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Structure and electrochemical properties of La-Mg-Ni system hydrogen storage alloys with different Co contents^①

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Abstract: The structure and electrochemical properties of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 - 1.05$) hydrogen storage alloys were investigated. The crystal structure and the lattice parameters of the alloys were analyzed by X-ray diffractometry and Rietveld method. Electrochemical properties of the alloys including $p - c - t$ curves, discharge capacity, discharge capacity retention were studied. The results show that (La, Mg)Ni₃ and LaNi₅ are the main phases of all the alloys. The plateau pressure for hydrogen absorption/desorption decreases and the hydrogen storage capacity firstly increases and subsequently decreases with increasing Co content. The values of the maximum discharge capacity of the alloy electrodes remain in range of 395.3 - 403.1 mA · h/g in spite of the change of Co content. The cycling stability of the alloy electrodes is greatly improved with increasing Co content, which is attributed to the suppression of the cell volume expansion during hydriding, leading the pulverization of the alloy particles lowered and the oxidation/corrosion of the active elements reduced.

Key words: La-Mg-Ni alloy; Ni/MH batteries; structure; hydrogen storage alloys; $p - c - t$ curve; electrochemical properties

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1 INTRODUCTION

To increase the discharge capacity of nickel/metal-hydride (Ni/MH) batteries, new types of hydrogen storage alloys with higher energy density have been paid considerable attention by researchers. Particularly, recent investigations on the R-Mg-Ni (R = rare earth or Ca element) system hydrogen storage alloys have led to a new series of ternary alloys with a high hydrogen storage capacity^[1-3]. Kohno et al^[4] found that the maximum discharge capacity of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ alloy electrode could reach 410 mA · h/g during the researches of the La_2MgNi_9 , $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ and $\text{La}_3\text{MgNi}_{14}$ alloy systems. Moreover, Liu et al^[5-8] also revealed that suitable heat treatment and partial substitution of Mn for Ni could improve the overall properties of the La-Mg-Ni-Co type electrode alloys, and the discharge capacity of 380 - 410 mA · h/g was reached. However, the cycling stability of this kind of alloys is still poor for commercial applications^[8-11], further investigations on the improvement of the cycling durability of the La-Mg-Ni-Co hydrogen storage alloys are highly necessary. It is known that the appearance of Co can effectively improve the cycling stability of the rare earth-based alloys due to the decrease of the pulverization of the alloy particles and the corrosion

of the alloy electrodes in alkaline solution^[12-15].

In this paper, at the aim of improving the cyclic lifetime, Co was selected to partially substitute Ni and the structure, hydrogen storage and electrochemical properties of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0, 0.3, 0.6, 0.75, 0.9, 1.05$) hydrogen storage alloys have been investigated systematically.

2 EXPERIMENTAL

$\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 - 1.05$) alloys were prepared by induction levitation melting in a water-cooled copper crucible under argon atmosphere. The purity of the metal components is higher than 99.5% (mass fraction). The ingots were turned over and remelted twice for homogeneity. Then the ingots were crushed and mechanically milled into powder of size of 30 - 80 μm for pressure-composition isotherm ($p - c - t$) and electrochemical measurements and X-ray diffraction (XRD) analyses of the crystal structure.

The X-ray data were obtained with an ARL X-ray diffractometer using Cu K_α radiation. Pressure-composition isotherms ($p - c - t$) for hydrogen absorption/desorption were measured by the Sieverts' method using an automatic Sieverts-type apparatus at 303 K.

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The alloy electrodes were prepared by mixing 0.1 g alloy powders with 0.4 g carbonyl nickel powder and then the mixture was cold pressed into a pellet up to pressure of 16 MPa. Electrochemical studies were carried out in a half-cell consisting of a working electrode (the MH electrode for studying), a sintered $\text{Ni(OH)}_2/\text{NiOOH}$ counter electrode and a Hg/HgO reference electrode. The electrolyte was 6 mol/L KOH solution. Each electrode was charged at 100 mA/g for 5 h followed by a 10 min rest and then discharged at 60 mA/g to the cut-off potential of -0.6 V (vs Hg/HgO).

