A374

Journal of The Electrochemical Society, **151** (3) A374-A380 (2004) 0013-4651/2004/151(3)/A374/7/\$7.00 © The Electrochemical Society, Inc.



# Structural and Electrochemical Properties of the $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$ Hydrogen Storage Electrode Alloys

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The effect of partial substitution of Mn for Ni on the structural and electrochemical properties of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys has been investigated systematically. The results of X-ray powder diffraction and Rietveld analyses showed that all alloys consisted of the (La, Mg)Ni<sub>3</sub> phase and the LaNi<sub>5</sub> phase, and the content of the (La, Mg)Ni<sub>3</sub> phase first remained unchanged ( $\sim 77$  wt %) and then decreased, but the content of the LaNi<sub>5</sub> phase increased progressively with increasing *x*. Meanwhile, the lattice parameters and cell volumes of the (La, Mg)Ni<sub>3</sub> phase and the LaNi<sub>5</sub> phase all increased with increasing Mn content. The pressure composition isotherms showed that the hydrogen storage capacity first remained almost unchanged and then decreased with increasing *x* from 0.0 to 0.5, and the equilibrium pressure decreased from 0.51 atm to 0.06 atm. The electrochemical measurements indicated that the maximum discharge capacity first remains unchanged ( $\sim 400$  mAh/g) with increasing *x* from 0.0 to 0.2 and then decreased when *x* increased further. Moreover, the high rate discharge-ability, the exchange current density  $I_0$ , the limiting current density  $I_L$ , and the hydrogen diffusion coefficient *D* of the alloy electrodes all increased first and then decreased with increasing *x*, which indicates that the kinetics of hydriding/dehydriding of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys increased first up to x = 0.1 and then decreased with further increasing *x*.

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Manuscript submitted April 28, 2003; revised manuscript received September 18, 2003. Available electronically January 26, 2004.

Hydrogen storage alloys have been successfully used as negative electrodes in nickel/metal-hydride (Ni/MH) secondary batteries. Besides the merits of higher energy density, higher charge and discharge ability, and longer charge/discharge cyclic life, the Ni/MH secondary batteries also have smaller memory effect and cause less environmental pollution compared with the rechargeable nickel/ cadmium (Ni/Cd) batteries.<sup>1-4</sup>

Recently, R-Mg-Ni (R = rare earth element, Ca or Y) system hydrogen storage electrode alloys for Ni/MH batteries have attracted our attention because of their higher hydrogen storage capacities than those of R-Ni alloys.<sup>5-9</sup> Chen *et al.*<sup>8</sup> found that the maximum discharge capacity of LaCaMgNi<sub>9</sub> alloy reached 356 mAh/g when worked on the structural and electrochemical characteristics of  $LaCaMg(NiM)_9$  (M = Al, Mn). Kohno *et al.*<sup>10</sup> have studied the electrochemical properties and structures of La-Mg-(NiCo)<sub>x</sub> (x = 3-3.5) system alloys and found that the discharge capacity of the  $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$  alloy reached 410 mAh/g, much higher than those of the conventional  $AB_5$ -type electrode alloys. Baddour-Hadjean *et al.*<sup>11</sup> have studied the structural and electrochemical properties of the R-Y-Ni (R = La, Ce) system electrode alloys and found the maximum discharge capacity to be 260 mAh/g. Moreover, in our previous work,<sup>12</sup> the structural and electrochemical properties of  $La_{0.7}Mg_{0.3}(Ni_{0.85}Co_{0.15})_x$  (x = 2.5-5.0) hydrogen storage alloy were investigated, and the results indicated that the maximum discharge capacity of La<sub>0.7</sub>Mg<sub>0.3</sub>(Ni<sub>0.85</sub>Co<sub>0.15</sub>)<sub>3.5</sub> electrode alloys reached 396 mAh/g. The study of the effect of the annealing treatment on the electrochemical properties and microstructure of the La-Mg-(NiCo)<sub>x</sub> ( $x = 3.0 \sim 3.5$ ) system alloys revealed that the discharge capacity of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.8</sub>Co<sub>0.5</sub> alloy annealed at 1123 K increased to 414 mAh/g.

