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# The electrochemical properties of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) hydrogen storage alloys

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## Abstract

$La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) alloys were prepared by a powder sintering method and the influence of partial substitution of Mg by La on the crystal structure and electrochemical performance of the alloys was investigated. The ternary alloys with different La/Mg ratio are related to the hexagonal $PuNi_3$-type structure. The increase of La/Mg ratio in the alloys leads to a linear increase of the unit cell volume. The La-rich alloys ($x=1.8$–$2.0$) show promising electrode properties including a large discharge capacity (~400 mAh/g), easy activation and good high-rate dischargeability, although the cycling stability needs further improvement.

*Keywords:* Hydrogen storage alloy; Crystal structure; X-ray diffraction; Electrochemical properties; Ni/MH batteries

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## 1. Introduction

To achieve an even higher energy density and better performance of the Ni–MH battery, one of the most important things is to increase the energy density of the electrode alloys with good overall properties. To date, two types of electrode alloys, namely the $AB_5$ ($CaCu_5$ type) and $AB_2$-type (Laves type) alloys have been extensively studied and used for commercial batteries. However, the $AB_5$-type mischmetal-based alloys have only limited capacity (~300 mAh/g), and the $AB_2$-type alloys suffer from slow activation and relatively low rate capacity [1,2].

Recently, the structure investigation of the $RMg_2Ni_9$ (where R is a rare earth element or Y, Ca) system indicated that some of the new series of R–Mg–Ni-based $AB_3$-type alloys with $PuNi_3$-type structure had higher capacity than that of the $AB_5$-type alloys and were thus regarded as promising candidates for reversible hydrogen storage [3–7]. Moreover, it is reported that some of the R–Mg–Ni-based $AB_3$-type alloys also exhibited promising electrode properties [8–10]. For example, the La–Mg–Ni–Co system $AB_x$ ($x=3.0$–$3.5$) type quaternary alloys were found to have large discharge capacities of 387–410 mAh/g, much higher than those of the commercially used $AB_5$-type alloys [8]. Therefore, the R–Mg–Ni-based $AB_3$-type alloys appear to be good potential candidates for the negative electrode materials of Ni–MH batteries.

It is reported that the alloy $LaMg_2Ni_9$ with the typical $PuNi_3$-type structure had very low hydrogen absorption capacity (~0.33 wt.%), but when both La and Mg were partially replaced by Ca, the hydrogen absorption capacity of the $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$ alloy went up to 1.87 wt.% accompanied with a large increase of the unit cell volume [6]. However, the electrode properties of these alloys have not yet been reported. In this paper, a series of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) ternary alloys were prepared by a powder sintering method, and the influence of partial substitution of La for Mg on the crystal structure and electrochemical properties of the alloys was investigated and reported.

## 2. Experimental

The $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) alloys were prepared by sintering the pressed powder mixture (3.0 g) of $LaNi_5$, $LaNi_3$, $MgNi_2$ and Ni (in suitable weight % ratio) at 600–1000 °C in 1.0 MPa Ar for 6 h, followed by annealing at 750 °C under Ar for 3 days to ensure good homogeneity. The starting alloys, $LaNi_5$ and $LaNi_3$ were prepared by induction melting followed by annealing at 750 or 1000 °C

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for 5 days. And the starting $MgNi_2$ alloy was prepared by sintering Mg and Ni powders at 850 °C in 1.0 MPa Ar for 12 h. All the starting metal powders had a purity higher than 99.5%. The X-ray powder diffraction patterns for the starting alloys $LaNi_5$, $LaNi_3$ and $MgNi_2$ agreed well with the data in JCPDS tables.

