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Effects of Ca-substitution and surface treatment on electrochemical performances of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy electrodes①

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Abstract: The influences of Ca-substitution for Ml and surface treatment on electrochemical performances of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy electrode were investigated. Ca-substitution with $x < 0.2$ for Ml could improve its discharge capacity, but Ca-substitution with $x > 0.2$ could decrease the capacity. It was also found that Ca-substitution deteriorates the electrocatalytic activity, high-rate dischargeability and cycling durability of the alloy electrode. In order to improve these properties of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloy electrode, the alloy was treated in 6 mol/L KOH + 0.02 mol/L KBH_4 solution. The results showed that the surface treatment improves the electrochemical performances such as the electrocatalytic activity, high-rate dischargeability and cycling durability of the alloy electrode.

Key words: hydrogen storage alloy; electrode; Ca-substitution; surface modification
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1 INTRODUCTION

Nickel-metal hydride (Ni/MH) batteries have attracted much attention because they have higher energy density and environmental advantage compared with Ni/Cd batteries. Many multicomponent AB_5-type hydrogen storage alloys have been developed to improve performances of Ni/MH batteries[1~4]. The $CaNi_5$-type alloy shows a high specific discharge capacity for battery[5]. The theoretical capacity of $CaNi_5$ can reach up to 482 mAh/g which is much higher than 372 mAh/g for $LaNi_5$. But the cycling durability of $CaNi_5$ alloy as a rechargeable electrode material is very poor because that Ca oxide is very easily formed on the surface of the alloy particles and converts to Ca hydroxide in aqueous solution. Owing to the poor protective effect of $Ca(OH)_2$ layer and the disproportionation of the alloy itself during charge-discharge cycling, the discharge capacity rapidly decreases. Li and Suda[6] found that the element substitution and fluorination could greatly improve the cycling durability of $CaNi_5$-type alloy electrode. But the fluorination decreased the discharge capacity because the fluoride formed on the surface was an insulator. Our previous researches[7,8] indicated that surface modification of $Ml(NiMnCoAl)_5$ alloy in alkaline solution have considerably improved its electrochemical performances.

In this paper, the influence of Ca-substitution on electrochemical performances of $Ml_{1-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy electrode was investigated. In order to improve their cycling durability, the alloys were treated in 6 mol/L KOH + 0.02 mol/L KBH_4 solution. The effect of surface treatment on the electrochemical performances of the alloy electrode was also discussed.

2 EXPERIMENTAL

The hydrogen storage alloys $Ml_{1.0-x}Ca_x$-

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$Ni_{4.0}Co_{0.6}Al_{0.4}$ (Ml = La-rich mischmetal, 64.6% La, 5.9% Ce, 26.6% Pr, 2.2% Nd, 0.7% others) were prepared by an inducing furnace under argon atmosphere. The purifies of the constituent metals are Ca 99.5%, Ni 99.9%, Co 99.5% and Al 99.6%. The ingots alloys were crushed mechanically to particles (50 ~ 74 μm). The plateau pressure of the alloy was measured at different temperatures by electrochemical method[9]. Both the enthalpy change (ΔH) and entropy change (ΔS) of the hydride formation were calculated from the plateau pressures (p) of alloys at different temperatures by following Van't Hoff Eqn.1

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{1}$$

Metal hydride (MH) electrodes were prepared by cold pressing the mixtures of 0.100 g hydrogen storage alloy powders with 0.200 g copper powders ($\leqslant 42$ μm) at 20 MPa to form pellets of 10 mm in diameter. Electrochemical measurements were carried out in open glass cell at room temperature, employing 6 mol/L KOH solution as electrolyte, a sintered nickel hydroxide electrode with electrochemical capacity much larger than that of MH electrode as counter electrode and an Hg/HgO electrode as a reference electrode. MH electrode was charged for 4 h and discharged to - 0.6 V vs Hg/HgO after a rest of 5 min at a constant current density of 100 mAh/g. The polarization resistance (R_p) and exchange current density (J_0) were measured by the linear sweep voltammetry at a scan rate of 1 mV/s nearly equilibrium potential ($\varphi_e \pm 10$ mV) (Solartron 1286 electrochemical interface). Before every measurement, MH electrode was adjusted to 50% depth of discharge. The polarization resistance (R_p) and exchange current density (J_0) were calculated by Eqn.2. The apparent activation energy (E_a) of the MH electrode reaction was calculated from J_0 at different temperatures using Eqn.3.

$$R_p = \frac{J}{\eta} = \frac{nFJ_0}{RT} \tag{2}$$

$$J_0 = A\exp\frac{-E_a}{RT} \tag{3}$$

In order to test the high-rate dischargeability of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloy electrode, MH electrode discharged at different current densities after charging at 100 mA/g for 4 h. The high-rate dischargeability was described by the ratio of the discharge capacity measured at different current densities to that at 100 mAh/g.