Although the La-Mg-Ni-Co system electrode alloys have high hydrogen storage capacity, the plateau pressure of absorption/ desorption hydrogen is too high and the cyclic stability is too low for a good electrode alloy. On account of those inadequacies, we have continued our study to improve their overall electrochemical properties. From previous studies, we have noticed that the partial element substitution is a very effective method. As for rare earthbased hydrogen storage electrode alloys, Mn is commonly present and has been found to be beneficial in many respects.<sup>14-18</sup> The partial substitution of Ni with Mn on the B side can increase the lattice parameters and the cell volume, and decrease the plateau equilibrium pressure of hydrogen.<sup>14,19,20</sup> In more recent studies, Mn is reported effective in improving the electrochemical properties of rare earth-based hydrogen storage electrode alloys, particularly the high rate dischargeability (HRD).<sup>15-18,20</sup> So we believe that Mn element would also play an important role in the La-Mg-Ni-Co system hydrogen storage electrode alloys.

In the present study, the structural and electrochemical properties of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage electrode alloys were studied systematically.

### Experimental

Alloy preparation.—Alloy samples of  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared from component metals with the purity all above 99% by vacuum magnetic levitation melting under argon atmosphere. To assure the homogeneity of the alloy, ingots were turned over and remelted twice. Then, the ingots were mechanically crushed and ground into the powder of 300 mesh size for electrochemical and X-ray diffraction (XRD) measurements. The average particle size of the resulting powder as measured by Malvern particle analyzer Mastersizer2000 is 26.24 µm.

Structure analyses and Pressure-composition isotherms (PCT) measurement.—The crystal structures, phase abundance and the lattice parameters were determined by X-ray diffraction with Cu K $\alpha$  radiation by the Rietveld method<sup>21</sup> using Rietan97 software. P-C-Ts were measured with an automatic Sieverts-type apparatus at 303 K after each alloy powder sample (about 1 g) has been activated by four hydriding/dehydriding cycles.

*Electrochemical measurements.*—A hydrogen storage alloy electrode was prepared each time by mixing a specific alloy powder with carbonyl nickel powder in the weight ratio of 1:4 and then cold pressing the mixture into a pellet under a pressure of 16 MPa. Electrochemical measurements were performed at 303 K in a standard open trielectrode electrolysis cell consisting of a working electrode

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**Figure 1.** Rietveld refinement of the XRD profiles of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys. The gray line is the calculated intensity and the points superimposed on it (+) are observed intensities. The tick marks below the profile indicate the positions of all allowed  $K_{\alpha 1}$  and  $K_{\alpha 2}$  peaks for the structure models adopted. The bottom solid line shows the difference between calculated and observed intensities. (a) x = 0.0, (b) x = 0.1, (c) x = 0.2, (d) x = 0.3, (e) x = 0.4, and (f) x = 0.5.

(the MH pellet electrode for studying), a sintered Ni(OH)<sub>2</sub>/NiOOH counter electrode, and a Hg/HgO reference electrode immersed in the 6 M KOH electrolyte. The discharge capacity and the cycle stability of each test electrode were determined by the galvanostatic method. 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 cutoff potential of -0.6 V *vs.* the Hg/HgO reference electrode. For investigating the HRD, the discharge capacities at several specific discharge current densities were measured. Electrochemical impedance spectroscopy (EIS) studies were conducted at 50% depth of discharge (DOD) using a Solartron SI1287 electrochemical interface with 1255B frequency response analyzer. Before EIS measurements, the electrodes were first completely activated by charging/ discharging for 5 cycles. The EIS spectra of the electrodes were obtained in the frequency range of 10 kHz to 5 mHz with an ac

amplitude of 5 mV under the open-circuit condition. The linear polarization curves and Tafel polarization curves of the electrodes were measured on a Solartron SI1287 potentiostat by scanning the electrode potential at the rate of 0.1 mV/s from -5 to 5 mV (*vs.* open circuit potential, OCP) and 5 mV/s from -500 to 500 mV (*vs.* OCP) at 50% DOD, respectively. For the potentiostatic discharge, the test electrodes in the fully charged state were discharged at +600 mV potential steps for 3600 s on a Solartron SI1287 potentiostat.