Alloy samples were ground mechanically to powder below 300 meshes. The X-ray diffraction (XRD) measurements were conducted on a Rikagu D/Max PC2500 X-ray diffractometer with Cu Kα radiation. The pellet-type alloy electrodes ($d$=10 mm) were prepared by cold pressing the mixture of alloy powder and nickel powder in a weight ratio of 1:4, and the cell assemblies for the electrochemical tests were the same as those reported in a previous paper [11]. All electrochemical measurements were conducted at 25 °C. For activation and charge/discharge cycling, each electrode was charged at 300 mA/g for 2 h, followed by discharging at 100 mA/g to −0.6 V vs. Hg/HgO. High-rate dischargeability (HRD) was determined from a ratio of the discharge capacity at a given discharge current density (400–1200 mA/g) to the discharge capacity at 100 mA/g. The electrochemical P–C isotherms at 25 °C were measured using the pulse charge/discharge method at 25 mA/g, and the equilibrium hydrogen pressure $P_{eq}$ was calculated from the measured equilibrium electrode potential $E_{eq}$ according to the Nernst equation [12]:

$$E_{eq}\ (\text{V vs. Hg/HgO}) = -0.925 - 0.03\log(P_{eq}).$$

## 3. Results and discussion

### 3.1. Crystal structure

Fig. 1 shows the XRD patterns of $La_xMg_{3-x}Ni_9$ ($x$=1.0–2.0) alloys. It can be seen that except for a few small peaks due to the impurity phases ($LaNi_5$ and $MgNi_2$), all the other peaks can be identified as the hexagonal $PuNi_3$-type structure with the unit cell dimensions shown in Table 1. The cell parameters of $LaMg_2Ni_9$ prepared in this study are very close to the previously reported data [3], and the progressive La substitution for Mg, which changes the formula of the alloy from $LaMg_2Ni_9$ to $La_2MgNi_9$ leads to an increase of both $a$ parameter (+1.94%) and $c$ parameter (+1.85%) and a subsequent expansion of the unit cell volume (+5.83%) owing to the atomic radius of La (2.74 Å) being larger than that of Mg (1.72 Å). The value of $c/a$ remained constant, being about 4.82 when the unit cell volume ($Å^3$) expanded from 503.3 ($x$=1.0) to 532.7 ($x$=2.0). It indicates that the structure of these alloys was kept isotropic when the cell expanded. Our results of Rietveld refinement, which will be presented in another paper, indicate that La atoms occupy the 3$a$ and Mg atoms occupy the 6$c$ sites, respectively, in $LaMg_2Ni_9$, but with the increase of La content in the alloys ($x$>1.0), some La atoms also occupy the 6$c$ sites.

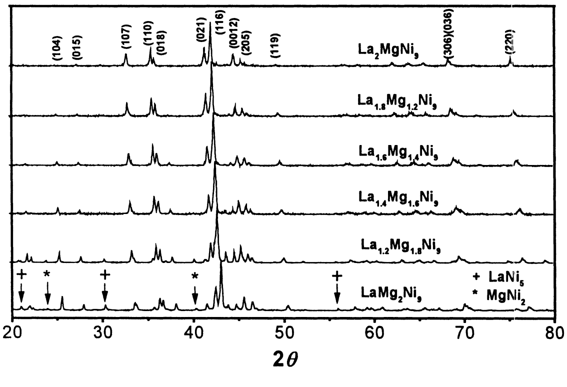

Fig. 1. X-ray diffraction patterns for the as-prepared $La_xMg_{3-x}Ni_9$ ($x$=1.0–2.0) alloys.

Table 1
Crystallographic data for $La_xMg_{3-x}Ni_9$ ($x$=1.0–2.0) alloys

| Alloys | Unit cell dimensions (Å) | | | Unit cell volume $V$ ($Å^3$) |
|---|---|---|---|---|
| | $a$ | $c$ | $c/a$ | |
| $x$=1.0 | 4.9380(3) | 23.8359(9) | 4.83 | 503.3 |
| $x$=1.2 | 4.9685(2) | 23.9410(8) | 4.82 | 511.8 |
| $x$=1.4 | 4.9818(3) | 23.9967(11) | 4.82 | 515.8 |
| $x$=1.6 | 5.0040(2) | 24.1020(8) | 4.82 | 521.9 |
| $x$=1.8 | 5.0162(2) | 24.1839(7) | 4.82 | 527.0 |
| $x$=2.0 | 5.0336(4) | 24.2759(14) | 4.82 | 532.7 |

