

Influence of magnesium content on structure and electrochemical properties of $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ hydrogen storage alloys

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Abstract: $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ ($x=0.07, 0.08, 0.10, 0.13, 0.15$) alloys were prepared by high-frequency inductive method, and then their structure and electrochemical properties were investigated systematically. The XRD analysis revealed that the alloys consisted of LaNi_5 phase and $\text{La}_4\text{MgNi}_{19}$ ($\text{Ce}_5\text{Co}_{19} + \text{Pr}_5\text{Co}_{19}$) phase, and the introduction of Mg could promote the formation of $\text{La}_4\text{MgNi}_{19}$ phase. The observation of microstructure showed that all the alloys processed dendritic structure, which was refined with the increase of x value. The electrochemical measurements showed that all the alloys could be activated within 2 cycles, and with increasing x , the maximum discharge capacity obviously increased from 254.00 mAh/g ($x=0.07$) to 351.51 mAh/g ($x=0.15$), but the cycling stability (S_{80}) decreased somehow from 78.4% to 73.9%. Meanwhile, the appropriate addition of Mg could improve the high-rate discharge capacity (HRD) of the alloy electrodes, which was mainly controlled by the electrochemical reaction rate on the surface of the alloys.

Keywords: A_5B_{19} -type; hydrogen storage alloy; phase structure; electrochemical properties; rare earths

With the rapid development of industry and the increasing attention on the environment, the demand for the higher performance and greenness of batteries has grown a lot. The nickel/hydride (Ni/MH) batteries have many advantages, such as environmental friendliness, high energy density and better cyclic stability^[1,2], and have been widely applied in portable electronic devices, electric vehicles and so on. As the negative electrode materials for the Ni/MH secondary batteries, the hydrogen storage alloys are the key factor affecting the properties of the batteries^[3,4]. Now, the commercial hydrogen storage alloy is mischmetal-based AB_5 -type alloy, which has no potential to increase its maximum discharge capacity and can hardly meet the demand for new-type batteries^[5].

The R-Mg-Ni system alloys have been considered as one of the most promising negative electrode materials for the Ni/MH storage battery since RMg_2Ni_9 ($\text{R}=\text{La, Ce, Pr, Ca, Y}$) alloys were found to absorb-desorb 1.7 wt.%–1.8 wt.% H_2 ^[6]. Ternary La-Mg-Ni alloys are mainly composed of PuNi_3 -type phase, Ce_2Ni_7 -type phase or $\text{Pr}_5\text{Co}_{19}$ -type phase. The types of the phase are determined by n [LaNi_5] units and m [LaMgNi_4] units which alternatively stack along c -axis in certain ratios. Compared with other types of alloys, the A_5B_{19} -type ($\text{Ce}_5\text{Co}_{19} + \text{Pr}_5\text{Co}_{19}$, space groups are $R\bar{3}m$ and $P6_3/mmc$ respectively) alloys possess preferable maximum discharge capacity and better high-rate discharge property^[7–9]. How-

ever, the cycle life of the A_5B_{19} -type alloys needs to be further improved.

In the past decades, a lot of methods to improve the properties of the A_5B_{19} -type hydrogen storage alloys have been studied, such as the element substitution, element addition^[10–12], heat treatment^[13,14] and surface modification^[15]. Mg element is the key factor which influences the properties of the hydrogen storage alloys. The relevant researches revealed that the appropriate addition of Mg can improve the maximum discharge capacity, the structural stability and the thermodynamic property of AB_3 -type and $\text{AB}_{3.5}$ -type alloys^[16–18]. However, Mg element is volatile and uncontrollable during melting. To make the control of the composition of alloys more accurate and stable, La-Mg, Mg-Ni and La-Ni intermediate alloys were used instead of Mg and La. The intermediate alloys could reduce burnt loss of Mg element and accelerate the melting rate of alloys. Meanwhile, the intermediate alloys were beneficial to the accurate addition of Mg element, which could make the alloys consistent with the composition designed. In the previous work, our group found that the addition of Co could improve the electrochemical performance of A_5B_{19} -type alloy electrodes and increase the abundance of A_5B_{19} -type phase^[19]. Thus, the high-Co low-Ni A_5B_{19} -type $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ ($x=0.07, 0.08, 0.10, 0.13, 0.15$) alloys were studied to find the appropriate ratio of Mg to Ni.

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1 Experimental

The $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ alloys ($x=0.07-0.15$) were melted by vacuum levitation (under argon atmosphere) and the purity of the materials was above 99 wt.%. The alloys need to be turned over and remelted three times to ensure its high homogeneity. La-Mg, Mg-Ni and La-Ni intermediate alloys were used instead of Mg and La to reduce the loss of Mg element and the oxidation of La. Meanwhile, a slight excess of La and Mg was added to the alloys to recover the burning loss of La and Mg during melting.