## **Results and Discussion**

*Crystal structures.*—Figure 1 shows the XRD patterns and the Rietveld analysis patterns of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys. Besides the very small amounts of some particular phases, each alloy is com-

Samples	Phases	Space group (no.)	Phase abundance (wt %)		Lattice parameter (Å)		$\begin{array}{c} \text{Cell volume} \\ (\text{\AA}^3) \end{array}$
x = 0.0	(La, Mg)Ni <sub>3</sub>	<i>R</i> -3 <i>m</i> (166)	78.9	a = 5.041		c = 24.21	532.93
	LaNi <sub>5</sub>	P6/mmm (191)	18.9	a = 5.034		c = 3.99	87.55
	LaNi	Fd3m (227)	2.2	a = 3.849	b = 10.825	4.36	181.67
x = 0.1	(La, Mg)Ni <sub>3</sub>	R-3m (166)	77	a = 5.055		c = 24.273	537.25
	LaNi <sub>5</sub>	P6/mmm (191)	23	a = 5.04		c = 4.0	88.162
x = 0.2	(La, Mg)Ni <sub>3</sub>	<i>R</i> -3 <i>m</i> (166)	75.2	a = 5.07		c = 24.32	541.31
	LaNi <sub>5</sub>	P6/mmm (191)	24.8	a = 5.049		c = 4.012	88.58
x = 0.3	(La, Mg)Ni <sub>3</sub>	R-3m (166)	65.9	a = 5.077		c = 24.36	543.75
	LaNi <sub>5</sub>	P6/mmm (191)	34.1	a = 5.054		c = 4.024	89.03
x = 0.4	(La, Mg)Ni <sub>3</sub>	<i>R</i> -3 <i>m</i> (166)	62.9	a = 5.097		c = 25.01	562.86
	LaNi <sub>5</sub>	P6/mmm (191)	36.6	a = 5.064		c = 4.042	89.79
	MnO <sub>2</sub>	Pnma (62)	0.5	a = 9.29	b = 2.838	4.545	119.83
x = 0.5	(La, Mg)Ni <sub>3</sub>	R-3m (166)	56.5	a = 5.107		c = 25.033	565.369
	LaNi <sub>5</sub>	P6/mmm (191)	42.4	a = 5.067		c = 4.054	90.134
	$MnO_2$	<i>Pnma</i> (62)	1.1	a = 9.29	b = 2.838	c = 4.546	119.92
x = 0.5	MnO <sub>2</sub> (La, Mg)Ni <sub>3</sub> LaNi <sub>5</sub> MnO <sub>2</sub>	Pnma (62) R-3m (166) P6/mmm (191) Pnma (62)	0.5 56.5 42.4 1.1	a = 9.29 a = 5.107 a = 5.067 a = 9.29	b = 2.838 $b = 2.838$	4.545  c = 25.033  c = 4.054  c = 4.546	119.83 565.369 90.134 119.92

Table I. The characteristics of alloy phases in the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys.<sup>a</sup>

<sup>a</sup> The Rietveld refinement program Rietan97 was used.

prised of a (La, Mg)Ni<sub>3</sub> phase with the PuNi<sub>3</sub>-type rhombohedral structure and a LaNi<sub>5</sub> phase with the CaCu<sub>5</sub>-type hexagonal structure. The phase abundance, lattice parameters, and cell volumes for the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  hydrogen storage alloys are listed in Table I. It can be seen that the lattice parameters and cell volumes of the (La, Mg)Ni3 phase and LaNi5 phase all increase with the increase of Mn content (as can be seen in Table I), which can be attributed to the larger atomic radius of Mn (1.79 Å) than that of Ni (1.62 Å). Thus the increase of Mn content with increasing x leads to the crystal lattice expansion of both the (La, Mg)Ni3 phase and the LaNi<sub>5</sub> phase and the increase of phase abundance of LaNi<sub>5</sub> phase. Moreover, from Table I, it can be seen that the content of (La, Mg)Ni<sub>3</sub> phase first remains almost unchanged (~77 wt %) when x increases from 0.0 to 0.2. However, as x increases further, the content of (La, Mg)Ni3 phase decreases from 65.9 wt % (x = 0.3) to 56.5 wt % (x = 0.5). In contrast, the content of LaNi<sub>5</sub> phase increases progressively from 18.9 to 42.4 wt % with increasing x from 0.0 to 0.5, which also confirms that Mn promotes the formation of LaNi<sub>5</sub> phase in the alloy.

