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Studies on the electrochemical properties of $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride alloy electrodes

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Abstract

In this paper, the electrochemical properties of $MlNi_{4.3-x}Co_xAl_{0.7}$ electrode alloys, including high rate dischargeability, exchange current density I_0, limiting current density I_L, and diffusion coefficient of hydrogen in the hydride D_α by means of linear polarization, anodic polarization, and electrochemical impedance spectroscopy were systematically studied. The results indicate that, with the increase of Co content, the cyclic stability is improved markedly, which agrees with previous investigation. However, activation becomes more difficult, and the high rate dischargeability decreases. The linear polarization and anodic polarization results suggest that the exchange current density I_0 and limiting current density I_L decrease from the 395 ($x=0$) to 33 mA g^{-1} ($x=1.3$) and from 2263 ($x=0$) to 308 mA g^{-1}, respectively. The electrochemical impedance spectroscopy result also reveals that the diffusion coefficient of hydrogen in the alloys decreases rapidly with the increase in Co content in $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride alloy electrodes.

Keywords: Electrochemical properties; AB_5 type alloy; Hydrogen storage alloy electrode

1. Introduction

Nickel–metal hydride (Ni–MH) batteries have been extensively investigated and produced because of their high energy density, high charge and discharge rate ability, long cycle life, no dendrite formation, and environmental compatibility [1–3].

Two classes of metal hydride alloys currently being developed are AB_5 type intermetalic compounds, where A represents rare earth elements and B includes any of late transition or p-shell elements [4,5], and AB_2 type Laves phases, where A and B both denote early transition elements [6]. Although the AB_2 alloys are reported to exhibit higher specific energy than that of AB_5 alloys, state-of-the-art commercial Ni–MH batteries are predominately use AB_5 alloys because of their better overall electrochemical properties.

Although $LaNi_5$ alloys has a high absorption and desorption hydrogen capacity, easy electrochemical activation and good charge and discharge kinetics [7], the storage capacity of this alloy declines rapidly during charge and discharge cyclings because the La on its surface is oxidized to $La(OH)_3$ easily. A breakthrough was made by Willems and Buschow [4] who found that partial substitution of Ni by Co was very effective to enhance the cycle life of $LaNi_5$ alloy. Since then, many scientists have investigated the influence of Co on the cycle life of $LaNi_5$ based alloys [8–15]. Up to now, cobalt has been thought to be indispensable for AB_5 type battery electrodes. However, the effect of Co on the electrochemical properties rather than cycle life and activation has not been systematically investigated.

2. Experimental

Hydrogen storage alloys of nominal composition $MlNi_{4.3-x}Co_xAl_{0.7}$ ($x=0.0$, 0.5. 0.7, 0.9, 1.1, 1.3) were prepared by arc melting under an argon atmosphere. The Ml stands for lanthanum-rich misch metal which composed of 80 wt% La, 10 wt% Ce, 6 wt% Pr, and 5 wt% Nd. The purity of the other metals is above 99.7%. Ingots were turned over and remelted five times for homogeneity during melting. The ingots were mechanically pulverized and ground into fined powders with an average size of 40 μm for to be used as electrode materials.

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The metal hydride electrode was made by first mixing thoroughly 0.5 g of alloy powder with 0.2 g of carbonyl nickel powder, then 3% PVA solution was added to the mixture as binder. The mixture was cold pressed onto an Ni mesh under pressure of 20 MPa. The apparent surface area of the electrode was 1.5×1.5 cm^2 with a thickness of ≈1.5 mm. The electrode for the cyclic lifetime study was sandwiched with two Ni meshes to prevent stripping of the alloys [16].

The cell for electrochemical measurement consisted of a working electrode (metal hydride), a counterelectrode ($NiOOH/Ni(OH)_2$ electrode), and a reference electrode (Hg/HgO). The Hg/HgO electrode was equipped with Luggin tube to reduce the IR drop in the polarization and electrochemical impedance spectroscopy measurements. The electrolyte was 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. For activation and cyclic lifetime investigation, the electrode was charged and discharged at 50 mA. For polarization and electrochemical impedance spectroscopy measurements, the hydrogen storage alloy electrode was first activated completely (20 cycle) and then was charged and discharged to the 50% SOD. The average particle size of hydride electrode after activation was determined by scanning electron microscopy (SEM).

