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Influence of concentration of KOH solution containing 0.02 M borohydride on the kinetic properties of hydrogen storage alloys

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Abstract

In this paper the effect of concentration of KOH solution containing 0.02 M borohydride on the electrochemical properties of $Ml(NiCoAl)_5$ hydrogen storage alloys, including the high rate dischargeability, exchange current density I_0, limiting current density I_L, and diffusion of hydrogen in the hydride, by means of linear polarization, anodic polarization, cathodic polarization, and electrochemical impedance spectroscopy, was studied in detail. The results show that high rate dischargeability, the exchange current density i_0, and limiting current density I_L increase, and the anodic and cathodic polarization decrease with the increase in concentration of KOH. The size of a semicircle of electrochemical impedance spectroscopy decreased with increase in concentration of KOH, which indicates that the diffusion coefficient of hydrogen increases. Within the range of the experimentation, it can be concluded that the higher the concentration of KOH, the better the electrochemical properties of $Ml(NiCoAl)_5$ hydrogen storage alloys.

Keywords: Pretreatment; Concentration of alkaline; Electrochemical properties; Hydrogen storage alloy electrodes

1. Introduction

Nickel–metal hydride battery industry has been developing due to the demand for a power source with high energy density, high rate capacity, long cycle life, and better environmental compatibility. A number of alloys, and intermetallic compounds capable of forming hydrides have been extensively studied as hydrogen storage materials, among which the rare earth-based alloys [1], titanium based alloys [2] and zirconium based alloys [3] are considered most promising.

$LaNi_5$ has a high absorption and desorption hydrogen capacity, good electrochemical activation properties and good charge and discharge kinetics, but the storage capacity of this alloy declines rapidly during charge and discharge cyclings, because the La on the surface transforms readily and its pressure plateau is too high [4]. In order to improve the cycle life of $LaNi_5$ alloys and/or lower the pressure plateau, various metallic elements were introduced to substitute Ni in $LaNi_5$ alloys, such as Co, Mn, Al, Si, Cu, Sn, Fe, and Cr [4–11] or substitute La by Ti and Zr [1,12]. The benefit of substitutions are also accompanied by the undesirable decrease in hydrogen absorption and adsorption capacity, poor activation, and slow kinetics of hydrogen absorption and adsorption [9]. Therefore, In order to improve these electrochemical properties, various surface modifications were introduced to solve these problems. Suda et al. [13–15] treated the hydrogen storage alloys with F-containing aqueous solution or hydrazine in an alkaline solution. Ogawa et al. [15] and Uchida et al. [16,17] reported treating the alloys with a hot and dense alkaline solution. Kuriyama et al. [18] reported the electrodes modified by an alkaline solution containing $Co(OH)_2$ and Iwakura et al. [19,20] reported the electrodes modified by an alkaline solution containing hypophosphite or potassium borohydride. Among them, surface modification by an alkaline solution containing potassium borohydride is a very effective method. In a previous paper, the effect of the 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 electrodes was reported [21], In this paper, the results of a systematic study of the concentration of KOH solution containing 0.02 M borohydride on the kinetic properties of hydrogen storage alloys is presented.

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2. Experimental

The ingots of hydrogen storage alloy with the composition of $\mathrm{MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}}$ was prepared by induction melting under argon atmosphere. The Ml stands for lanthanum-rich misch metal with 64.6 wt% La, 5.89 wt% Ce, 26 wt%Pr, and 2.24 wt% Nd. The purity of the other metals is all above 99.9 weight percent. After melting ingots were mechanically crushed and ground into fined powder with an average size of 40 μm.

The alloy powders were modified with y (y=3, 4, 5, 6) M KOH solution containing 0.02 M $\mathrm{KBH_4}$. The modification temperature was 80°C and the time 5 h. After treatment, the alloy powders 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 compacted into a pellet of 10 mm in diameter under pressure of 20 MPa for electrochemical measurements..