In a word, the increase of Mn element content affected the phase composition of alloy only moderately, but increased the lattice parameters and cell volumes of the main phases and thus affected the overall electrochemical properties of the alloy electrodes noticeably.

P-C-Ts.—Figure 2 shows the hydrogen absorption/desorption P-C-Ts of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$ = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys at 303 K. As shown in Fig. 2, the equilibrium pressure of hydrogen desorption decreases from 0.51 atm to 0.06 atm as x for Mn content increases from 0.0 to 0.5, which is in good agreement with the results reported previously about the rare earth-based hydrogen storage alloys by Lartigue *et al.*<sup>14</sup> The hydrogen storage capacity decreases with increasing x. To make the comparison more exact, the maximum hydrogen desorption capacity  $C_{\rm max}$  is defined as the hydrogen desorbed from the alloy at 303 K between 5 atm and 0.1 atm. It can be seen that the hydrogen desorption capacity maintains almost unchanged at first with x increasing from 0.0 to 0.2. Then, the hydrogen desorption capacity decreases while x increasing from 0.3 to 0.5. The change of hydrogen storage capacity can be attributed to the change of the phase abundance of the alloys. According to the work of Oesterreicher<sup>22</sup> and Takeshita,<sup>23</sup> the hydrogen storage capacity of the LaNi<sub>3</sub> phase is larger than that of the LaNi<sub>5</sub> system alloy. Therefore, with the decrease of the (La, Mg)Ni<sub>3</sub> phase in the alloys, the absorption/desorption capacity would decrease accordingly. In the present investigation, the change of hydrogen storage capacity agreed well with the change of phase abundance obtained from Rietveld analysis.

Electrochemical characteristics.—Figure 3a shows the discharge capacity vs. the cycle number of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> hydrogen storage alloy electrodes. Table II summarizes the electrochemical properties of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> alloy electrodes. All alloy electrodes can be activated very easily, namely within two cycles. The maximum discharge capacities of the alloy electrodes first remain almost unchanged (~400 mAh/g) and then decrease to 362.5 mAh/g when the x for Mn content increases from 0.3 to 0.5, which agrees with the result of the P-C-T measurement. Figure 3b shows the capacity retention rate of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> hydrogen storage alloy electrodes after 60 charge/discharge cycles. It can be seen that the capacity retention of alloy electrodes remains almost unchanged ( $\sim 46\%$ ) after 60 cycles when x increases from 0.0 to 0.4 (Mn/Ni = 0.00  $\sim 0.11$ , atomic ratio) and then increases to 54.5% when x reaches 0.5 (Mn/Ni = 0.20), which can be attributed to increasing of the



**Figure 2.** The absorption/desorption P-C isotherms of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys at 303 K.



**Figure 3.** (a) Discharge capacity *vs.* cycle number for the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes at 303 K. (b) The capacity retention of the alloy electrodes after 60 charge/discharge cycles at 303 K.

content of LaNi<sub>5</sub> phase. Previous studies have ascertained that the Mg atoms only occupy 6c sites if La is partially substituted by Mg in PuNi<sub>3</sub>-type rhombohedral structure,<sup>24</sup> and that Mg atoms do not occupy the La sites in LaNi<sub>5</sub> phase.<sup>25</sup> As it is generally accepted that the Mg element would be corroded very easily in KOH solution and

Table	II. The	electrochemica	l properties	of	the
La <sub>0.7</sub> Mg <sub>0</sub> loy electr	<sub>3</sub> Ni <sub>2.975-x</sub> C rodes.	$\cos_{0.525} \mathrm{Mn}_x (x) =$	0.0, 0.1, 0.2, 0.3	, 0.4, 0.	5) al-

Samples	C <sub>max</sub> (mAh/g)	$N_a^{\ a}$	$\binom{C_{60}/C_{\max}}{(\%)}$	$\underset{(\%)}{\overset{\text{HRD}_{1500}}{\overset{\text{b}}{\overset{\text{b}}{\overset{\text{b}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{\text{c}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}{\overset{{}}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}{\overset{{}}}}}{\overset{{}}}}{$
x = 0.0	406.4	2	47.1	66.7
x = 0.1	404.2	2	47.2	70.2
x = 0.2	400.1	2	44.6	61.9
x = 0.3	398.0	1	46.1	58.8
x = 0.4	387.8	1	48.6	51.8
x = 0.5	362.5	1	54.5	50.0

<sup>a</sup> The cycle numbers needed to activate the electrodes.