3 RESULTS AND DISCUSSION

3.1 Thermodynamic properties of hydrogen storage alloy

The Van't Hoff plots for the alloys are illustrated in Fig.1. At first, it can be seen from Fig.1 and Table 1 that the replacement of Ml by Ca (x = 0.1 ~ 0.3) causes the plateau pressure to increase slightly at same temperature. Wang *et al*[10] have found that the cell volume of the $Ml_{1.0-x}Ca_xNi_5$ decreased linearly with increasing Ca content. So, it can be believed that the

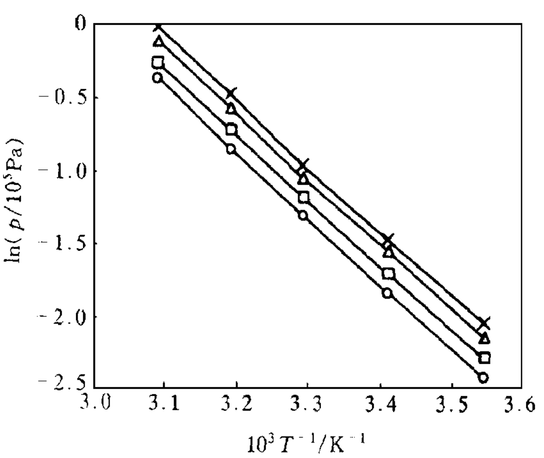

Fig.1 Van't Hoff plots of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloys

○ — $MlNi_{4.0}Co_{0.6}Al_{0.4}$;

□ — $Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$;

△ — $Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$;

× — $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$

Table 1 Thermodynamic properties of hydrogen storage alloy

Hydrogen storage alloy	ΔH/ (kJ·mol^{-1})	ΔS/ (J·mol^{-1}·K^{-1})	p/kPa (30 ℃)
$MlNi_{4.0}Co_{0.6}Al_{0.4}$	- 37.77	113.71	27.2
$Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$	- 37.28	113.12	30.8
$Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$	- 37.42	114.80	35.2
$Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$	- 37.60	116.18	38.4

increase in plateau pressure is caused by the cell volume of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ decreases with increasing Ca content. In general, the larger the cell volume of the hydrogen storage alloy, the stabler the metal hydride, and the more negative enthalpy change (ΔH) of hydride formation. But Table 1 shows there is no an obvious change in ΔH with increasing Ca content. It is likely to be caused by two kinds of contrary effects of Ca-substitution on ΔH . On one hand with increasing Ca content the decrease of the cell volume of the alloy causes a positive variation of ΔH, on the other hand, the increase of Ca content causes a negative variation of ΔH because Ca with hydrogen forms stable metal hydride. Both of the contrary influences are partly cancelled out each other.

3.2 Activation, discharge capacity of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloy electrode

The activation properties and discharge capacities of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloys electrodes are listed in Table 2. The first discharge capacity (C_0) decreased with increasing Ca content, because the Ca oxide or $Ca(OH)_2$ on the alloy surface affects the activation property of MH electrode[6]. A small amount of Ca-substitution can improve the discharge capacity, and the maximum capacity of $Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$ alloy reaches up to 329 mAh/g. However, when Ca-substitutes are excessive, the discharge capacity tends to decrease. Table 2 also shows that the surface treatment of the alloys can improve activation properties of MH electrodes. The surface treatment increases the first discharge capacity and decreases activation number.

The effects of Ca-substitution and surface treatment on the polarization resistance of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloys electrodes are shown in Fig.2. As shown in Fig.2, the polarization resistance increases gradually with increasing Ca content especially at first cycle. At first cycle, the polarization resistance of the untreated $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$ alloy electrode is 10.3 Ω, while that of untreated $MlNi_{4.0}Co_{0.6}Al_{0.4}$ alloy electrode is 7.8 Ω. This is attributed to that the Ca oxide or $Ca(OH)_2$ on the alloy surface causes the polarization overpotential to increase[6]. After surface treatment of the alloys, the polarization resistance of MH electrode decrease greatly. The polarization resistance of the treated $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$ and $MlNi_{4.0}Co_{0.6}Al_{0.4}$ alloys electrodes decrease to 4.7 Ω and 2.6 Ω, respectively. This was caused by that the oxide film on the alloy surface would be

