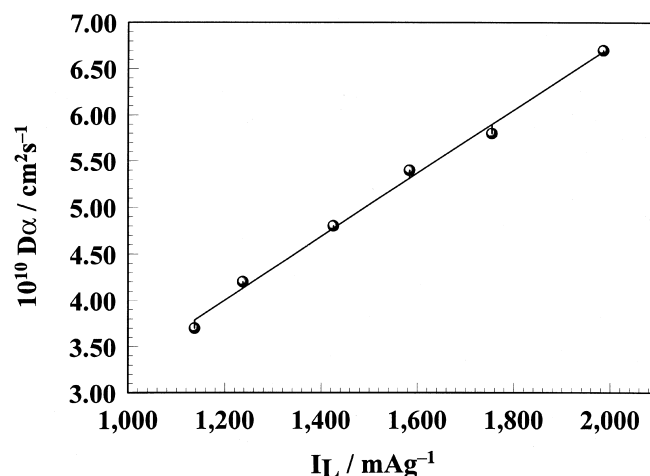
Fig. 6. Relationship of limiting current density I_L with diffusion coefficient of hydrogen D_α in the α-phase.

According to Wang et al. [20], the limiting current density I_L can be expressed as

$$I_L = \frac{3FD_\alpha C_{\alpha\beta}}{r_0^2 \rho}[(1 - SOD)^{-1/3} - 1]^{-1} \tag{7}$$

where SOD is the state of discharge. It can be expressed as

$$SOD = \frac{Q_d}{Q_{max}} \tag{8}$$

It can be seen that, when r_0 and SOD are constants, the I_L increases linearly with D_α. If neglected the effect of treatment on $C_{\alpha\beta}$, the I_L should increase linearly with D_α. Fig. 6 shows the relationship between I_L and D_α.

The total anodic polarization can be expressed as [25]

$$\eta = \eta_e + \eta_c \tag{9}$$

where

$$\eta_e = \frac{RT}{\beta F}\ln\left(\frac{I_d}{I_0}\right) \tag{10}$$

$$\eta_c = \frac{RT}{\beta F}\ln\left(\frac{I_L}{I_L - I_d}\right) \tag{11}$$

Substituted Eqs. (10) and (11) into Eq. (9), the following expression can be obtained [25]

$$\eta = \frac{RT}{\beta F}\ln\left(\frac{I_L}{I_0}\right) + \frac{RT}{\beta F}\ln\left(\frac{I_d}{I_L - I_d}\right) \tag{12}$$

According to Eq. (12), a plot of η vs. $\ln(I_d/I_L - I_d)$ should produce a straight line with its slope being $RT/\beta F$. Therefore, symmetry factor in the oxidation direction β can be calculated from data of I_L and T. The calculated β is also listed in Table 1. It can be seen that the symmetry factors are almost constant.

Eq. (10) can not be used to calculate electrochemical overpotential when the discharge current density is not enough large, but concentration polarization η_c and electrochemical polarization η_e of anodic polarization can be calculated by the following expressions [26]:

$$\eta_c = \frac{RT}{\beta F}\ln\frac{I_L}{I_L - I_d} \tag{13}$$

$$\eta_e = \eta - \frac{RT}{\beta F}\ln\left(\frac{I_L}{I_L - I_d}\right) \tag{14}$$

where η is the experimental value of total polarization.

The concentration polarization η_c of anodic polarization calculated by Eq. (13) and electrochemical polarization η_e calculated by Eq. (14) when the powder is treated with different y concentrations of KBH$_4$ are shown in Figs. 7 and 8, respectively. It is apparent that at the low discharge current densities, the electrochemical polarization η_e is greater than the concentration
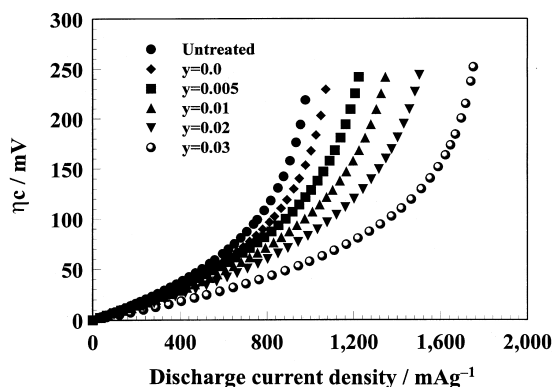

