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Crystal structure and electrochemical properties of rare earth non-stoichiometric AB_5-type alloy as negative electrode material in Ni-MH battery

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Abstract

The $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ ($0.05 \leqslant x \leqslant 0.35$) system compounds have been prepared by arc melting method under Ar atmosphere. X-ray diffraction (XRD) analysis reveals that the as-prepared alloys have different lattice parameters and cell volumes. The electrochemical properties of these alloys have been studied through the charge–discharge recycle testing at different temperatures and discharge currents. It is found that the $La_{0.85}Mg_{0.25}Ni_{4.5}Co_{0.35}Al_{0.15}$ alloy electrode is capable of performing high-rate discharge. Moreover, it has very excellent electrochemical properties as negative electrode materials in Ni-MH battery at low temperature, even at −40°C.

Keywords: Hydrogen storage alloy; Crystal structure; Electrochemical property; High-rate discharge

1. Introduction

Air pollution and depletion of natural petroleum reserves have spurred the renewed interest in electric vehicles. Due to the high specific energy, Ni-MH battery has been widely investigated and applied in portable computers, cellular telephones, new cordless appliances and hybrid electric vehicles and so on [1–3]. The most important part in Ni-MH battery is negative electrode. AB_5-typed hydrogen storage alloys have been extensively studied and applied as negative electrode materials in Ni-MH battery [4–6]. However, in order to be used as vehicle power source in some cold places, such as north-east of china, Russia etc., the abilities of high-rate discharge and low temperature discharge for AB_5-typed hydrogen storage alloys still need to be further improved so that to meet the requirement of the extended applications.

Notten and Percheron-Guegan et al. indicated that the electrochemical properties of hydrogen storage alloy, such as the storage capacity, cycling stability and discharge efficiency, can be significantly changed by non-stoichiometric and elemental substitution [7–10]. Moreover, the non-stoichiometry method is a special doping technique for intermetallic compounds, and it is very simple and easy to do. In this paper, we describe the synthesis and crystal structure and electrochemical properties of non-stoichiometry $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ ($0.05 \leqslant x \leqslant 0.35$) system in order to obtain hydrogen storage alloys which are capable of performing high-rate discharge and being used in low-temperature environment.

2. Experimental details

2.1. Alloy preparation, X-ray diffraction

All alloys were prepared by arc-melting the component metals or master alloy on a water-cooled copper hearth under argon atmosphere. The purity of the metals, i.e., La, Mg, Ni, Co and Al, is higher than 99.9%. The samples were all inverted and remelted 5 times to ensure good homogeneity. Thereafter, these alloys were crushed into fine powders of 200–300 mesh

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in mortar. Commercial $LaNi_5$ powder, which is supplied by Shanghai Institute of Metallurgy, were used to do the contradistinctive experiment.

Crystallographic characterization of the hydrogen storage alloys were carried out by XRD analysis utilizing CuKá radiation on a Ragaku D/max 2500 V PC X-ray diffractometer. The cell parameters of the alloys were calculated by Cell program [11].

2.2. Electrochemical measurement

The well-mixed alloy powder and nickel powder in weight ratio of 1:5 were pressed into the tablets as metal hydride electrodes, which have the diameter of 13 mm and thickness of 1.5 mm, and each electrode was about 0.9 g. The electrochemical properties were then measured in a standard trielectrode cell consisting of a working electrode (metal hydride electrode), a counter-electrode ($NiOOH/Ni(OH)_2$ electrode) and a reference electrode (Hg/HgO, OH^-). The electrolyte in the cell was 6 M KOH aqueous solution. Charge and discharge tests were carried out on a DC-5 battery testing instrument controlled by computer. The charge/discharge tests were emphasis on the electrochemical capacity and stability of the negative electrode, thus the capacity of the positive electrode plate was designed to be much higher than that of the negative electrode. These experimental cells were firstly charged at a current of 60 mA/g for 5.5 h, and then, after 5 min break, were discharged at different discharge currents and temperatures end to the voltage of −0.60 V vs. Hg/HgO.