3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 \sim 1.05$) hydrogen storage alloys. Fig. 2 shows the example of XRD patterns and Rietveld analysis patterns of the alloy with $x = 0.75$. It can be seen from Fig. 1 that $(\text{La, Mg})\text{Ni}_3$ and LaNi_5 are the main phases of all of the alloys, additionally, minor phase of LaNi was also detected.

Table 1 lists the lattice parameters and cell volumes of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 \sim$

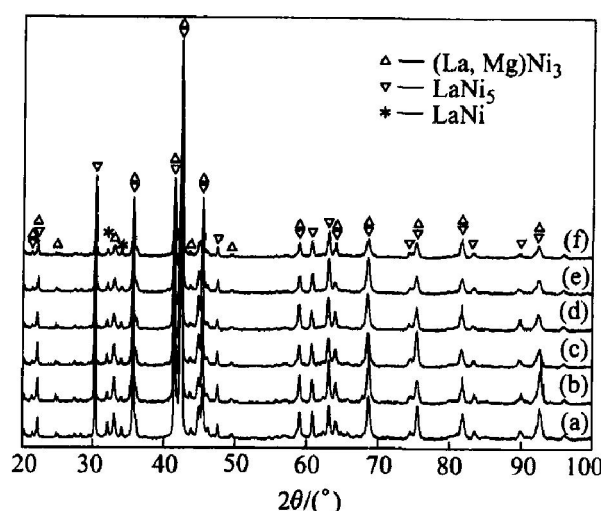


Fig. 1 XRD patterns of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 \sim 1.05$) hydrogen storage alloys
(a) $x = 0$; (b) $x = 0.30$; (c) $x = 0.60$;
(d) $x = 0.75$; (e) $x = 0.90$; (f) $x = 1.05$

1.05) alloys, which was calculated from the data of Fig. 1 by using Rietveld method. Data in Table 1 show that parameters of a and c of both $(\text{La, Mg})\text{Ni}_3$ phase and LaNi_5 phase increase with

Table 1 Characteristics of alloy phases in $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 \sim 1.05$) hydrogen storage alloys

x	Phase	a/nm	b/nm	c/nm	Cell volume/ nm^3
0	$(\text{La, Mg})\text{Ni}_3$	0.503 9		2.423 2	0.533 07
	LaNi_5	0.503 5		0.399 7	0.087 78
	LaNi	0.383 8	1.074 4	0.445 8	0.183 89
0.30	$(\text{La, Mg})\text{Ni}_3$	0.504 3		2.424 9	0.534 12
	LaNi_5	0.503 6		0.399 8	0.087 79
	LaNi	0.383 6	1.074 1	0.445 7	0.183 67
0.60	$(\text{La, Mg})\text{Ni}_3$	0.505 1		2.426 0	0.536 04
	LaNi_5	0.503 9		0.400 1	0.088 01
	LaNi	0.383 7	1.074 0	0.445 7	0.183 65
0.75	$(\text{La, Mg})\text{Ni}_3$	0.505 2		2.426 2	0.536 98
	LaNi_5	0.504 4		0.400 2	0.088 22
	LaNi	0.383 7	1.074 0	0.445 7	0.183 65
0.90	$(\text{La, Mg})\text{Ni}_3$	0.506 0		2.427 0	0.538 30
	LaNi_5	0.504 8		0.400 5	0.088 40
	LaNi	0.383 9	1.074 7	0.446 0	0.184 06
1.05	$(\text{La, Mg})\text{Ni}_3$	0.506 1		2.428 0	0.538 75
	LaNi_5	0.504 9		0.400 6	0.088 44
	LaNi	0.383 9	1.076 1	0.445 7	0.184 13

Rietveld refinement program RIETICA is used.

