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Influence of the substitution Ce for La on structural and electrochemical characteristics of $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ (x=0, 0.05, 0.1, 0.15, 0.2 at. %) hydrogen storage alloys

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ABSTRACT

Structural and electrochemical performances of $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ (x = 0, 0.05, 0.1, 0.15, 0.2 at.%) alloys prepared by an induction melting under helium atmosphere followed by annealing treatment at 1173 K in a vacuum furnace for 8 h are studied. Rietveld refinement results from the XRD data suggest that the alloys are mainly composed of (La, Mg)Ni_3, (La, Mg)$_2Ni_7$ and $LaNi_5$ phases. Increasing the content of Ce, the amounts of (La, Mg)Ni_3 phase and (La, Mg)$_2Ni_7$ phase decrease, while the amount of $LaNi_5$ phase increases. Electrochemical performance measurement results show that the $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ alloys are completely activated within 2 cycles, and the cyclic stability after 100 charge/discharge cycles of the alloys increases from 62.39% to 84.94% with the rising of Ce content, and the discharge capacity of the 100th cycle reaches the maximum value of 259 mAh/g when Ce content is 0.1 at.%. Meanwhile, the high rate discharge ability of the alloy electrodes increases to the maximum value when Ce content is 0.1 at.%, and then decreases. Thus, the $La_{0.65}Ce_{0.1}Mg_{0.25}Ni_3Co_{0.5}$ alloy exhibits optimum comprehensive electrochemical properties.

1. Introduction

As a clean energy, hydrogen energy has attracted more and more attention [1], among which the growing environmental pollution concerns from vehicle exhaust have brought in an increasing need for green energy automobiles such as hybrid electric vehicle (HEV), etc. In other words, developing high efficient, low-cost, long-life, and durable advanced rechargeable batteries has become one great challenge to achieve the change from petroleum-powered vehicles to green energy automobiles [2,3]. During the last decades, the Ni-MH batteries have been establishing a large market share owing to their high energy density, long cycle life and environmentally friendly characteristics, and its basic cell reaction is stated as follow [4].

$$M + xNi(OH)_2 \underset{discharge}{\overset{charge}{\Leftrightarrow}} MH_x + xNiOOH$$

Nowadays, La-Mg-Ni-based A_2B_7-type hydrogen storage alloys have been considered as promising candidates for negative electrode materials of Ni-MH rechargeable batteries [5–8], but the poor cycling stability of this type of alloys hinders its practical application [9,10].

It has been one of the challenges faced by researchers in this area to continuously improve the comprehensive properties of A_2B_7-type hydrogen storage alloys through different methods [11,12], including elemental substitution, rapid quenching, and composite alloying, etc. and the elemental substitution has been thought as one of the effective methods to improve the cycle life of La-Mg-Ni system hydrogen storage alloys [13–17], and many scholars have done a lot of valuable researches during recent years [18–21]. Adzic et al. [22,23] pointed out that the replacement of La by Ce might give the La-Mg-Ni system alloy a satisfactory cycle lifetime due to the significant corrosion decreasing caused by addition of Ce. Cheng et al. [24] revealed that the $La_{0.76-x}Ce_xMg_{0.24}Ni_{3.15}Co_{0.245}Al_{0.105}$ (x = 0–0.4 at. %) alloy exhibits excellent cyclic stability (S_{35} = 350/366.67 = 95.45%), and the HRD_{3000} reaches 58.11%. Zhang et al. [25] reported that the S_{70} and HRD_{1200} of $La_{0.7-x}Ce_xMg_{0.3}Ni_{2.8}Co_{0.5}$ (x = 0–0.5 at. %) alloy could reach 87.3% and 67.5%, respectively. Pan et al. [26] found that the $La_{0.7-x}Ce_xMg_{0.3}Ni_{2.875}Mn_{0.1}Co_{0.525}$ (x = 0–0.5 at%) alloy possesses

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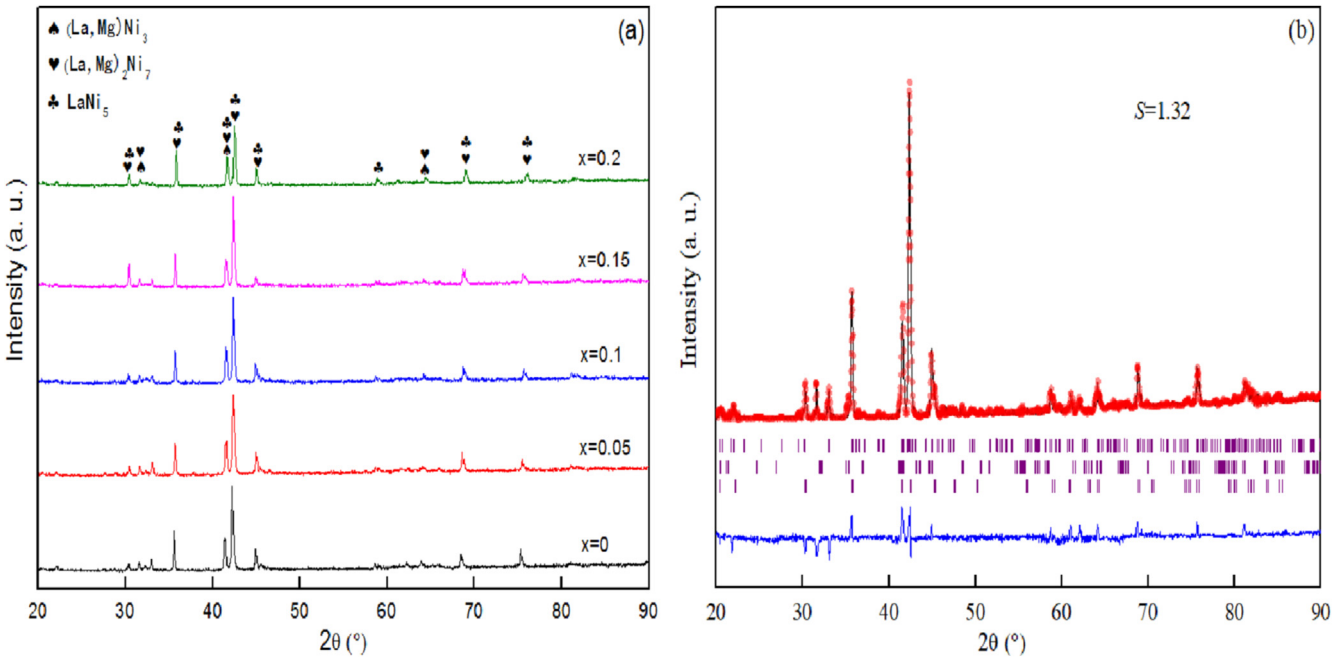