### 3.2. Electrochemical properties

Fig. 2 shows the electrochemical P–C isotherms of the $La_xMg_{3-x}Ni_9$ ($x$=1.0–2.0) alloys at 25 °C. The results illustrate that with increasing La/Mg ratio (from $x$=1.0 to 2.0) in the alloys, the plateau pressure for hydrogen absorption and desorption lowers noticeably (desorption plateau pressure decreased from 2.5 to ~0.06 atm), and the plateau region becomes much wider and flatter, leading to the increase of the hydrogen storage capacity (H/M) from 0.17 to 1.05. This means that the La-rich alloys form the more stable hydrides and have a greater number of

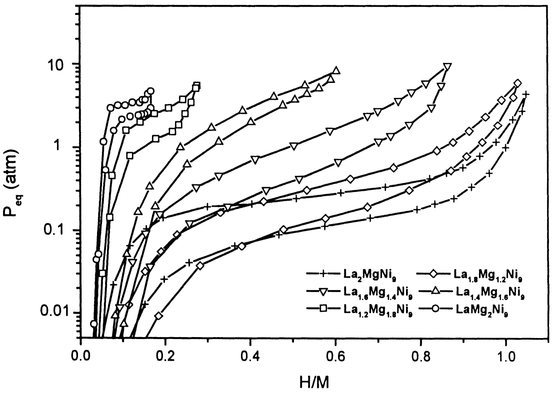

Fig. 2. The electrochemical isotherms of $La_xMg_{3-x}Ni_9$ ($x$=1.0–2.0) alloys at 25 °C.

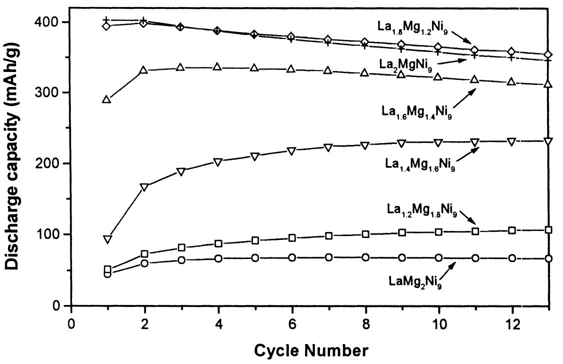

Fig. 3. Activation profiles of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) electrodes (25 °C, discharge at 100 mA/g).

available sites for hydrogen storage than the Mg-rich alloys because the unit cell volume increases with increasing La/Mg ratio.

Fig. 3 shows the activation profiles of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) alloy electrodes. It can be seen that the La-rich alloys ($x=1.6$–$2.0$) can be easily activated to their maximum discharge capacity within three cycles, while the Mg-rich alloys ($x<1.6$) need about 6–10 cycles. Among the electrodes studied, the $LaMg_2Ni_9$ electrode exhibits the lowest discharge capacity of 68.4 mAh/g, which is very close to the reported hydrogen absorption capacity ($H/M=0.2$, at 30 °C) [6]. However, as the La/Mg ratio in the alloys increases, the discharge capacity of these electrodes greatly increases also. The discharge capacity of $La_{1.6}Mg_{1.4}Ni_9$ electrode goes up to 335 mAh/g, while that of the $La_{1.8}Mg_{1.2}Ni_9$ and $La_2MgNi_9$ electrode reach 398 and 403 mAh/g, respectively, which are notably larger than that of the commercialized $AB_5$-type alloys. The higher discharge capacity of the La-rich alloys is attributed to the increased H/M values and the decreased plateau pressure ($<1$ atm), both being advantageous for electrochemical application.

