

Effects of Boron Addition on Structural and Electrochemical Properties of La-Mg-Ni-Co System Hydrogen Storage Electrode Alloys

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Abstract: The structural and electrochemical properties of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) hydrogen storage electrode alloys were investigated systematically. The results from XRD show that all of the alloys consist of a (La, Mg) Ni_3 phase and a LaNi_5 phase. With the increase of B content, the abundance of the (La, Mg) Ni_3 phase increases, accordingly that of the LaNi_5 phase decreases, and the cell volumes of the two phases decrease. Electrochemical studies indicate that B addition can effectively improve the high rate dischargeability (HRD) of the alloy electrode, and the optimal value of HRD_{1000} reaches 57.1% as x being 0.04. With the addition of small amount of B, the cycling stability and activation properties of the alloy electrodes keep almost unchanged, but the maximum discharge capacity (C_{max}) decreases. In addition, the electrochemical kinetics investigations including the linear polarization and anodic polarization were also performed in detail.

Key words: hydrogen storage alloys; La-Mg-Ni-based hydrides; structure; electrochemical properties

It is well known that hydrogen storage alloys have been used widely as the negative materials of the MH/Ni batteries because of their high reversible discharge capacity, long cycle life, good charge/discharge kinetics and excellent environment-friendly properties. Several types of hydrogen storage alloys have been studied extensively, including AB_5 type alloys^[1], AB_2 type alloys^[2], AB type alloys^[3], A_2B type alloys^[4] and V-based solid solution alloys^[5]. However, all of the alloys mentioned above have their inherent disadvantages, such as the low energy density of AB_5 type alloys, the difficult activation of AB_2 type alloys, and the poor cycling stability of A_2B type alloys and V-based solid solution alloys. Therefore, new type hydrogen storage alloys with the good overall electrochemical properties are urgently needed to be developed.

In last decade, Kadir et al^[6-8] reported that the RMg_2Ni_9 ($R=\text{La, Ce, Ca or Y}$) hydrogen storage alloys with a PuNi_3 type rhombohedral structure might be more promising materials for the electrode of the MH/Ni secondary batteries owing to their high hydrogen storage capacity^[9]. Among the alloys

with the PuNi_3 structure, the effective hydrogen storage capacity of the $\text{La}_{0.65}\text{Ca}_{0.35}\text{Mg}_{1.32}\text{Ca}_{0.68}\text{Ni}_9$ alloy could reach 1.87 wt%, which was much higher than that of the AB_5 type alloys. Pan et al^[10-12] indicated that the proper anneal, the variation of the stoichiometry and the element substitution could improve the overall electrochemical properties of La-Mg-Ni-Co type hydrogen storage electrode alloys. Whereas, due to the corrosion and dissolution of the hydrogen absorbing elements (La and Mg) in the KOH solution and the pulverization of the alloy particles during charge/discharge cycling, the cycling stability of this type of alloy electrodes is poor. Recently, some investigations show that the addition of B in AB_5 type alloys could obviously improve the cycling stability, the high rate dischargeability and the activation properties of the alloy electrodes, but the maximum discharge capacity decreased slightly^[13-15].

Based on these investigations, in order to further improve the overall electrochemical properties of the La-Mg-Ni-Co type alloy electrodes, the alloys $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$

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($x=0-0.08$) were designed by the addition of a small amount of B in the pristine alloy. The influence of the B addition on the structural and electrochemical properties of the above alloy electrodes was studied in detail.

1 Experimental

The $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0, 0.02, 0.04, 0.08$) alloys were prepared by induction levitation melting in argon atmosphere and remelted four times for homogeneity. The purities of all the constituent metal elements were higher than 99.9%. Then, the alloys were crushed mechanically and grounded into powders with $<50\ \mu\text{m}$ used for X-ray powder diffraction (XRD) and electrochemical measurements. The detailed XRD and electrochemical properties measurements were described in our previous paper^[10].

2 Results and discussion

2.1 Crystal structures

Fig. 1 shows the XRD patterns of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) hydrogen storage alloys. It can be seen from Fig. 1 that the main phases in all of the alloys are the (La, Mg)Ni₃ phase with a rhombohedral PuNi₃-type structure and LaNi₅ phase with a hexagonal CaCu₅-type structure. The relative phase abundance, the lattice parameters and the unit cell volumes of the two phases in the alloys determined by the Rietveld analyses are listed in Table 1. Obviously, the relative abundance of the LaNi₅ phase decreases gradually from 32.8 wt% to 26.7 wt%, accordingly that of the (La, Mg)Ni₃ phase increases from 67.2 wt% to 73.3 wt% with increasing of x from 0 to 0.08. In addition, the lattice parameters and unit cell volumes of the (La, Mg)Ni₃ phase and LaNi₅ phase decrease gradually with increasing of B content.