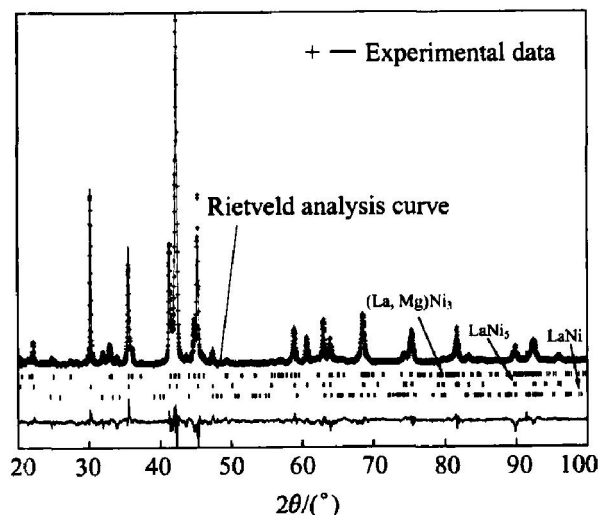


Fig. 2 XRD patterns and Rietveld analysis patterns of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ alloy with $x = 0.75$

increasing Co content, leading a subsequent expansion of the cell volumes, which was caused by the larger atomic radius of Co (0.167 nm) compared with Ni (0.162 nm).

Fig. 3 shows the pressure-composition isotherms (p - c - t) of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 - 1.05$) at 303 K. With increasing value of x from 0 to 1.05, the equilibrium pressure for hydrogen absorption/desorption of these alloys decreases gradually, which can be attributed to that the cell volumes are enlarged after the partial substitution of Co for Ni. In addition, the maximum hydrogen storage capacity of the alloys firstly increases from 1.44% ($x = 0$) to 1.55% ($x = 0.75$) and then decreases to 1.48% ($x = 1.05$), which is related to the change of the content of the (La, Mg)Ni₃ phase and the LaNi₅ phase in the alloys and the decrease of the plateau pressure for hydrogen absorption/desorption.

Fig. 4 shows the curves of discharge capacity vs cycle times of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 - 1.05$) alloy electrodes at 303 K. It can be seen that the maximum discharge capacities almost remain stable when the Co content increases from $x = 0$ to $x = 1.05$, just increase a little from 397.5 ($x = 0$) to 403.1 mA · h/g ($x = 0.75$) then decrease to 395.3 mA · h/g ($x = 1.05$). This is in good agreement with the result obtained from the p - c - t measurements and is also attributed to the reducing of the plateau pressure of hydrogen absorption/desorption and the different content of (La, Mg)Ni₃ phase and LaNi₅ phase. Fig. 4 further reveals that all of the alloy electrodes can be easily activated to their maximum discharge capacity within two cycles. Moreover, the cycling stability is greatly improved during the cycling.

Fig. 5 displays the discharge capacity retention

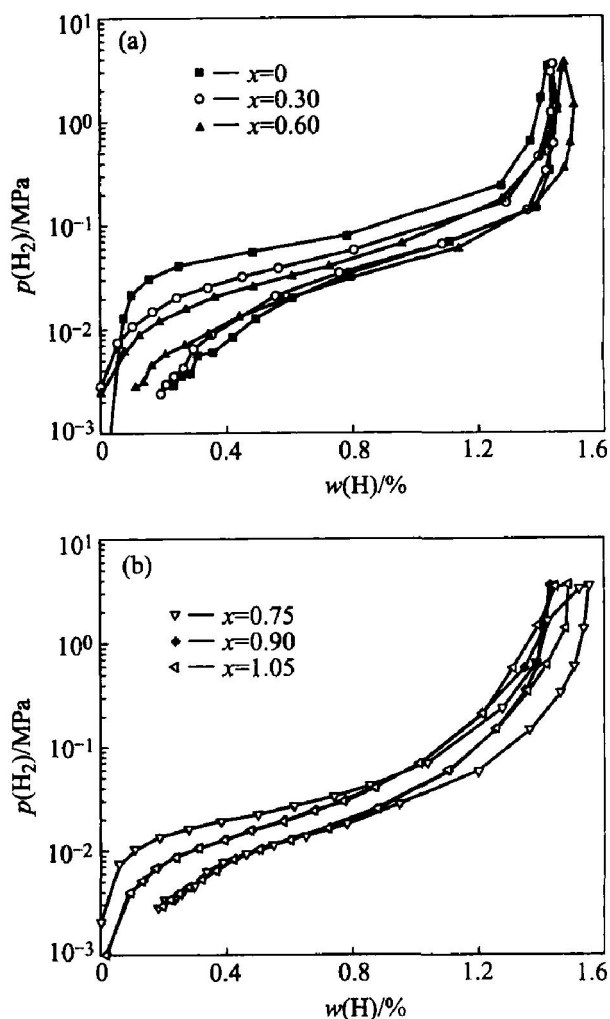


Fig. 3 p - c - t isotherms curves of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 - 1.05$) hydrogen storage alloys at 303 K