The electrochemical cell for electrochemical measurement consisted of the working electrode (metal hydride electrode), the counterelectrode ($\mathrm{NiOOH/Ni(OH)_2}$ electrode), and the reference electrode (Hg/HgO electrode). The Hg/HgO electrode was equipped with Luggin tube to reduce the IR drop during the 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 cutoff voltage for discharging was fixed at –600 mV with respect to the Hg/HgO electrode. Before polarization and electrochemical impedance spectroscopy measurements, the hydrogen storage hydride electrode was activated completely (10 cycles). The average particle size of hydride electrode was determined by scanning electron microscopy (SEM) after activation. In order to investigate high rate dischargeability, the discharge capacity at different discharge current density were measured.

3. Results and discussion

The kinetic properties of hydride electrodes can be characterized by the high rate dischargeability (HRD), which is defined as the ratio of the discharge capacity Q_i with cutoff voltage –0.6 V at the discharge current density Id to the maximum discharge capacity Q_max:

$$\mathrm{HRD} = (Q_\mathrm{i}/Q_\mathrm{max}) \times 100\% \qquad (1)$$

The effects of alloys powder treated by different concentration of KOH on the HRD are shown in Fig. 1. The HRD of the electrodes of the alloy powder treated by 3 M, 4 M, 5 M, and 6 M KOH is 3.1, 4.8, 5.7, and 6.1 times than that untreated, respectively. It can be seen that the HRD increases markedly with the increasing concentration of KOH when the concentration is lower than 5 M, but the increasing rate becomes much slower when the concentration of KOH is higher than 5 M.

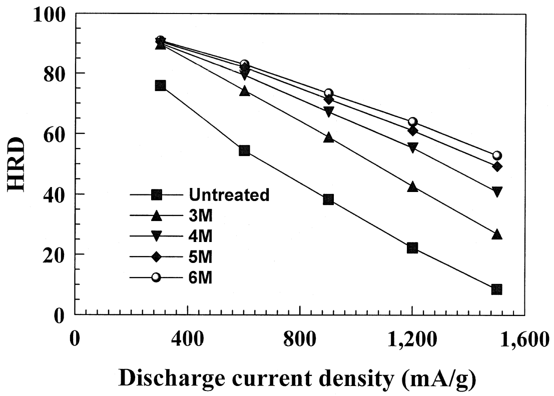

Fig. 1. Effect of the alloy powder treated by the y (y=3, 4, 5, 6) M KOH containing 0.02 M $\mathrm{KBH_4}$ solution on the high rate dischargeability HRD of $\mathrm{MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}}$ hydride electrode.

The hydrogen desorption process during discharge is composed of several partial steps in the alkaline solution [22,23]:

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.

$$\mathrm{MH_{abs}} \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} \mathrm{MH_{ads}} \qquad (2)$$

4. electrochemical oxidation of hydrogen, namely, occurring of electrochemical reaction at the electrode surfaces.

$$\mathrm{MH_{ads}} + \mathrm{OH^-} \underset{k_{-3}}{\overset{k_3}{\Leftrightarrow}} \mathrm{M} + \mathrm{H_2O} + \mathrm{e} \qquad (3)$$

Therefore, after activation, the HRD or the kinetic properties of hydride electrodes were mainly determined by the exchange current density I_0, diffusion coefficient of hydrogen in the α phase D_α or the limiting current density I_L.

Fig. 2 presents the linear polarization curves of the powder untreated, treated by 3 M, 4 M, 5 M, and 6 M KOH solution containing 0.02 M KBH4 under the following experimental conditions: the state of discharge (SOD) being 50% and the scanning rate 10 mV/s. It can be seen that the overpotential at the same discharge current density I_d becomes smaller with an increase in concentration of KOH.