The alloys were mechanically crushed into the powder of 300 mesh size for XRD analysis and electrochemical tests. The crystal structure of the alloys was determined by XRD (Rigaku D/max 2500/PC diffractometer) with Cu K α radiation. The range of the angle was from 18° to 75° at a speed of 3 (°)/min. All the pellet electrodes ($\Phi 10$ mm $\times$ 1 mm) were made by mixing 0.4 g carbonyl Ni powder and 0.1 g alloy powder uniformly and then cold pressing the mixture at 25 MPa. Electrochemical properties were tested in a conventional tri-electrode cell by LAND battery testing system. The tri-electrode cell was first charged at 120 mA/g for 4 h and then discharged at 60 mA/g after 5 min rest to test the maximum discharge capacity (C_{max}) and the activation performance. The cyclic stability was evaluated by charging/discharging at 300 mA/g and the capacity retention S_d was defined as:

$$S_d (\%) = C_d / C_{\text{max}} \times 100\% \quad (1)$$

where S_d is the capacity retention at the d th cycles and C_d is the discharge capacity at the d th cycles.

The high rate dischargeability (HRD) was defined as:

$$\text{HRD}_d = C_d / (C_d + C_{60}) \times 100\% \quad (2)$$

where C_d is the discharge capacity at the current density of i ($i=600, 900$ mA/g).

The high-rate dischargeability was investigated by

examining the discharge capacity at various discharge current densities after being activated fully.

For further study of electrochemical abilities of the electrodes, the linear polarization was plotted by scanning the electrode potential at a rate of 0.1 mV/s from -5 to 5 mV (versus open circuit potential) at 50% depth of discharge (DOD). And the diffusion coefficient of hydrogen was evaluated by the potentiostatic discharge via discharging the electrodes at the constant potential-step of 600 mV for 3000 s after being fully charged.

2 Results and discussion

2.1 Phase structure

Fig. 1 shows the XRD patterns of $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ alloy. According to the analysis by Jade 6.5, it can be found that all the alloys have multiphase structure, which includes LaNi_5 phase (CaCu $_5$ crystal structure, space group: $P6/mmm$) and A_5B_{19} phase ($\text{Ce}_5\text{Co}_{19} + \text{Pr}_5\text{Co}_{19}$ crystal structure, space group: $R-3m$ and $P6_3/mmc$).

The result of Rietveld whole pattern fitting is listed in Table 1. It revealed that the phase abundance of A_5B_{19} -

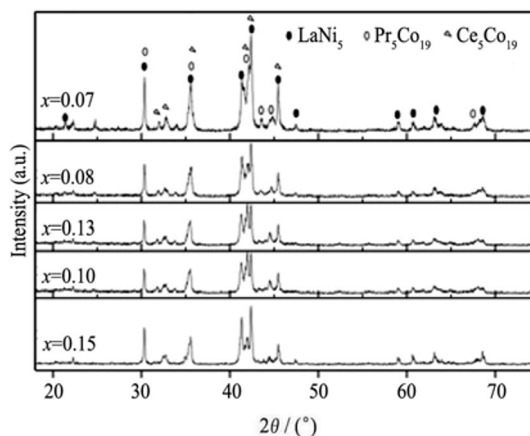


Fig. 1 XRD patterns of $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ alloy

Table 1 Phase structure and cell parameters of $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{1.75}\text{Co}_{2.05}$ alloy electrode

Samples	Phase	Space group	Phase abundance/ wt. %	Lattice constants/nm		Cell volume $V/10^{-3} \text{ nm}^3$
				a	c	
$x=0.07$	LaNi_5	$P6/mmm$ (191)	68.30	5.041	3.984	87.56
	$\text{Ce}_5\text{Co}_{19}$	$R-3m$ (166)	26.91	5.085	49.310	1105.34
	$\text{Pr}_5\text{Co}_{19}$	$P6_3/mmc$ (194)	4.79	5.060	32.64	721.560
$x=0.08$	LaNi_5	$P6/mmm$ (191)	51.85	5.042	3.985	87.72
	$\text{Ce}_5\text{Co}_{19}$	$R-3m$ (166)	34.80	5.095	49.150	1105.11
	$\text{Pr}_5\text{Co}_{19}$	$P6_3/mmc$ (194)	13.34	5.027	32.728	716.19
$x=0.1$	LaNi_5	$P6/mmm$ (191)	48.71	5.038	3.986	87.63
	$\text{Ce}_5\text{Co}_{19}$	$R-3m$ (166)	34.75	5.062	48.856	1084.03
	$\text{Pr}_5\text{Co}_{19}$	$P6_3/mmc$ (194)	16.54	5.095	32.943	740.62
$x=0.13$	LaNi_5	$P6/mmm$ (191)	46.76	5.044	3.991	87.92
	$\text{Ce}_5\text{Co}_{19}$	$R-3m$ (166)	30.21	5.102	49.46	1114.97
	$\text{Pr}_5\text{Co}_{19}$	$P6_3/mmc$ (194)	23.02	5.061	32.623	723.74
$x=0.15$	LaNi_5	$P6/mmm$ (191)	42.70	5.042	3.989	87.81
	$\text{Ce}_5\text{Co}_{19}$	$R-3m$ (166)	28.49	5.095	48.677	1094.31
	$\text{Pr}_5\text{Co}_{19}$	$P6_3/mmc$ (194)	28.81	5.043	32.628	718.73

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