In this paper, the stability of hydrogen storage alloy electrode after 250 cycle number [$S_{(250)}$] has been expressed in terms of the capacity ratio as follows:

$$S_{(250)} = \frac{C_{t(250)}}{C_{t(0)}} \times 100\% \quad (1)$$

3. Results and discussion

3.1. Effect of Co content on the thermodynamic properties

Fig. 1 shows the activation characteristics of $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes. The capacity of $MlNi_{4.3}Al_{0.7}$ hydride electrode decreases linearly with the cycle number. This can be attributed to the unstability of $MlNi_{4.3}Al_{0.7}$ hydride electrode in KOH solution and formatting to $La(OH)_3$ and nickel. The corrosion-resistance of the electrode increases rapidly with the Co content x increase from 0.0 to 0.5 in the $MlNi_{4.3-x}Co_xAl_{0.7}$ alloy electrodes, and the activation becomes rather difficult with the further increase of Co content.

The maximum capacities of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes are listed in Table 1. It should be emphasized that the maximum capacities of the $MlNi_{4.3}Al_{0.7}$ and $MlNi_{4.0}Co_{0.3}Al_{0.7}$ hydride electrodes are the maximum capacities after corrosion. Their real capacities should be higher than those listed in Table 1. As can be seen from Table 1 the capacity of the hydride electrode decreases with the increasing Co content in the alloys, but this decrease is not very large.

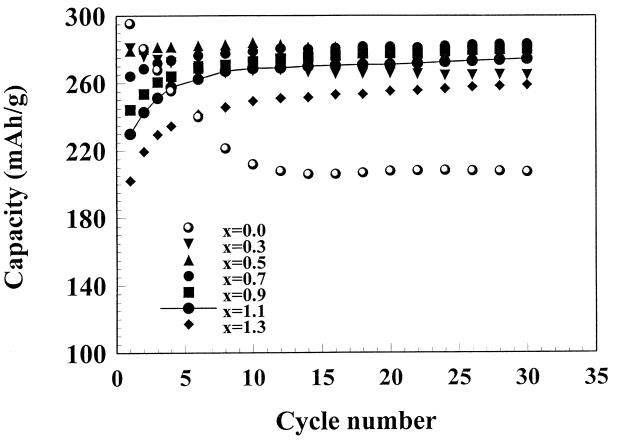

Fig. 1. Activation characteristics of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

The effect of Co content in the $MlNi_{4.3-x}Co_xAl_{0.7}$ alloys on the cycle life of $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes are shown in Fig. 2. The corresponding parameter $S_{(250)}$ are also listed in Table 1. The cycle life of hydride increases rapidly with the Co content from 0.0 to 0.7, but the improvement of cycle life becomes much less markedly with further increase of Co content.

3.2. Effect of Co content on the kinetic properties

One main parameter for the practical application of hydride electrodes is the rate capacity, i.e. the amount of charge which can be recovered during galvanostatic discharge. The high rate dischargeability (HRD) is 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}.

$$HRD = (Q_i/Q_{max}) \times 100\% \quad (2)$$

The high rate dischargeability is shown in Fig. 3. The HRD decreases with the increase of the Co content in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes, especially for high discharge current density. Furthermore, the effect of Co content on the HRD when the values of x is between 0.0 and 0.7 is smaller than that when the values of x is large than 0.7. In a word, the higher the content of Co content in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes, the lower the HRD.

After activation, the HRD or the kinetic properties of hydride electrodes were mainly determined by the exchange current density I_0, the diffusion coefficient of hydrogen in the α phase D_α or the limiting current density I_L [16].

Table 1
The capacity Q_{max}, cyclic stability $S_{(250)}$, exchange current density I_0, limiting current density I_L, symmetry β, and the apparent diffusion coefficient of hydrogen D_α in the α phase in $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes

Values of x in $MlNi_{4.3-x}Co_xAl_{0.7}$	Q_{max} (mA h g^{-1})	$S_{(250)}$	I_0 (mA g^{-1})	I_L (mA g^{-1})	β	D_α (cm^2 s^{-1})
0.0	295	6.4	395	2263	0.85	1.4×10^{-9}
0.3	301	14.8	233	1295	0.74	9.8×10^{-10}
0.5	292	44.9	147	1053	0.67	8.1×10^{-10}
0.7	285	63.6	91	805	0.64	5.4×10^{-10}
0.9	280	76.0	75	477	0.61	4.1×10^{-10}
1.1	271	85.3	45	390	0.57	3.2×10^{-10}
1.3	260	86.5	33	308	0.43	2.1×10^{-10}