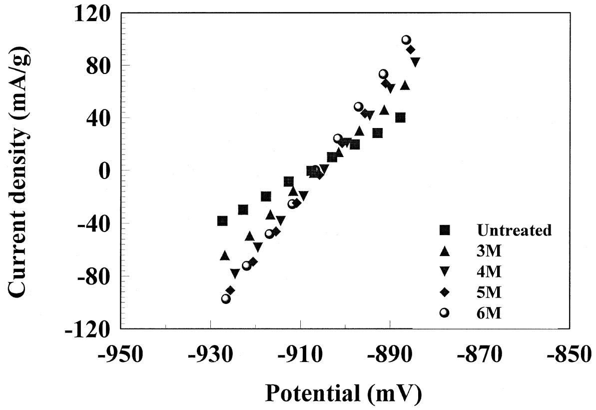

Fig. 2. Effect of the alloy powder treated by the y ($y=3$, 4, 5, 6) M KOH containing 0.02 M KBH_4 solution on the linear polarization of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydride electrode.

The exchange current density I_0 can be calculated according to the following expression [24]:

$$I_0 = \frac{I_d RT}{F\eta} \tag{4}$$

where R is gas constant, T is absolute temperature, F is Faraday constant, and η is total overpotential.

The calculated exchange current density I_0 is listed in Table 1. It can be seen that, similar to the effect of the concentration on the high rate dischargeability, the exchange current density I_0 increases markedly with the increase of the concentration of KOH. The I_0 increases from 58.4 mA/g to 130.6 mA/g with the concentration of KOH increase from 3 M to 6 M

During galvanostatic discharge, the apparent diffusion coefficient of hydrogen in α phase (including hydrogen diffusion through the oxidation film on the surface of particles) can be calculated [25]:

$$D_\alpha = \frac{r_0^2 I_d}{15(Q_0 - \tau I_d)} \tag{5}$$

Where Q_0, I_d, τ, and r_0 is 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.

Table 1
Effect of the alloy powder treated by the y ($y=3$, 4, 5, 6) M KOH containing 0.02 M KBH_4 solution on the exchange current density I_0, limiting current density I_L, and the apparent diffusion coefficient of hydrogen D_α of the electrode

	I_0 (mA/g)	I_L (mA/g)	D_α (cm^2/s)
untreated	50.0	1034.0	3.7×10^{-10}
3 M	58.4	1155.0	4.5×10^{-10}
4 M	77.4	1341.7	4.8×10^{-10}
5 M	110.0	1492.3	5.4×10^{-10}
6 M	130.6	1595.5	5.8×10^{-10}

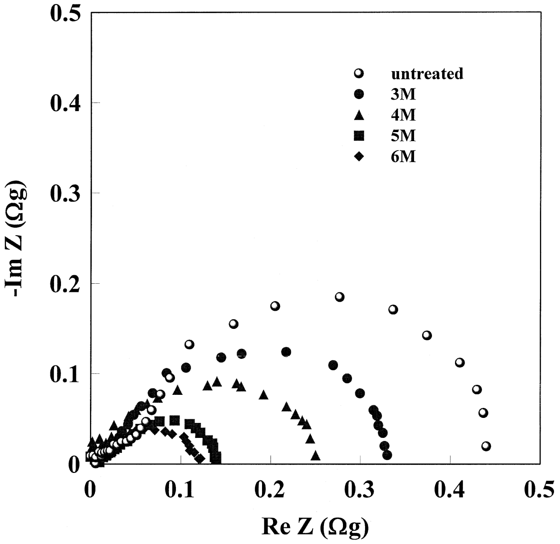

Fig. 3. Effect of the alloy powder treated by the y ($y=3$, 4, 5, 6) M KOH containing 0.02 M KBH_4 solution on the electrochemical impedance spectra of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydride electrode.