Fig.2 Polarization resistance (R_p) as a function of cycle number

●, ○ —Untreated and treated $MlNi_{4.0}Co_{0.6}Al_{0.4}$;
■, □ —Untreated and treated $Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$;
▲, △ —Untreated and treated $Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$;
+, × —Untreated and treated $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$

Table 2 Effects of Ca-substitution and surface treatment on activation properties and discharge capacity of $Ml_{1.0-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ alloy electrodes

Alloys	C_0/(mAh·g^{-1})(at 1st)		C_{max}/(mAh·g^{-1})		Activation number	
	untreated	treated	untreated	treated	untreated	treated
$MlNi_{4.0}Co_{0.6}Al_{0.4}$	261	290	307	310	3	2
$Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$	230	274	325	329	5	3
$Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$	225	270	319	321	6	4
$Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$	195	254	292	294	6	4

reduced or eliminated by surface treatment and a Ni-rich surface layer with high electrochemical activity was produced by preferential dissolution of Al or Ca[7,8].

3.3 High-rate dischargeability and exchange current densities of alloys electrodes

The high-rate dischargeabilities of the alloy electrodes can be described by the ratio of discharge capacity measured at different current densities to the capacity of 100 mAh/g. The test results of high-rate dischargeabilities are listed in Table 3 and Fig.3. It can be seen from Table 3 and Fig.3 that Ca-substitution has deteriorated the high-rate dischargeability of the alloy electrode. At the discharge current density of 600 mAh/g, the high rate dischargeabilty of $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$ alloy has decreased from 75.5% of $MlNi_{4.0}Co_{0.6}Al_{0.4}$ to 51.0%. Table 3 and Fig.3 also show that the surface treatment improves considerably the high-rate dischargeabilities of the alloys electrodes. After the surface treating, the high rate dischargeability of $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$ has increased from 51.0% to 69.1%, and that of $MlNi_{4.0}Co_{0.6}Al_{0.4}$ has increased from 75.5% to 85.6%.

Table 3 High-rate dischargeability of electrodes(at 600 mAh/g)

Alloys	HRD/% (600 mAh/g)	
	untreated	treated
$MlNi_{4.0}Co_{0.6}Al_{0.4}$	75.5	85.6
$Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$	71.6	81.8
$Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$	62.6	78.7
$Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$	51.0	69.1

Fig.3 High-rate dischargeabilities of alloys electrodes

●, ○ — Untreated and treated $MlNi_{4.0}Co_{0.6}Al_{0.4}$;
■, □ — Untreated and treated $Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$;
▲, △ — Untreated and treated $Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$;
+, × — Untreated and treated $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$

The influences of Ca-substitution and the surface treatment on the electrocatalytic activity of MH electrodes are listed in Table 4. The electrocatalytic activity is usually described by the exchange current density (J_0) and activation energy (E_a) of the electrode reaction. It can be seen from Table 4 that the exchange current density of the alloy electrode reaction decreased, while the activation energy increases with increasing Ca content. The facts indicate that the Ca-substitution deteriorates the electrocatalytic activity of MH electrode.

MH electrode reaction includes:

(1) the electron transfer step on the electrode surface ($H_2O + M + e \underset{\text{discharge}}{\overset{\text{charge}}{\Leftrightarrow}} M\text{-}H_{ad} +$

Table 4 Exchange current density (J_0) and activation energy (E_a) of MH electrode reaction

Alloys	$J_0/(mA\cdot g^{-1})(20\ ^\circ C)$		$E_a/(kJ\cdot mol^{-1})$	
	untreated	treated	untreated	treated
$MlNi_{4.0}Co_{0.6}Al_{0.4}$	138.3	244.2	21.3	17.8
$Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$	129.3	191.3	24.1	22.1
$Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$	118.7	166.5	25.4	23.0
$Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$	103.6	143.1	27.5	25.2

OH^-)';

(2) the adsorption of the hydrogen on the surface;

(3) the hydrogen diffusion step ($M\text{-}H_{ad} \underset{\text{discharge}}{\overset{\text{charge}}{\Leftrightarrow}} M\text{-}H_{ab}$).

The electrochemical reaction of MH electrode must take place on its surface by the absorption of hydrogen atom. The adsorption of hydrogen on the surface is a middle step of the charging-discharging reaction. Therefore, the adsorption strength of hydrogen on the surface has an important influence on the rate and activation energy of electrode reaction. It is usually believed that the more poor or stronger adsorption of hydrogen on the surface, the lower its electrocatalytic activity. When the adsorption bond strength of $M\text{-}H_{ad}$ is suitable, the electrode has higher electrocatalytic activity. The relationship between the electrocatalytic activity of the electrode and the adsorption bond energy of hydrogen on its surface is so called as "volcano effect". As the oxide layer or $Ca(OH)_2$ on the alloy surface suppresses the adsorption of hydrogen on the surface, the electrocatalytic activity of MH electrode decreases with increasing Ca content.