<sup>b</sup> The high rate dischargeability with discharge current density  $I_{\rm d}$  = 1500 mA/g.



**Figure 4.** (a) The high rate dischargeability (HRD) of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes at 303 K. (b) The HRD of the alloy electrodes with  $I_d = 1500$  mA/g.

form a permeable Mg(OH)<sub>2</sub> passive film, which results in the rapid capacity degradation during cycling.<sup>26</sup> In the present study, according to Rietveld analyses, as *x* increased, the content of (La, Mg)Ni<sub>3</sub> phase at first remained almost unchanged and then decreased with further increase of *x*, and the content of LaNi<sub>5</sub> phase increased progressively, so the effect of Mg corrosion weakened, and the cycling stability of the alloy improved noticeably when x = 0.5.

Figure 4a shows the HRD of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> alloy electrodes. Figure 4b shows the HRD of the alloy electrodes at the very high discharge current density of 1500 mA/g. It can be seen that the HRD of the alloy electrodes first increases from 66.7% (x = 0.0) to 70.2% (x = 0.1) and then decreases to 50.0% with further increase of x, and the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.875</sub>Co<sub>0.525</sub>Mn<sub>0.1</sub> alloy electrode shows the highest value of HRD even when  $I_d = 1500$ mA/g. It is well known that, for the rare earth-based hydrogen storage electrode alloys, Mn partial substitutions for Ni improves the HRD because the dissolution of Mn into electrolyte leads to the increase of Ni content on the alloy surface,<sup>17</sup> which has good electrocatalytic activity for the electrochemical decomposition of H<sub>2</sub>O on the surface of the electrode. In the present study, the total Ni content in the alloy decreased when the Mn content increased. It is believed that an optimum ratio between Mn element and Ni element in the alloys could be found for improving the HRD of the alloy electrodes by means of a plot as shown in Fig. 4b.



**Figure 5.** Electrochemical impedance spectra of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes measured at the 50% DOD and 298 K.

Figure 5 shows the electrochemical impedance spectra of the  $La_{0.7}Mg_{0.3}Ni_{2.975-{\it x}}Co_{0.525}Mn_{\it x}$  alloy electrodes at 50% DOD at 298 K. It can be seen that, for all alloy electrodes, each EIS spectrum is consisted of two circular arcs and a sloped straight line. According to the model of Kuriyama et al.,<sup>27</sup> the smaller arc in the highfrequency region represents the contact impedance between the foamed Ni substrate and the alloy particles, the larger arc in the low-frequency region represents the charge-transfer resistance on the alloy surface, and the low-frequency straight line is attributed to the Warburg impedance. From Fig. 5, it can be seen that the contact impedance remains almost unchanged for the alloy electrodes with different values of x, but the radius of the larger arc in the lowfrequency region decreases first and then increases with increasing x, which indicates that the charge-transfer resistance of the alloy electrode decreased first and then increased with increasing Mn content in alloys. There is an optimum value of Mn substitution for Ni (x = 0.1) for the kinetics of electrochemical reaction of the alloy electrodes.

Figure 6a shows the linear polarization curves of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> alloy electrodes. From the slope of the specific line, the polarization resistance of any alloy electrode can be determined, which is listed in Table III. The polarization resistance of the alloy electrode decreases first from 141.0 mΩ (x = 0.0) to 119.9 mΩ (x = 0.1) and then increases with further increase of x to 148.1 mΩ (x = 0.5). According to Notten *et al.*,<sup>28</sup> the exchange current density  $I_0$ , generally used to measure the kinetics of the electrochemical hydrogen reaction, can be calculated by the following formula

$$I_0 = \frac{I_d R T}{F \eta}$$
[1]