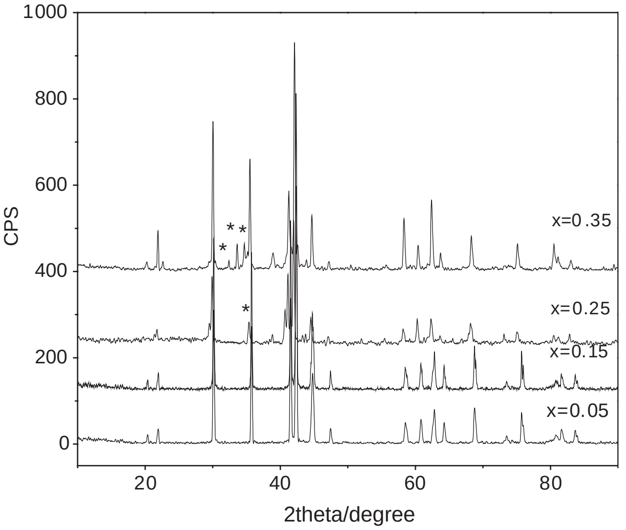

Fig. 1. XRD patterns of the $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ compounds as the function of Mg content.

Table 1
Lattice parameter, cell volume and density for $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ compounds

Mg-stoichiometry	Lattice parameter		Cell volume (nm^3)	Density (g/cm^3)
	a (nm)	*c* (nm)		
0.05	5.04927	4.04903	88.35	8.3020
0.15	5.02224	4.04865	88.3	8.2502
0.25	5.01964	3.98428	87.03	8.1317
0.35	5.01806	3.91713	86.49	8.1274

3. Results and discussions

3.1. Structure characterization

Fig. 1 shows the XRD patterns of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ ($0.05 \leqslant x \leqslant 0.35$) compounds. The sharp peaks indicate a long-range crystallographic order and excellent crystallinity. Both the stoichiometric ($La_{0.85}Mg_{0.15}Ni_{4.5}Co_{0.35}Al_{0.15}$) and B-rich ($La_{0.85}Mg_{0.05}Ni_{4.5}Co_{0.35}Al_{0.15}$) compounds have the single $CaCu_5$-type phase, while the B-poor ($La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$, $0.25 \leqslant x \leqslant 0.35$) compounds consist of two phases, one is $CaCu_5$-type phase and the other is identified to be La_2Ni_7 phase, which is marked with the symbol "*" in Fig. 1. There are some slight differences between the relative intensities of Bragg peaks in 20–25 2θ and 55–60 2θ ranges. The results indicate that the composition of compound strongly affects the structure of the compound and non-stoichiometry may relate to appearance of new phase. There are some slight shifts between the patterns of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ ($0.05 \leqslant x \leqslant 0.35$) because of the different content of Mg. The lattice parameters and cell volumes of compounds are listed in Table 1. It can be found that both the lattice parameters and the cell volumes are decreased with increasing x. That's mostly because that the radius of Mg is smaller than that of La.

3.2. Electrochemical properties

3.2.1. Discharge ability

The typical detail time–potential curves at the first cycle of $La_{0.85}Mg_{0.25}Ni_{4.5}Co_{0.35}Al_{0.15}$ at 293 and 233 K during charging and discharging processes are shown in Figs. 2 and 3, respectively. It can be clearly seen that the charge potential of the electrode becomes more and more negative resulting from the formation of hydrogen solid solution and hydride, moreover, the charge potential at 233 K is more negative than that at room temperature, however, the situation is reverse during the discharge process. Those are mostly because of the decrease of electrolyte activity at low temperature which reasonably lead to the increase of hydrogen diffusion resistance and thus the obviously decrease of the charge efficiency and discharge efficiency, and then inevitably bring out the decrease of the discharge capacity of the electrodes.