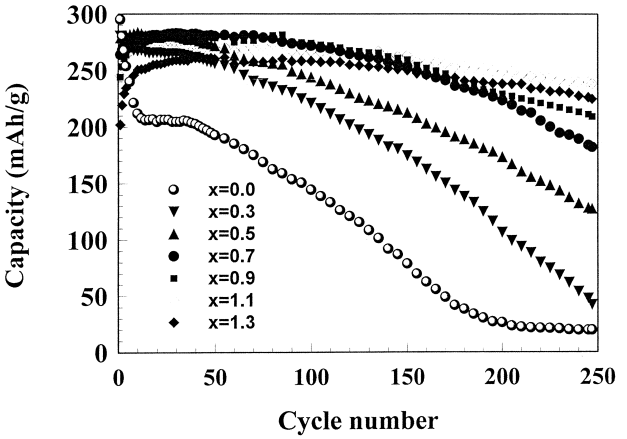

Fig. 2. Cycle life of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

In order to determine the exchange current density I_0 and the polarization resistance, the linear polarization experiment was conducted at 50% SOD and scanning rate of 5 mV s^{-1}. The results are presented in Fig. 4, which reveals that the polarization increases with the increase in Co content in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes. The exchange current density I_0 can be calculated according to the following formula [17]:

$$I_0 = \frac{I_d RT}{F\eta} \tag{3}$$

where F, R, and T are the Faraday constant, the gas constant, and absolute temperature, respectively, and η is the total polarization at the discharge current density I_d.

The exchange current density I_0 calculated by Eq. (3) are listed in Table 1. The exchange current density I_0 decreases from 395 mA g^{-1} for $x=0.0$ to 33 mA g^{-1} for $x=1.3$, respectively. This means that, with the increase in Co content x, the I_0 decreases seriously.

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 by the equation followed [18]:

$$D_\alpha = \frac{r_0^2 I_d}{15(Q_0 - \tau I_d)} \tag{4}$$

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.

The calculated values of D_α according to Eq. (4) are also presented in Table 1. Fig. 5 shows the relationship of D_α with the Co content. It can be seen that the apparent

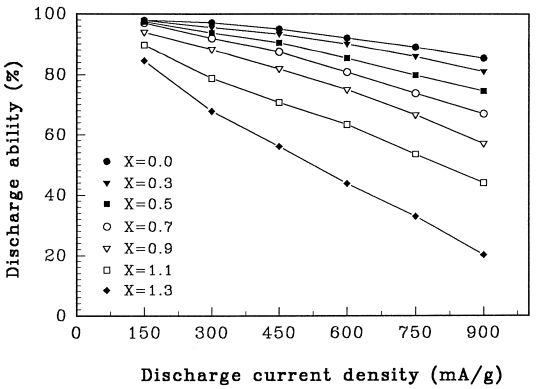

Fig. 3. High rate dischargeability HRD of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

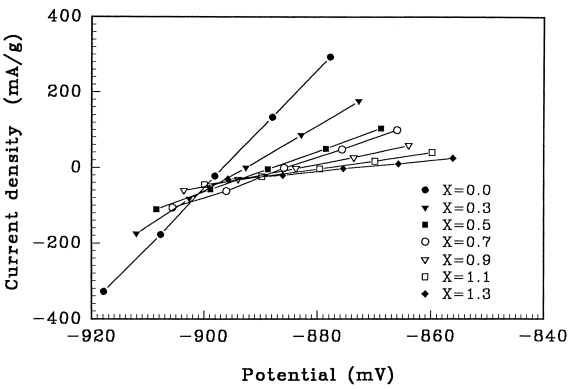

Fig. 4. Linear polarization curves of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