Fig. 4 illustrates the effect of the discharge current density (100–1200 mA/g) on the discharge capacity of the three La-rich alloy electrodes ($x=1.6$–$2.0$) with initial capacities all higher than 330 mAh/g. It is found that among these electrodes $La_2MgNi_9$ electrode has the best high-rate dischargeability. At the discharge rate of 400 mA/g, the high-rate dischargeability (HRD) of $La_2MgNi_9$ electrode reaches 95.5%, and it was 89.9% and 85.8% for the $La_{1.6}Mg_{1.4}Ni_9$ and $La_{1.8}Mg_{1.2}Ni_9$ electrode, respectively. When the discharge rate goes up to 1200 mA/g, the HRD of the $La_{1.6}Mg_{1.4}Ni_9$ and $La_{1.8}Mg_{1.2}Ni_9$ electrodes reduce to much lower values (58.4–64.3%) than that of the $La_2MgNi_9$ electrode (80.7%). This may be due to the higher rate of decrepitation and the better catalytic activity of the $La_2MgNi_9$ alloy than the other two alloys.

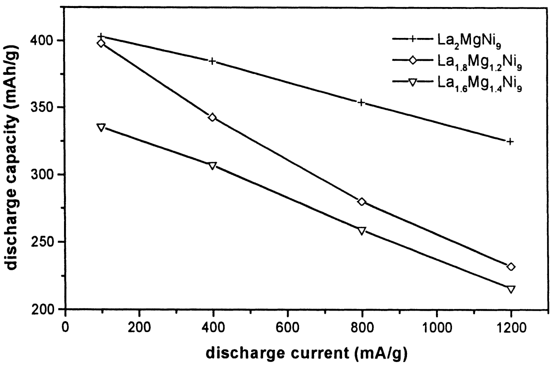

Fig. 4. Discharge capacities of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) electrodes versus the discharge current densities at 25 °C.

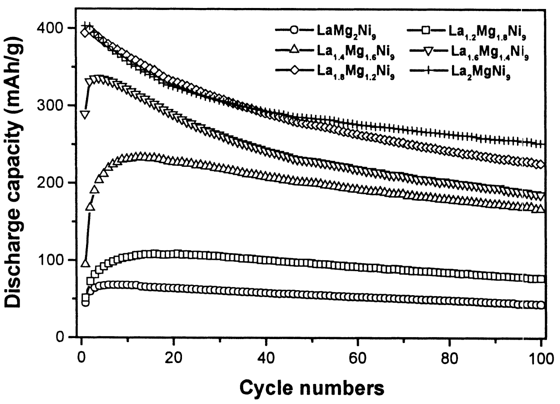

Fig. 5. Cycling stability of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) electrodes (25 °C, discharge at 100 mA/g).

Fig. 5 shows the cycling stability of $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) alloy electrodes. The results reveal that the increase of La/Mg ratio in the alloys results in a faster cycling capacity degradation or a lower capacity retention rate $S_{100}$ (%) as denoted by the ratio of the discharge capacity after being cycled 100 cycles to the maximum capacity after being fully activated. It is found that the capacity retention rate ($S_{100}$) of the Mg-rich electrodes ($x=1.0$–$1.4$) with lower initial capacities reaches 63–71% at the discharge current density of 100 mA/g, while the $S_{100}$ of the La-rich electrodes ($x=1.6$–$2.0$) with a higher initial capacity ($>330$ mAh/g) drops to 55–62%, suggesting that the La-rich alloys have a higher degree of decrepitation and hence a higher corrosion rate than that of the Mg-rich alloys. In addition, the difference in rate of capacity decay is also attributable to the difference of the change in phase structure of the alloys during the repeated cycling. Further investigation in the degradation mechanism and optimization in both alloy composition and phase structure to improve the cycling stability of these alloys is in progress.

## 4. Conclusions

The $La_xMg_{3-x}Ni_9$ ($x=1.0$–$2.0$) alloys with different La/Mg ratio are confirmed to be of the $PuNi_3$-type structure. It is found that the unit cell dimensions and electrochemical properties are influenced largely by the La/Mg ratio in the alloys. Among the alloys studied, the $La_{1.8}Mg_{1.2}Ni_9$ and $La_2MgNi_9$ alloys show the largest discharge capacity (~400 mAh/g), the most rapid activation and good high-rate dischargeability, but higher capacity decay in cycling. The results suggest that the La–Mg–Ni-based $AB_3$-type alloys are good potential candidates for the negative electrode materials for Ni/MH batteries if the cycle life of the alloys is further improved.

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