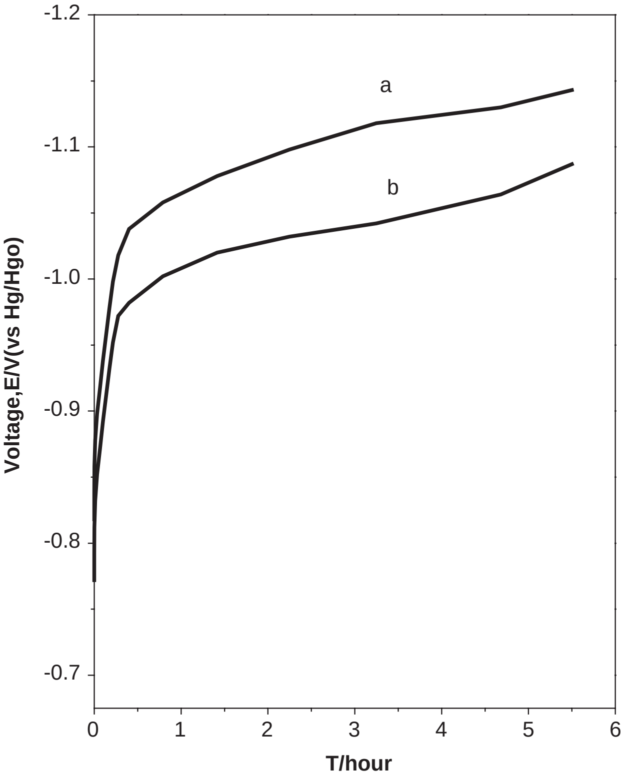

Fig. 2. Electrochemical charge curves at the current of 60 mA/g for $La_{0.85}Mg_{0.25}Ni_{4.5}Co_{0.35}Al_{0.15}$: (a) at 233 K; (b) at 293 K.

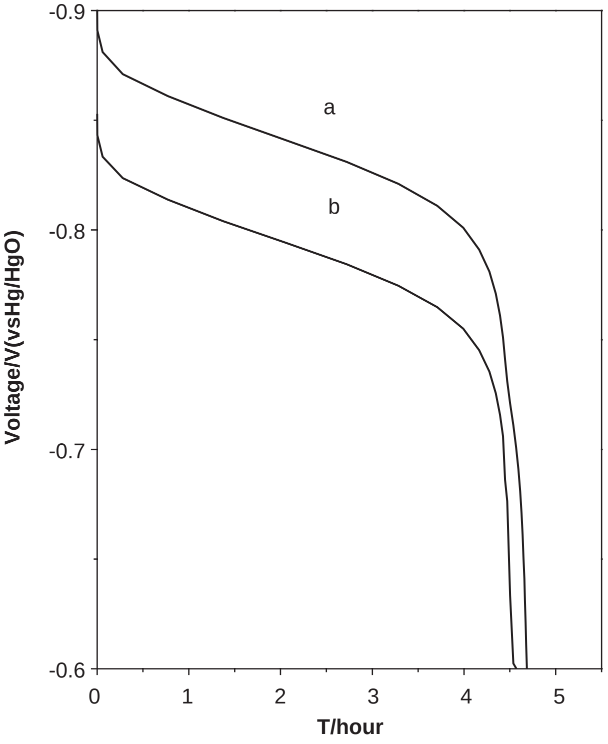

Fig. 3. Electrochemical discharge curves at the current of 60 mA/g for $La_{0.85}Mg_{0.25}Ni_{4.5}Co_{0.35}Al_{0.15}$: (a) at 293 K; (b) at 233 K.

3.2.2. Activation and maximum capacity

Fig. 4 shows the activation profiles of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ electrodes. It seems that the activation of B-rich compounds is easier than that of B-poor samples. The activation of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy electrodes in the range of $0.05 \leqslant x \leqslant 0.15$ only need 3 cycles, while $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy electrodes in the range of $0.25 \leqslant x \leqslant 0.35$ complete their activations after 5 cycles. The easy activation may probably attribute to the addition of Ni which is very useful to the metal hydride decomposes. Fig. 4 also shows that, with the increase of Mg content, the specific capacity of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy electrodes decrease first and then increase. The specific capacity of the alloy electrodes decrease when the Mg content changes from 0.05 to 0.15. However, with further increase in Mg content, the specific capacity is greatly increased to a value what is even larger than that of $La_{0.85}Mg_{0.05}Ni_{4.5}Co_{0.35}Al_{0.15}$. This is an indication of the occurrence of two opposing factors that contribute to the specific capacity. To elucidate this phenomenon, the chemical elemental characteristics of La and Mg must be considered. As the atomic radius and atom volume of Mg are smaller than that of La, the addition of Mg will inevitably cause the decrease of the lattice cell and therefore decrease the interstitial space of the lattice cell and this will detrimental to the hydrogen-storage process, and perhaps there is some extra Mg within the structure that adds to the molecular weight when x greater than 0.15 in $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy.