Fig. 1. XRD patterns (a) of $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ alloys and Rietveld analysis pattern (b) of the $La_{0.65}Ce_{0.1}Mg_{0.25}Ni_3Co_{0.5}$ alloy. Bottom labels for the Rietveld analysis pattern correspond to $(La, Mg)_2Ni_7$: $P6_3/mmc$, (La, Mg)Ni_3: R-3m, and $LaNi_5$: $P6/mmm$, (top to bottom, respectively).

Table 1
Summary of refinement data of $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ alloys.

Alloys	Phase type	Space group	Phase abundance/(wt.%)	Lattice constant			Unit-cell volume/Å^3
				a/Å	c/Å	c/a	
x = 0	(La, Mg)Ni_3	R-3m	3.09%	5.096	25.709	5.045	578.131
	$(La, Mg)_2Ni_7$	$P6_3/mmc$	91.18%	5.049	24.245	4.802	535.256
	$LaNi_5$	$P6/mmm$	5.73%	5.051	4.010	0.794	88.603
x = 0.05	(La, Mg)Ni_3	R-3m	2.48%	5.082	25.697	5.056	574.818
	$(La, Mg)_2Ni_7$	$P6_3/mmc$	85.85%	5.037	24.220	4.809	532.134
	$LaNi_5$	$P6/mmm$	11.67%	5.039	4.001	0.794	87.999
x = 0.1	(La, Mg)Ni_3	R-3m	2.09%	5.072	25.670	5.061	571.860
	$(La, Mg)_2Ni_7$	$P6_3/mmc$	81.26%	5.028	24.207	4.815	529.900
	$LaNi_5$	$P6/mmm$	16.65%	5.032	3.997	0.794	87.663
x = 0.15	(La, Mg)Ni_3	R-3m	1.58%	5.067	25.654	5.063	570.307
	$(La, Mg)_2Ni_7$	$P6_3/mmc$	73.94%	5.013	24.190	4.826	526.392
	$LaNi_5$	$P6/mmm$	24.48%	5.023	3.990	0.794	87.181
x = 0.2	(La, Mg)Ni_3	R-3m	1.03%	5.051	25.599	5.068	565.677
	$(La, Mg)_2Ni_7$	$P6_3/mmc$	65.52%	5.009	24.179	4.827	525.320
	$LaNi_5$	$P6/mmm$	33.45%	5.014	3.982	0.794	86.714

good electrochemical properties (S_{80} = 75/94.8 = 79.1%, HRD_{1250} = 56%). Liu et al. [27] revealed that the S_{90} of the $La_{0.8-x}Ce_xMg_{0.2}Ni_{2.8}Co_{0.6}$ (x = 0–0.3 at. %) alloy reaches 77% when x = 0.1. Luo et al. [28] reported that the $(LaCeMg)(NiCoAlZn)_{3.5}$ alloy exhibits good cyclic stability (S_{100} = 253.37/285 = 88.9%), and the HRD_{900} reaches 65.32%. Zou et al. [29] also found that the S_{100} and HRD_{900} of $La_{0.6}Ce_{0.2}Mg_{0.2}(NiCoAlMn)_{3.3}$ alloy nearly reach 90% and 66%, respectively, but the capacity reduces nearly to 250 mAh/g when S_{100} reaches the maximum value. Lin et al. [30] revealed that the S_{100} of $La_{0.65}Ce_{0.1}Mg_{0.25}Ni_{3.5}Si_{0.15}$ could reach 74.17%, and the HRD of the alloy is also excellent (HRD_{300} = 91.90%, HRD_{600} = 87.77%, HRD_{900} = 85.43%, HRD_{1200} = 82.70%). Shen et al. [31] also found that the S_{100} of $La_{0.8-x}Ce_xMg_{0.2}Ni_{3.5}$ (x = 0–0.2) alloy reaches 73.33%.

As above-mentioned, the studies in the electrochemical properties of the A_2B_7 type alloys doped by Ce are still not sufficient, and the range of doping amount of Ce is also a bit broad to a certain degree, hence more detailed researches are still needed to be carried out. In the present work, the annealed Ce-added $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ alloys are prepared, and a systematic study about Ce content on structural and electrochemical properties of the alloy is carried out.

2. Experimental

2.1. Sample preparation

Ingots of $La_{0.75-x}Ce_xMg_{0.25}Ni_3Co_{0.5}$ (x = 0, 0.05, 0.1, 0.15, 0.2 at.%) alloys were prepared by induction melting according to the nominal compositions under 0.3 MPa helium atmosphere, purity of all the component metals is at least 99.99 wt%. 10 wt% of extra Mg were added to compensate for the elemental loss during melting process. Afterwards, the samples were annealed at 1173 K in a vacuum furnace for 8 h, and then crushed and grinded into