Fig. 7. Effect of the alloy powder treated with the 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the concentration polarization η_c.
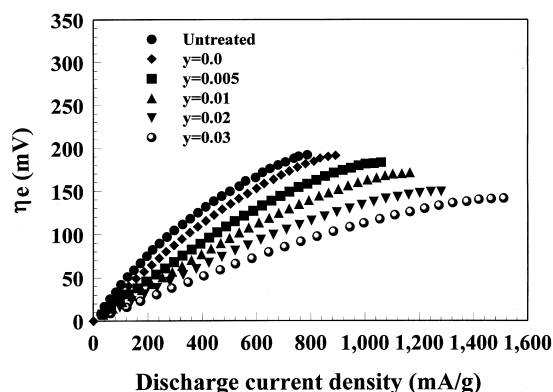
Fig. 8. Effect of the alloy powder treated with 6 M KOH + y M KBH$_4$ (y = 0.0, 0.005, 0.01, 0.02 and 0.03) solution on the electrochemical polarization η_e.

Fig. 10. Galvanostatic discharge curves of MlNi$_{3.7}$Co$_{0.6}$Mn$_{0.4}$Al$_{0.3}$ hydride electrode, where the powder is untreated, treated with the 6 M KOH solution and 6 M KOH + 0.03 M KBH$_4$ solution; discharge current density is 600 mA/g.

polarization η_c, whereas at high discharge densities η_c becomes dominant. This means that, at low discharge current densities, the charge transfer is the rate determining step, whereas at high discharge current densities, the release of hydrogen (diffusion of hydrogen in α-phase) is the rate determining step. It also can be found that the concentration polarization η_c and electrochemical polarization η_e decrease with the increasing concentration of KBH$_4$. The difference of the η_e or η_c of the alloys treated with different concentration of KBH$_4$ becomes much larger with the increasing discharge current density. Therefore, among the electrodes investigated, the powder treated with 0.03 M KBH$_4$ have the best kinetic properties.

The effect of the powder treated with y (y = 0.0, 0.03) concentration of KBH$_4$ on the galvanostatic polarization when the discharge current density I_d is 60, 600 and 1200 mA/g are presented in Figs. 9–11, re-
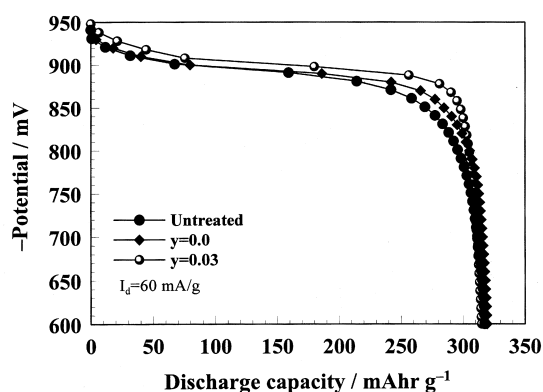
spectively. For comparison, the galvanostatic polarization of the untreated powder at different I_d are also shown in corresponding figures. The polarization of the untreated powder is similar to that treated with the 6 M KOH solution, but the discharge potential of the powder treated with 0.03 M KBH$_4$ is negative slightly compared with that of powder treated with the 6 M KOH solution, When the I_d is 60 mA/g. With the increase in I_d, the polarization decreases in sequence of the powder untreated, treated with the 6 M KOH solution and treated with the 0.03 M KBH$_4$. For example, when I_d = 600 mA/g, the discharge plateau is about −700, −760 and −825 mV for the powder untreated, treated with the 6 M KOH solution and 6 M KOH + 0.03 M KBH$_4$ solution, respectively. It can be found that, when the discharge current density I_d is