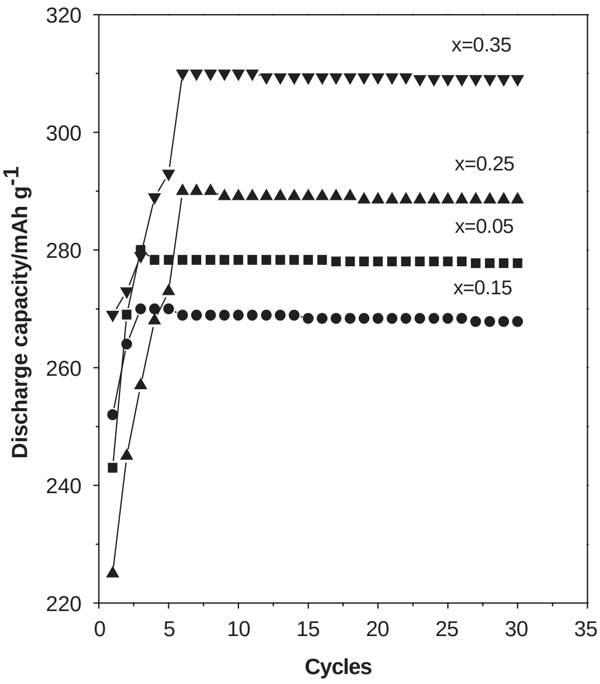

Fig. 4. Activation profiles of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ hydride electrodes.

On the other hand, owing to the light weight of Mg as compared to La, that can also be seen from the density of the alloys shown in Table 1, the compound molecular weight decreases with increasing x, and therefore the electrode material capacity is enhanced as long al the amount of uptake hydrogen atoms remains constant. Therefore, it is reasonable to assume that, with an Mg addition of lower than a certain amount; the decrease of the lattice cells is dominant and will cause a decrease in the specific capacity. When the addition of Mg excess the certain amount, though there is some extra Mg within the structure that adds to the molecular weight when x greater than 0.15 in $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy, the increase in the number of lattice cells per unit weight of the alloys will become dominant and will give rise to an increase in the specific capacity. Overall, the combined effect of the two opposite factors will inevitably result in an optimal value for the specific capacity. In the case of $La_{0.85}Mg_{0.25}Ni_{3.5}Co_{0.35}Al_{0.15}$ electrode, the capacities reach its maximum of 290 mA h/g after 5 cycles. The results, electrochemical properties of hydrogen storage are strongly dependent on the non-stoichiometric, are in good agreement with those found by Notten and Percheron-Guegan et al. [7–10].

3.2.3. High-rate discharge

As an electrode for battery, it is very important to holdback the decrease of the discharge capacity even at high discharge current density. Fig. 5 shows the discharge capacities of the $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloys comparable to the commercial $LaNi_5$ alloy at various discharge current densities. As seen from Fig. 5, the high-rate discharge ability of the $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloys decrease with the increase content of Mg. The rate discharge ability of those alloys electrodes were mainly determined by the charge transfer process at the electrode surface and the mass transfer process in electrode body. Because of the smaller lattice parameters, cell volume which are detrimental to the hydrogen diffusion, moreover, equilibrium hydrogen pressure in the La_2Ni_7 system is very low which are also detrimental to hydrogen desorbing during the discharge process, the high-rate discharge ability decrease with the increase of Mg content for $La_{0.85}Mg_xNi_{3.5}Co_{0.35}Al_{0.15}$ alloys electrodes. An additional comparison of the discharge capacities at the discharge current of 4200 mA/g is given in Table 2. In the case of $La_{0.85}Mg_{0.25}Ni_{3.5}Co_{0.35}Al_{0.15}$ alloy electrode, it can still discharge 197 mA h/g which is over 68% of maximum capacity and more than four times than that of commercial $LaNi_5$ alloy. Considering the excellent high-rate discharge ability, $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloys doubtlessly has the potential to be used as electrode material in electric vehicles in future.

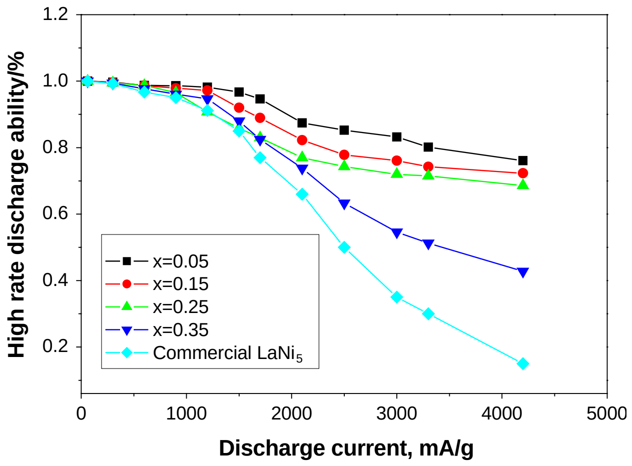

Fig. 5. High-rate discharge ability of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ electrodes as the function of Mg.