where *R* is the gas constant, *T* the absolute temperature,  $I_d$  the applied current density, *F* the Faraday constant and  $\eta$  the total overpotential. The exchange current density  $I_0$  calculated with Eq. 1 is listed in Table III. Figure 6b also shows the variation of the exchange current density  $I_0$  with increasing the atomic ratio between Mn and Ni. As shown in Table III, the exchange current density  $I_0$  of the alloy electrodes increases first from 182.1 mA/g (x = 0.0) to 214 mA/g (x = 0.1) and then decreases to 173.3 mA/g (x = 0.5) with increasing *x*, which indicates that the kinetics of the electrochemical hydrogen reaction in alloy electrodes increases first and then decreases with increasing Mn content in alloys. There also exists a most optimum ratio between the Mn content and the Ni



**Figure 6.** (a) Linear polarization curves for the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes with a scan rate 0.1 mV/s measured at the 50% DOD and 298 K. (b) The exchange current density of the alloy electrodes at 298 K.

content at which the kinetics of the electrochemical hydrogen reaction in alloy electrodes is the highest as shown in Fig. 6b.

Figure 7 shows the Tafel polarization curves of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  alloy electrodes. It can be seen in Fig. 7 that each Tafel polarization curve contains an anode polarization branch, which corresponds to the hydrogen desorption, and a cathode polarization branch, which corresponds to the hydrogen absorption. The anode polarization slope ( $B_a$ ) and the cathode polarization slope ( $B_c$ ) obtained from the curves are listed in Table III. Both  $B_a$  and  $B_c$  increase first with *x* increasing from 0.0 to 0.1 and then decrease with further increasing *x*. The exchange current density  $I_0$  can be obtained from Tafel polarization curves according to the Tafel equation

$$I = I_0 (10^{E - E_0 / B_a} + 10^{-E - E_0 / B_c})$$
[2]

in which *I* the measured current ( $I_{anodic}$ - $I_{cathodic}$ ),  $I_0$  the exchange current density, *E* is the applied potential,  $E_0$  the open circuit potential (OCP),  $B_a$  the anodic Tafel slope,  $B_c$  the cathodic Tafel slope, respectively. The exchange current density  $I_0$  obtained from Eq. 2 is also listed in Table III. It can be seen that the  $I_0$  increases from 181.8 mA/g (x = 0.0) to 221.0 mA/g (x = 0.1) and then decreases to 166.2 mA/g when x reaches 0.5, which is consistent with the result obtained from the line polarization curves. Moreover, all the

Table III. The polarization resistance  $R_D$ , the exchange current density  $I_0$ , the limiting current density  $I_L$  and the hydrogen diffusion coefficient D of La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes.

	Polarization	Linear polarization exchange current density	Tafel (mV	slope /dec)	Tafel polarization exchange current density	Limiting current density	Hydrogen diffusion
Samples	$(m \ \Omega)$	(mA/g)	B <sub>a</sub>	B <sub>c</sub>	(mA/g)	(mA/g)	$(\times 10^{-11} \text{ cm}^2/\text{s})$
x = 0.0	141.0	182.1	169	155	181.8	2098.5	9.49
x = 0.1	119.9	214.0	206	187	221.0	2399.4	9.85
x = 0.2	133.1	192.7	182	179	206.6	2002.6	8.57
x = 0.3	133.3	192.6	174	174	199.8	2000.3	7.28
x = 0.4	146.4	175.4	173	169	171.5	1552.9	7.23
x = 0.5	148.1	173.3	170	165	166.2	1400.1	6.61

curves show that, during the anode polarization process, the anodic current increases first with increasing overpotential and finally reaches a maximum, which is defined as the limiting current density  $I_{\rm L}$ , which represents the hydrogen diffusion ability of the alloy electrode. The limiting current density  $I_{\rm L}$  of the electrodes made of different alloys (Table III) increases first from 2098.5 mA/g (x = 0.0) to 2399.4 mA/g (x = 0.1) and then decreases to 1400.1 mA/g (x = 0.5), indicating that the hydrogen diffusion in alloy increases first and then decreases with increasing x, and the variation in hydrogen diffusivity is in agreement with the variation of the exchange current density and the HRD.