Fig. 9. Galvanostatic discharge curves of MlNi$_{3.7}$Co$_{0.6}$Mn$_{0.4}$Al$_{0.3}$ hydride electrode, where the powder is untreated, treated with the 6 M KOH solution and 6 M KOH + 0.03 M KBH$_4$ solution; discharge current density is 60 mA/g.
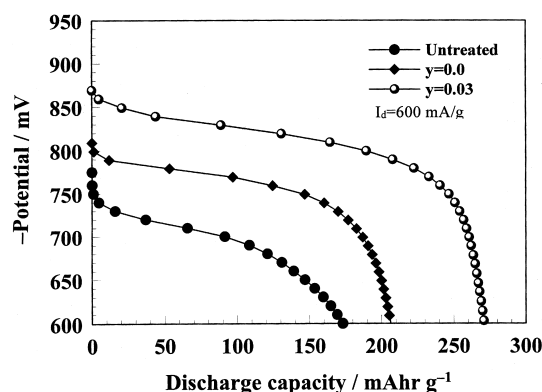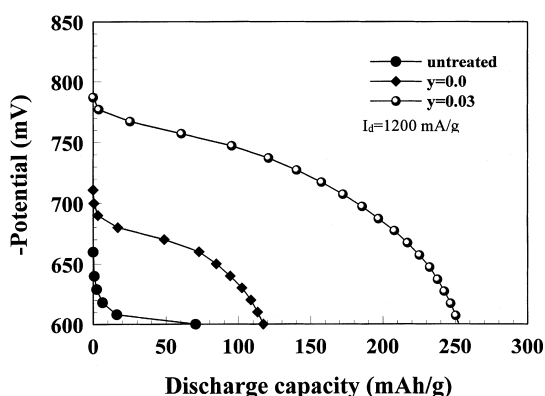

Fig. 11. Galvanostatic discharge curves of MlNi$_{3.7}$Co$_{0.6}$Mn$_{0.4}$Al$_{0.3}$ hydride electrode, where the powder is untreated, treated with the 6 M KOH solution and 6 M KOH + 0.03 M KBH$_4$ solution; discharge current density is 1200 mA/g.

small, for example, $I_d = 60$ mA/g, the potential initially drops slowly and then changes abruptly at the end of the discharge, which indicated that the determining step changes from charge transfer reaction to the diffusion of hydrogen in α-phase, but this change becomes more close to the end of discharge in sequence of the powder untreated, treated with the 6 M KOH solution and the 6 M KOH + 0.03 M KBH_4 solution. With increasing I_d, for example, $I_d = 600$ mA/g, the rate determining step for the untreated powder becomes the electrochemical (charge transfer) reaction and diffusion of hydrogen during the whole polarization process, but for the powder treated with the 6 M KOH solution and 6 M KOH + 0.03 M KBH_4 solution, like the small discharge current density it is remains the electrochemical determination for the small drop of potential and diffusion of hydrogen determination for the sudden drop of potential at the end of discharge and if the discharge current density increases continuously, for example $I_d = 1200$ mA/g, the whole discharge process is controlled by electrochemical reaction for the untreated powder, but it is controlled by electrochemical reaction and diffusion of hydrogen during the whole polarization process for the powder treated with the 6 M KOH solution and 6 M KOH + 0.03 M KBH_4 solution.

4. Conclusions

In conclusions, the kinetic parameters of electrodes of high rate dischargeablilty HRD, the exchange current density I_0, the limiting current density I_L increase markedly with the increase in the concentration of KBH_4, the electrochemical polarization η_e and concentration polarization η_c decrease rapidly with increasing y value, but the symmetry factor β is almost constant. The kinetic properties of the $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydride electrode are markedly improved when the powder is treated with the 6 M KOH solution containing KBH_4 as reducing agent.

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