3.2.4. Temperature effect

Alloys used as negative electrode material in Ni-MH battery should be capable of working at wide temperature range. Fig. 6 shows the discharge ability of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ at different temperatures. It

Table 2
Discharge capacity of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy electrodes with different Mg contents at the discharge current of 4200 mA/g

x	0.05	0.15	0.25	0.35
Discharge capacity (mA h/g)	189	175	197	130

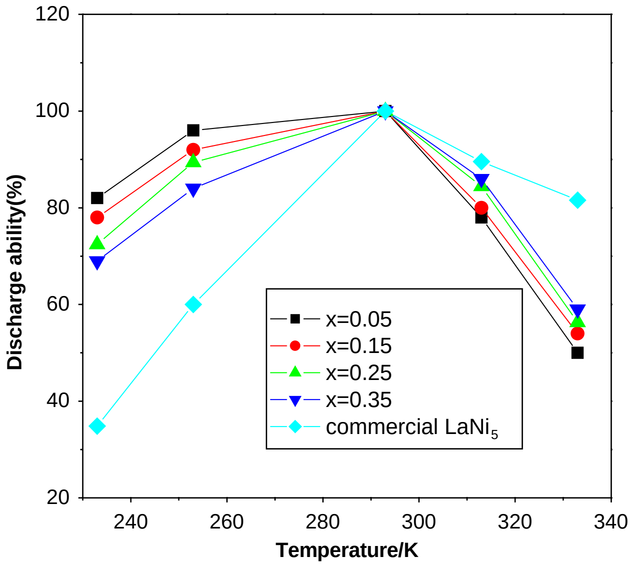

Fig. 6. Discharge ability of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ and commercial $LaNi_5$ as the function of temperature at the discharge current of 60 mA/g.

can be easily found that the discharge capacities are sensitive to temperature. The electrodes reach their maximum discharge capacities at room temperature (293 K) then decrease sharply with the decrease and increase of temperature. All the $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy electrodes can only discharge less than 60% of their maximum capacity at high temperature (333 K). Those tell us that Mg-substituted electrodes suffer from poor high-temperature performance because the 60% is even quite smaller than 81.576% for commercial $LaNi_5$ electrode. Fig. 6 also shows us that low-temperature discharge abilities of the $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ alloy electrodes are quite different. Hydrogen can diffuse easily at mass alloys with large lattice parameter and cell volume, thus low-temperature discharge ability is greatly improved because it is hydrogen diffusion control reaction. However, owing to large lattice parameter and cell volume, hydrogen evolution became easier during charge and the rates of self-discharge become larger during discharge, the specific capacity at high-temperature decrease with the increase of the lattice parameter and cell volume. The high-temperature discharge ability of $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ should be improved to meet the extended applications.

4. Summary

The $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ ($0.05 \leqslant x \leqslant 0.35$) system compounds have been prepared by arc melting method under Ar atmosphere. The X-ray diffraction (XRD) analysis reveals that the as-prepared alloys have different cell parameter from that of $LaNi_5$ alloy. The electrochemical properties of these alloys have been studied through the charge–discharge recycle testing at both low- and high-temperature.

The results obtained are summarized as follows:

(1) The lattice parameters and cell volume decrease with the increase of Mg content in $La_{0.85}Mg_xNi_{4.5}Co_{0.35}Al_{0.15}$ ($0.05 \leqslant x \leqslant 0.35$).

(2) Large lattice parameter and cell volume are benefit to the high-rate discharge and low-temperature discharge ability. However, it detrimental to the high-temperature discharge ability of the electrodes.

(3) The $La_{0.85}Mg_{0.25}Ni_{4.5}Co_{0.35}Al_{0.15}$ system alloys are capable of performing high-rate discharge and have very excellent electrochemical properties as negative electrode materials in Ni-MH battery at low temperature, even at −40°C.

Acknowledgments

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