of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 - 1.05$) alloy electrodes after 90 charge/discharge cycles. The discharge capacity retention of the alloy electrodes increases obviously from 25.5% to 47.9% with Co content increasing from $x = 0$ to $x = 1.05$. This is mainly attributed to the lowering of the cell volume expansion ($\Delta V/V$) and a reducing of the oxidation/corrosion of the active elements in the alloys^[12-15].

Fig. 6 shows the XRD patterns of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0, 0.6, 0.75, 0.9$) alloys after be fully charged. It can be seen that the hydride phases of the (La, Mg)Ni₃ and LaNi₅ remain the original PuNi₃-type structure and CaCu₅-type structure, respectively. Moreover, the diffraction peaks of hydride phases shift toward larger angles with increasing Co content, indicating that the cell volume expansion caused by hydrogenation reduces.

Table 2 lists the lattice parameters and unit cell volumes of the (La, Mg)Ni₃ phase and LaNi₅ phase after charging, which was calculated from the data of Fig. 6 by using Rietveld method. It is

Table 2 Characteristics of hydride phases in $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$
($x = 0 \sim 1.05$) hydrogen storage alloys

x	Hydride phases	a/nm	b/nm	Cell volume/ nm^3	$\Delta V/\text{nm}^3$	$\Delta V/V$
0	(La, Mg)Ni ₃ -H	0.539 4	2.571 4	0.648 117	0.115 047	0.215 8
	LaNi ₅ -H	0.538 9	0.426 9	0.107 409	0.019 629	0.223 6
0.60	(La, Mg)Ni ₃ -H	0.536 9	2.564 6	0.640 267	0.104 227	0.194 4
	LaNi ₅ -H	0.538 6	0.422 1	0.106 079	0.018 069	0.205 3
0.75	(La, Mg)Ni ₃ -H	0.536 1	2.560 8	0.637 610	0.100 630	0.187 3
	LaNi ₅ -H	0.538 2	0.419 8	0.105 339	0.017 119	0.194 0
0.90	(La, Mg)Ni ₃ -H	0.535 9	2.547 9	0.633 942	0.095 642	0.177 7
	LaNi ₅ -H	0.537 4	0.415 4	0.103 914	0.015 514	0.175 4

Rietveld refinement program RIETICA is used.

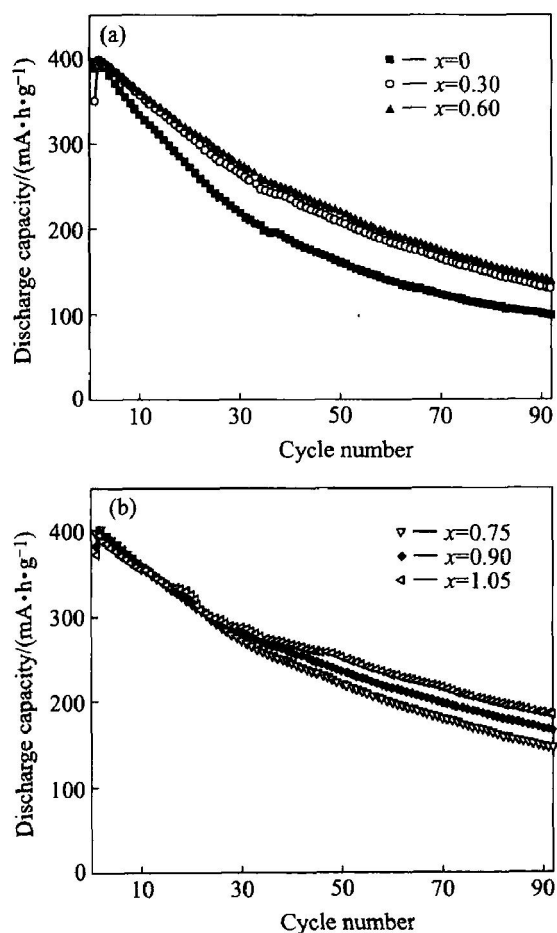


Fig. 4 Discharge capacity vs cycle numbers of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 \sim 1.05$) alloy electrodes at 303 K