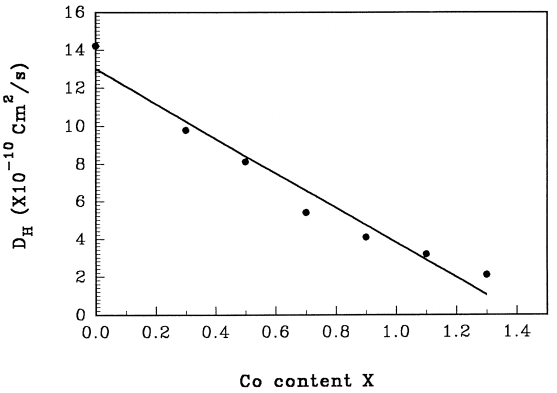

Fig. 5. Relationship between D_α and Co content in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

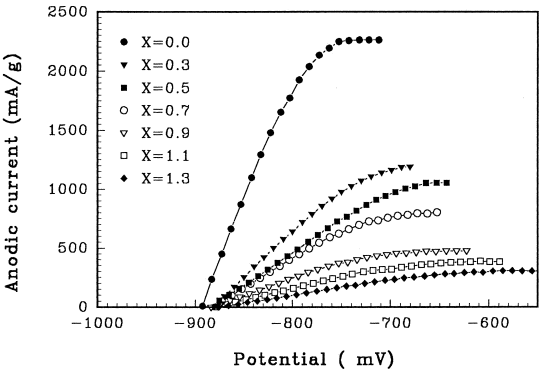

Fig. 7. Anodic polarization of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

diffusion coefficient of hydrogen in the α phase D_α is almost inversely proportional to the Co content in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes. The apparent diffusion coefficient of hydrogen in α phase D_α decreases with the increase in Co content. For example, the D_α at $x=0.0$ is nine times higher than that at $x=1.3$. This result also can be confirmed by the results of electrochemical impedance spectra. Fig. 6 shows the electrochemical impedance spectra of in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes at $x=0.3$, 0.7, 0.9, 1.1, and 1.3. According to Wang's mathematical model [19], the low frequency semicircle in the electrochemical impedance spectra is attributed to the hydrogen diffusion in the α phase. The radius of this semicircle increases with increasing Co content means that the apparent diffusion coefficient of hydrogen in α phase D_α decreases with the increase of Co content x in $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

Fig. 7 shows that the anodic current density in response to the overpotential of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes at 50% SOD. The total overpotential at same discharge current density increases with increasing Co content x. The corresponding limiting current density I_L at different values of x is listed in Table 1. The limiting current density I_L decreases dramatically with the increase in x, i.e. the limiting current density I_L at $x=0.0$ is about eight times higher compared with that at $x=1.3$ in the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes.

The overpotential of anodic polarization can be expressed as [20]:

$$\eta = \frac{RT}{\beta F}\ln\left(\frac{I_L}{I_0}\right) + \frac{RT}{\beta F}\ln\left(\frac{I_d}{I_L - I_d}\right) \quad (5)$$

According to Eq. (5), a plot of η vs. $\ln(I_d/I_L - I_d)$ should be a straight line with $RT/\beta F$ as its slope. Therefore, symmetry factor in the oxidation direction 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 factor in the oxidation direction β decreases with increasing Co content x.

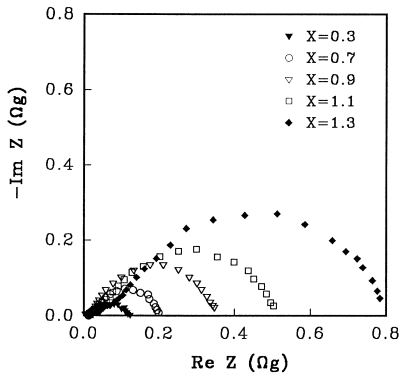

Fig. 6. Electrochemical impedance spectra of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes at $x=0.3$, 0.7, 0.9, 1.1, and 1.3.

4. Conclusions

In this paper, the effect of Co content on the thermodynamic and kinetic properties of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes have been systematically studied. The results show that, with an increase of Co content, the cyclic stability is improved markedly, the activation becomes more difficult, and the high rate dischargeability decreases. The linear polarization and anodic polarization results indicate that the exchange current density I_0 and limiting current density I_L decrease from the 395 ($x=0$) to 33 mA g^{-1} ($x=1.3$) and from 2263 ($x=0$) to 308 mA g^{-1} in the $MlNi_{4.3-x}Co_xAl_{0.7}$ electrode alloys, respectively. The electrochemical impedance spectroscopy result also reveals that the diffusion coefficient of hydrogen in the alloys is much lower than that for $x=0$ in the alloy.

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