According to our SEM results, this kind of surface treatment almost makes effect of the particle size of electrodes not noticeable anymore. The effect of the concentration of KOH on the apparent diffusion coefficient D_α is also listed in Table 1. It can be seen that the D_α also increases with the increase of the concentration of KOH. It is apparent that the surface treatment does not affect the real diffusion coefficient of hydrogen in α phase D'_α, but it changes the structure and depth of oxide film and its ability of absorption and desorption of hydrogen, which leads to a higher apparent diffusion coefficient of hydrogen in the α phase. The influence of treatment on the D_α was also confirmed by electrochemical impedance spectroscopy. Fig. 3 presents the corresponding results. The semicircle corresponding to the low frequency in the electrochemical impedance spectra is attributed to the hydrogen diffusion in the α phase according to Wang's mathematical model [26]. The radius of this semicircle decreases with increasing concentration of KOH means that the apparent diffusion coefficient of hydrogen in α phase D_α increases with the increase in KOH concentration. It should be noted that the effect of surface treatment on the exchange current density I_0 is larger than that on the D_α.

The effects of surface treatment on the anodic and cathodic polarization are shown in Figs. 4 and 5, respectively. It is apparent that the anodic and cathodic overpotential decrease rapidly with the increasing concentration of KOH. The anodic limiting current densities I_L obtained from Fig. 4 are also shown in Table 1. The anodic limiting current density is improved by surface treatment and it increases with the increase of concentration of KOH.

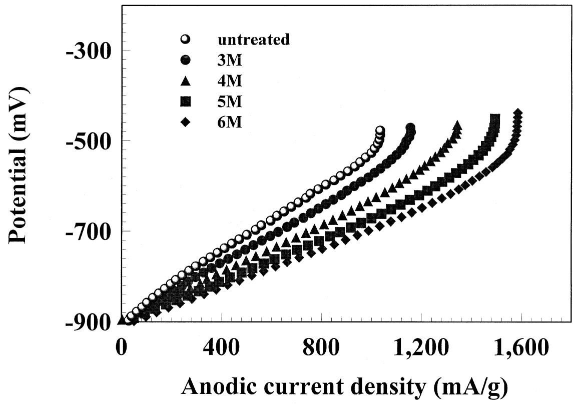

Fig. 4. Effect of the alloy powder treated by the y ($y=3$, 4, 5, 6) M KOH containing 0.02 M KBH_4 solution on the anodic polarization.

4. Conclusions

The influence of the concentration of KOH solution containing 0.02 M KBH_4 on the kinetic properties of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydrogen storage alloy electrode has been studied. The results show that high current dischargeability, the exchange current density i_0, and limiting current density I_L all increase, and, the anodic and cathodic polarization decrease with the increase in concentration of KOH. The size of the semicircle of electrochemical impedance spectroscopy decreases also with the increase in concentration of KOH, which implies that the diffusion coefficient of hydrogen increases. In the range of the experimentation, it can be concluded that the higher the concentration of KOH, the better the electrochemical properties of $MlNi_{3.7}Co_{0.6}Mn_{0.4}Al_{0.3}$ hydrogen storage alloys are.

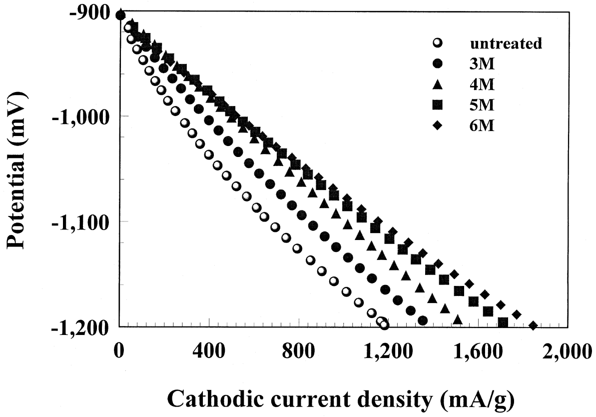

Fig. 5. Effect of the alloy powder treated by the y ($y=3$, 4, 5, 6) M KOH containing 0.02 M KBH_4 solution on the cathodic polarization.

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