Figure 8 shows the semilograrithmic curves of anodic current *vs.* time responses of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  alloy electrodes. As shown in Fig. 8, it can be distinguish the current responses in two time regions. The first one is the shorter time region in which the current density declines rapidly, and the other is the longer time region in which the current density decreases slowly in a linear.<sup>29-30</sup> Using a spherical diffusion model,<sup>29</sup> the linear response in the longer time region can be treated as the finite diffusion of hydrogen inside the alloy particle. In this case, the diffusion coefficient of the hydrogen atoms in the bulk of the alloy can be estimated according to following expression<sup>31</sup>

$$\log i = \log \left[ \frac{6FD}{da^2} (C_0 - C_s) \right] - \frac{\pi^2}{2.303} \frac{D}{a} t$$
 [3]



Figure 7. Tafel polarization curves for the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes with a scan rate 5 mV/s measured at the 50% DOD and 298 K.

where *i*, *D*, *C*<sub>0</sub>, *C*<sub>s</sub>, *a*, *d* and *t* are the diffusion current density (A/g), the hydrogen diffusion coefficient (cm<sup>2</sup>/s), the initial hydrogen concentration in the bulk of the alloy (mol/cm<sup>3</sup>), the hydrogen concentration on the surface of the alloy particles (mol/cm<sup>3</sup>), the alloy particle radius (cm), the density of the hydrogen storage alloy (g/cm<sup>3</sup>), and the discharge time (s), respectively. By taking that the average particle radius as 13.12 µm, the values of hydrogen diffusion coefficient, *D*, of alloys with different *x* values are calculated by Eq. 3 and tabulated in Table III. The hydrogen diffusion coefficient increases from  $9.49 \times 10^{-11}$  cm<sup>2</sup>/s (x = 0.0) to  $9.85 \times 10^{-11}$  cm<sup>2</sup>/s (x = 0.1) and then decreases to  $6.61 \times 10^{-11}$  cm<sup>2</sup>/s (x = 0.5), which is consistent with the result of the Tafel polarization examination, with the electrochemical kinetics of the alloy electrodes increasing first and then decreasing with increasing *x* from 0.0 to 0.5.

As the performance of a hydrogen storage alloy electrode is determined by both the kinetics of the processes at the alloy/electrolyte interface and the rate of hydrogen diffusion in the bulk of the alloy, the exchange current density  $I_0$ , the limiting current density  $I_L$ , and the *D* are the three important parameters for charactering the kinetics of alloy hydriding. In the present study, the exchange current density  $I_0$ , the limiting current density  $I_L$ , and the *D* of the alloy electrodes all increased first and then decreased with increasing Mn content due to the increasing ratio of Mn content and Ni content in the alloy. From the above results, the kinetics of hydriding of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys is affected by changing *x*, with the optimum composition around x = 0.1, which is consistent with the variation of HRD.



**Figure 8.** Semilograrithmic plots of anodic current *vs.* time responses of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) alloy electrodes at 298 K.

## Conclusions

The structural and electrochemical properties of the  $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$  (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) hydrogen storage alloys have been studied. All alloys mainly consisted of the (La, Mg)Ni<sub>3</sub> phase and the LaNi<sub>5</sub> phase. The relative content of the (La, Mg)Ni<sub>3</sub> phase and that of the LaNi<sub>5</sub> phase varied with x. Meanwhile, the lattice parameters and cell volumes of both the (La, Mg)Ni3 phase and the LaNi5 phase all increased with increasing Mn content. The P-C isotherms indicate that the hydrogen storage capacity first remained almost unchanged and then decreased with increasing x from 0.0 to 0.5, and the equilibrium pressure decreased with increasing x continuously. The electrochemical measurements show that the maximum discharge capacity first remained unchanged and then decreased. Moreover, the HRD, the exchange current density  $I_0$ , the limiting current density  $I_L$ , and the D of the alloy electrodes all increased first and then decreased with increasing x, which is attributed to the dissolution of Mn into electrolyte leading to the increase of Ni content on the alloy surface. Therefore, the kinetics of hydriding of the La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>2.975-x</sub>Co<sub>0.525</sub>Mn<sub>x</sub> hydrogen storage alloys was affected by changing x, with the optimum composition around x = 0.1.

#### Acknowledgment

This work was supported by the National Nature Science Foundation of China (50131040).

Zhejiang University assisted in meeting the publication costs of this article.

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