2.2 Electrochemical properties

Fig. 2 and Table 2 show the activation properties (N_a), maximum discharge capacity (C_{max}) and cycling stability (C_{60}/C_{max}) of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) alloy electrodes. It can be found that all the alloy electrodes are fully activated within two cycles and the C_{60}/C_{max} of the

alloy electrodes are around 73%-75%, which means that the addition of B has no obvious effect on their activation properties and the cycling stability. Whereas, the C_{max} of the alloy electrodes decreases from 368.1 mAh/g to 322.5 mAh/g with the increase of x value from 0 to 0.08. It is well accepted that the C_{max} can be related to the cell volumes of the main phases of the hydrogen storage electrode alloys^[16]. The alloy electrodes with larger cell volumes of the main phases have the higher C_{max} . Moreover, Lee et al^[15] reported that the interaction between B and H in the interstitial sites decreased the hydrogen storage properties of the TiFe based alloys. So the decrease of the C_{max} may be ascribed to the decrease of the cell volumes of the main phases and the interaction between B and H in the interstitial sites of the alloy electrodes.

Fig. 3 shows the high rate dischargeability (HRD) of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) alloy electrodes. The HRD can be calculated from the following equation:

$$\text{HRD} = \frac{C_d}{C_d + C_{60}} \times 100\% \quad (1)$$

where C_d is the discharge capacity with the cut-off potential of $-0.6\ \text{V}$ vs. Hg/HgO reference electrode at the discharge current density I_d , and C_{60} is the residual discharge capacity with cut-off potential of $-0.6\ \text{V}$ vs. Hg/HgO reference electrode

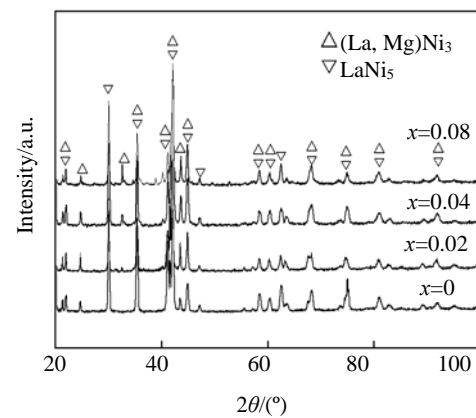


Fig.1 XRD patterns of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) alloys

Table 1 Characteristics of the phase structures in the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) alloys

Alloys	Phases	Phase abundance/wt%	Lattice parameter/ $\times 0.1\ \text{nm}$		Cell volume / $\times 0.001\ \text{nm}^3$
			a	c	
$x=0$	(La, Mg)Ni ₃	67.2	5.088	24.934	559.0
	LaNi ₅	32.8	5.067	4.038	89.8
$x=0.02$	(La, Mg)Ni ₃	68.8	5.085	24.934	558.4
	LaNi ₅	31.2	5.062	4.040	89.7
$x=0.04$	(La, Mg)Ni ₃	71.7	5.074	24.870	554.5
	LaNi ₅	28.3	5.060	4.037	89.5
$x=0.08$	(La, Mg)Ni ₃	73.3	5.070	24.861	553.4
	LaNi ₅	26.7	5.059	4.034	89.4

at the discharge current density I_{60} after the alloy electrode has been fully discharged at the large discharge current density under investigation. As can be seen from Fig. 3, the HRD of the alloy electrodes increases firstly and then decreases with increasing of x value from 0 to 0.08, and the optimal value of the HRD is obtained as x value being 0.04. For example, at a discharge current density of 1000 mA/g, the HRD_{1000} of the alloy electrodes firstly increases from 49.1% ($x=0$) to 57.1% ($x=0.04$) and then decreases to 52.5% ($x=0.08$). Ye et al [17] also reported that the proper addition of B in the $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ hydrogen storage electrode alloy could improve its electrochemical activity and then increase