The oxide layer including Ca oxide on the alloy surface would be reduced or eliminated by the surface modification, while a Ni-rich surface layer is produced by preferential dissolution of Al or Ca. Ni-rich layer exits in form of Ni-cluster or Raney-Ni, enhances adsorbability of hydrogen on the surface and has higher electrochemical activity. In addition, our previous research[4] found that the surface treatment enlarged the specific surface area of the alloy. It is also benefit to the adsorption of hydrogen on the electrode surface. It can be seen from Table 4 that the exchange current density of the treated alloy increases and its activation energy decreases, compared with the original untreated alloy. The facts confirm that the surface treatment can improve the electrocatalytic activity of the MH electrode reaction.

3.4 Cycling durability of alloy electrode

The variations of discharge capacities of the alloy electrodes with cycle number are shown in Fig.4. It can be seen from Fig.4 that the rate of the capacity deterioration increase with increasing Ca content. The cycling durability of the alloy electrode can be evaluated by the ratio of its discharge capacity at 300th cycle to the maximum capacity. The higher the ratio, the better the cycling durability. As listed in Table 5, the cycling durability of the alloy electrode decreases with increasing Ca content. For example, the discharge capacity of the $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$ alloy at 300th cycle has decreased to 144 mAh/g, only 47.9% of its maximum. This is likely to be caused by the poor protective effect and increase of $Ca(OH)_2$ layer during cycling. It also can be seen from Table 5 that the surface treatment improves the cycling durability of the alloy electrodes to different degree. This is due

Table 5 Cycling durability of alloy electrode

Alloys	C_{300th}/(mAh·g^{-1})		(C_{300th}/C_{max})/%	
	untreated	treated	untreated	treated
$MlNi_{4.0}Co_{0.6}Al_{0.4}$	239	254	77.8	82.1
$Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$	213	248	65.3	75.5
$Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$	168	233	52.7	72.5
$Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$	140	201	47.9	68.3

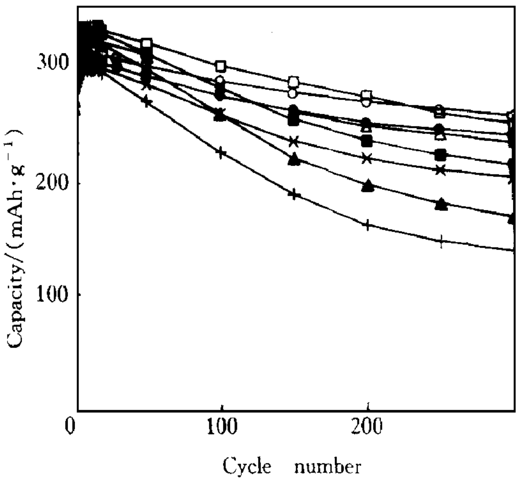

Fig.4 Discharge capacity of alloy electrode as a function of cycle number

●, ○ —Untreated and treated $MlNi_{4.0}Co_{0.6}Al_{0.4}$;

■, □ —Untreated and treated $Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}Al_{0.4}$;

▲, △ —Untreated and treated $Ml_{0.8}Ca_{0.2}Ni_{4.0}Co_{0.6}Al_{0.4}$;

+, × —Untreated and treated $Ml_{0.7}Ca_{0.3}Ni_{4.0}Co_{0.6}Al_{0.4}$

to a rich-nickel layer on the treated alloy surface has a certain protective effect on the alloy electrode in electrolyte.

4 CONCLUSIONS

(1) The replacement of Ml by a small amount of Ca ($x = 0.1$) can improve the discharge capacity of the alloy electrode, but Ca-substitution with excessive content ($x > 0.2$) will trend to deteriorate it. $Ml_{0.9}Ca_{0.1}Ni_{4.0}Co_{0.6}$-$Al_{0.4}$ has the maximum discharge capacity of 329 mAh/g compared with other alloys.

(2) Ca-substitution for Ml will deteriorate the electrocatalytic activity, high-rate dischargeability and cycling durability of the alloy electrode because of the effect of $Ca(OH)_2$ on its surface.

(3) The surface modification can improve electrochemical performance of the alloy electrode to different degrees. The changes of the treated alloy surface enhance the adsorption of hydrogen on the surface.

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