obvious that the volume expansion ratio ($\Delta V/V$) of the (La, Mg)Ni₃-H phase decreases from 21.58% to 17.76% when the Co content increasing from $x = 0$ to $x = 0.9$, and that of the LaNi₅-H phase decreases from 22.36% to 17.54%. This reveals that the alloy electrodes undergo a smaller cell volume expansion and contraction in each charge/discharge cycle with increasing Co content, and lower pulverization of the alloy particles. Thus, the oxidation/corrosion of the active elements in the alloys is reduced. The improvement of the cycling dura-

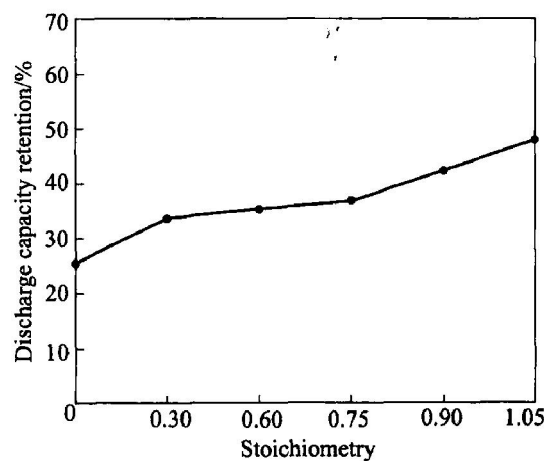


Fig. 5 Discharge capacity retention of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}$ ($x = 0 \sim 1.05$) alloy electrode after 90 charge/discharge cycles

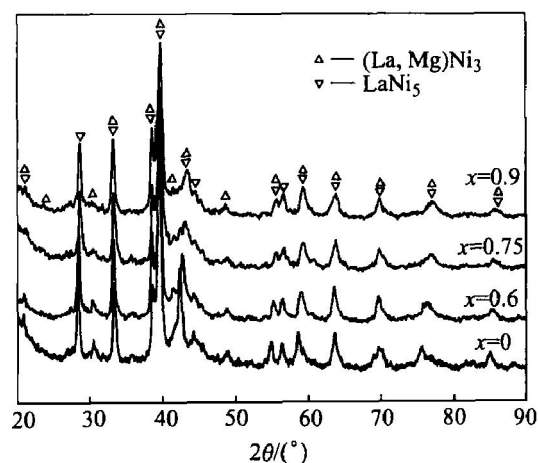


Fig. 6 XRD patterns of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Co}_x$ ($x = 0, 0.60, 0.75, 0.90$) hydrides

bility of the alloy electrodes with increasing Co content can also be obviously seen from Fig. 4.

4 CONCLUSIONS

(La, Mg)Ni₃ and LaNi₅ phase are the main phases of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.4-x}\text{Mn}_{0.1}\text{Co}_x$ ($x = 0 \sim 1.05$)

hydrogen storage alloys, additionally, small amount of the LaNi phase was also existed. The lattice parameters and cell volumes of the (La, Mg)-Ni₃ phase and the LaNi₅ phase all increase with increasing Co content. The equilibrium pressure for hydrogen decreases gradually with increasing Co content. The maximum electrochemical discharge capacity is almost in the same value, being of about 400 mA · h/g when the Co content varies from $x = 0$ to $x = 1.05$. But the cyclic stability of the alloy electrodes was significantly improved with increasing Co content, which was attributed to the suppression of the cell volume expansion during hydriding, leading the pulverization of the alloy particles lowered and thus the oxidation/corrosion of the active elements reduced.

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