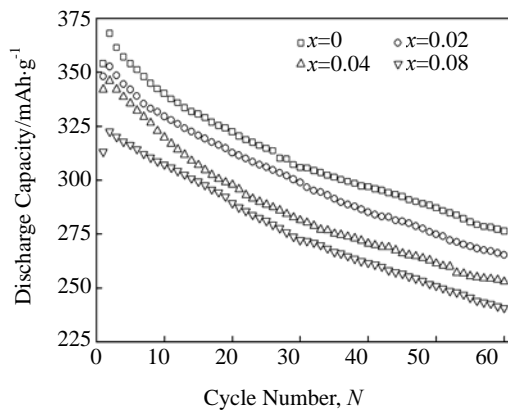


Fig.2 Discharge capacity vs. cycle number for the $La_{0.7}Mg_{0.3}Ni_{2.65}Co_{0.75}Mn_{0.1}Al_{0.2}B_x$ ($x=0-0.08$) alloy electrodes

Table 2 Electrochemical characteristics of the $La_{0.7}Mg_{0.3}Ni_{2.65}Co_{0.75}Mn_{0.1}Al_{0.2}B_x$ ($x=0-0.08$) alloy electrodes

Alloys	N_a^a	Capacity/mAh·g ⁻¹	$C_{60}/C_{max}/\%$	$HRD_{1000}^b/\%$	$I_0/mA·g^{-1}$	$I_l/mA·g^{-1}$
$x=0$	2	368.1	75.03	49.1	226.4	2542.6
$x=0.02$	2	352.6	75.2	50.9	240.2	2857.9
$x=0.04$	2	346.1	73.1	57.1	264.3	2970.3
$x=0.08$	2	322.5	74.6	52.5	235.0	3185.4

^a The cycle number needed to activate the electrode

^b The high rate dischargeability with discharge current density $I_d=1000$ mA/g

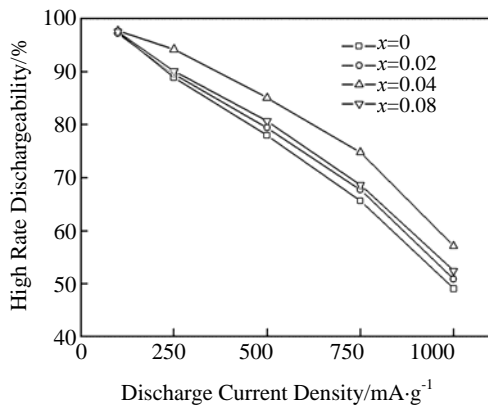


Fig.3 HRDs of the $La_{0.7}Mg_{0.3}Ni_{2.65}Co_{0.75}Mn_{0.1}Al_{0.2}B_x$ ($x=0-0.08$) alloy electrodes

its high rate dischargeability (HRD).

In general, the HRD can represent the electrochemical kinetic performances of the alloy electrodes, which is mainly determined by the charge-transfer rate of hydrogen at the surface of the alloy electrodes and the hydrogen diffusion rate in the bulk alloy [18, 19]. In order to further make clear the variation tendency of the electrochemical kinetics of the alloy electrodes, the linear polarization and anodic polarization were investigated.

Fig. 4 shows the linear polarization curves of the $La_{0.7}Mg_{0.3}Ni_{2.65}Co_{0.75}Mn_{0.1}Al_{0.2}B_x$ ($x=0-0.08$) alloy electrodes. Obviously, the polarization current density is almost linearly dependent on the overpotential within a small range of overpotential (± 5 mV). The values of the exchange current density I_0 which can be calculated by the following equation [20]:

$$I_0 = \frac{IRT}{F\eta} \quad (2)$$

are listed in Table 2, where I , R , T , F and η denote the polarization current density, the gas constant, the absolute temperature, the Faraday constant and the overpotential, respectively. As listed in Table 2, the I_0 increases from 226.4 mA/g ($x=0$) to 264.3 mA/g ($x=0.04$) and then decreased to 235.0 mA/g ($x=0.08$) with increasing x value. This indicates that the electrochemical reaction resistance of the alloy electrode decreases firstly and then increases. The electrochemical reaction rate of the alloy electrode with x being 0.04 is the fastest.

Fig. 5 shows the anodic polarization curves of the

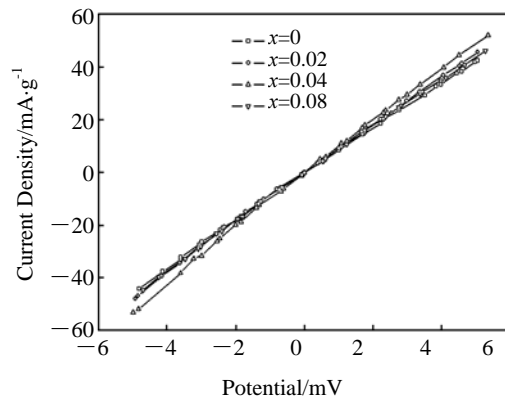


Fig.4 Linear polarization curves of the $La_{0.7}Mg_{0.3}Ni_{2.65}Co_{0.75}Mn_{0.1}Al_{0.2}B_x$ ($x=0-0.08$) alloy electrodes

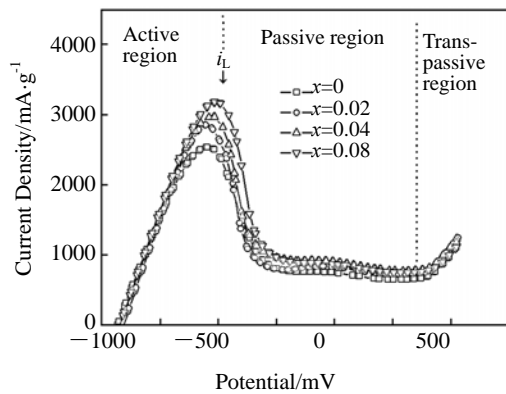


Fig.5 Anodic polarization of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) alloy electrodes

$\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) alloy electrodes. As can be seen in Fig. 5, the anodic current density increases with increasing of the overpotential, and then reaches a limiting value defined as the limiting current density I_L , which was controlled by the hydrogen diffusion in the bulk alloy^[21]. The limiting current density I_L listed in the Table 2 increases from 2542.6 mA/g ($x=0$) to 3185.4 mA/g ($x=0.08$) with increasing of x value, which indicates the diffusion rate of H atom into the bulk alloy increases gradually.

Generally, the exchange current density (I_0) can evaluate the electrochemical reaction rate of the alloy electrode, and the limiting current density (I_L) can evaluate the diffusion rate of the H atom into the bulk alloy^[20, 21]. In this paper, the results from linear polarization and anodic polarization indicate that the value of I_0 increases firstly and then decreases, while the value of I_L increases gradually with the increase of B content. The variation tendencies of the I_0 and I_L with x value do not accord with that of the HRD, so we can conclude that the electrochemical kinetics are controlled with both the charge transfer resistance and the hydrogen diffusion resistance.

3 Conclusions

1) The hydrogen storage electrode alloys $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0-0.08$) consist of the (La, Mg)Ni₃ phase with a rhombohedral PuNi₃-type structure and LaNi₅ phase with a hexagonal CaCu₅-type structure.

2) With the addition of B, the activation properties and cycling stability of the alloy electrodes keep almost unchanged, but the maximum discharge capacity decreases from 368.1 mAh/g to 322.5 mAh/g.

3) With increasing of x value, the high rate dischargeability (HRD) and exchange current density (I_0) of the alloy electrodes increase firstly and then decreases, and both HRD and I_0 reach the optimal values as x being 0.04.

4) The limiting current density (I_L) of the alloy electrodes increases gradually with the increase of B content. The electrochemical kinetics properties of the alloy electrodes are controlled with both the charge transfer resistance and the hydrogen diffusion resistance.

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硼添加对 La-Mg-Ni-Co 系贮氢电极合金的微结构及电化学性能的影响

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摘 要: 系统研究了贮氢电极合金 $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.65}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.2}\text{B}_x$ ($x=0, 0.02, 0.04, 0.08$) 的微结构与电化学性能。XRD 结果显示, 所有合金均由 (La, Mg)Ni₃ 相与 LaNi₅ 相组成, B 含量的增加导致 (La, Mg)Ni₃ 相的丰度不断增加, 相应地 LaNi₅ 相的丰度逐渐下降。此外, 合金的晶格参数与晶胞体积均随 B 含量的增加而减小。电化学测试分析表明, B 的添加可以显著改善合金电极的高倍率放电性能, 当 B 含量为 0.04 时达到最佳。微量 B 的加入对合金的循环稳定性能与活化性能影响很小, 但降低合金电极的最大放电容量。此外还采用线性极化与阳极极化对合金电极的动力学性能进行了进一步研究。

关键词: 贮氢合金; Ni/MH 二次电池; 微结构; 电化学性能

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