Preparation and Electrochemical Hydrogen Storage of the Nanocrystalline $LaMg_{12}$ Alloy with Ni Powders

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Many alloys are capable of reversibly storing large amounts of hydrogen via absorbing gaseous hydrogen at certain pressure and temperatures or by electrochemistry to form metal hydride (MH).[1] Rechargeable alkaline Ni−MH batteries using metal hydride as negative materials have become the dominant advanced battery technology for portable electronic devices, electric tools, electric vehicle (EV), and hybrid electric vehicle (HEV) applications due to their high reversible energy storage capacity, excellent long-term cycling stability, and good electrochemical reaction kinetics. The various alloy families including AB_5, AB_2, AB, AB_3, Mg-based alloy, V-based solid solution, and their composites have been largely investigated as negative materials of Ni/MH batteries.[2−11] Recently, numerous investigations have been conducted to search for a new hydrogen storage alloy with a desire to have a high discharge capacity for performance improvements of Ni/MH batteries. Mechanical alloying (MA) is a way to synthesize new alloy materials with a metastable amorphous or nanocrystalline structure. It was found that amorphous Mg-based alloys after being ball-milled were formed which could be charged and discharged readily at room temperature and showed a high discharge capacity of 500 mA·h/g.[7] The amorphous quaternary $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy ball-milled with Ni powders in a weight ratio of 1:1 for 50 h was also demonstrated to have a high electrochemical capacity of about 1000 mA·h/g ($La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ as active materials).[12]

The $LaMg_{12}$ intermetallic compound is a promising candidate as a hydrogen storage material since it has a high hydrogen storage capacity of 3.7−5.5 wt %.[13,14] However, the practical hydrogen absorption and desorption process of $LaMg_{12}$ intermetallic compound at high temperature and high hydrogen pressure is hard to carry out due to an irreversible or disproportionation reaction as shown below:

$$2LaMg_{12} + 27H_2 \rightarrow 2LaH_3 + 24MgH_2$$

$$2LaH_3 + 24MgH_2 \leftrightarrow 2LaH_x + 24Mg + (27-x)H_2$$

Among all hydrogen storage alloys as negative electrode materials, metallic Ni is indispensable due to its high electrocatalytic activity and good corrosion resistance in an alkaline solution. Therefore, addition of metallic Ni in La−Mg intermetallic compounds is essential for decreasing the hydride stability, improving the poor electrocatalytic activity, and enhancing the corrosion resistance of Mg in electrochemical reactions. In this communication, we made an attempt to prepare the nanocrystalline alloys through ball-milling $LaMg_{12}$ alloys with Ni powders and to investigate their electrochemical properties to search for new negative materials.

The $LaMg_{12}$ alloy was synthesized through a melt−salt−cover−melting process by melting a stoichiometric mixture of metallic La and Mg and then pulverizing the ingot to 200 mesh. Negative electrode materials were prepared by further mechanical milling of $LaMg_{12}$ alloy and carbonyl nickel powders (255 INCO). The ratio of carbonyl nickel powders and $LaMg_{12}$ alloys by weight was set to be 1.5, 2, and 3 (total mass of 6 g), respectively. All ball-milling processes were performed with a weight ratio of ball to powders of 20:1 at 580 rmp in a cyclohexane solution in a planetary-type ball-mill for 11 h. The microstructure analysis of the alloy powders was performed by X-ray diffraction (XRD, Rigaku D/max-2500) and transmission electron microscopy (TEM, FEI Tecnai 20). Negative electrodes were constructed through mixing as-prepared composites with carbonyl nickel powders in a weight ratio of 1:3. The powder mixture was pressed under 30 MPa pressure into a small pellet of 10 mm in diameter and 1.5-mm thick. Electrochemical measurements were conducted in a three-compartment cell using a Land battery test instrument. A sintered nickel electrode with a large capacity and an Hg/HgO electrode in a 6 M KOH solution served as counter and reference electrodes, respectively. The electrodes were charged at a current density of 1000 mA/g for 80 min and then discharged at a current density of 50 mA/g to −0.6 V (vs Hg/HgO)

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(1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.
(2) Willems, J. J. G. *Philips J. Res.* **1984**, *39*, 1.
(3) Kuriyama, N.; Sakai, T.; Miyamura, H.; Uehara, I.; Ishikawa, H. *J. Alloys Compd.* **1993**, *202*, 183.
(4) Park, H. Y.; Chang, I.; Cho, W. I.; Cho, B. W.; Jang, H.; Lee, S. R.; Yun, K. S. *Int. J. Hydrogen Energy* **2001**, *26*, 949.
(5) Gao, X. P.; Song, D. Y.; Zhang, Y. S.; Zhou, Z. X.; Zhang, W.; Wang, M.; Shen, P. W. *J. Alloys Compd.* **1995**, *229*, 268.
(6) Jurczyk, M.; Jankowska, E.; Nowak, M.; Jakubowicz, J. *J. Alloys Compd.* **2002**, *226*, 265.
(7) Lei, Y. Q.; Wu, Y. M.; Yang, Q. M.; Wu, J.; Wang, Q. D. *Z. Phys. Chem.* (*Munich*) **1994**, *183*, 379.
(8) Kuriyama, N.; Chartouni, D.; Tsukahara, M.; Takahashi, K.; Takeshita, H. T.; Tanaka, H.; Schlapbach, L.; Sakai, T.; Uehara, I. *Electrochem. Solid-State Lett.* **1998**, *1*, 37.
(9) Chen, J.; Kuriyama, N.; Takeshita, H. T.; Tanaka, H.; Sakai, T.; Haruta, M. *Electrochem. Solid-State Lett.* **2000**, *3*, 249.
(10) Pan, H. G.; Liu, Y. F.; Gao, M. X.; Zhu, Y. F.; Lei, Y. Q. *Int. J. Hydrogen Energy* **2003**, *28*, 1219.
(11) Gao, X. P.; Wang, F. X.; Liu, Y.; Pan, G. L.; Li, S.; Qu, J. Q.; Wu, F.; Yuan, H. T.; Song, D. Y. *J. Electrochem. Soc.* **2002**, *149*, A1616.
(12) Chen, Y.; Sequeira, C.; Chen, C. P.; Wang, Q. D.; *J. Alloys Compd.* **2003**, *354*, 120.
(13) Pal, K. *Int. J. Hydrogen Energy* **1997**, *22*, 799.
(14) Sun, D. L.; Gingl, F.; Nakamura, Y.; Enoki, H.; Bououdina, M.; Akiba, E. *J. Alloys Compd.* **2002**, *333*, 103.

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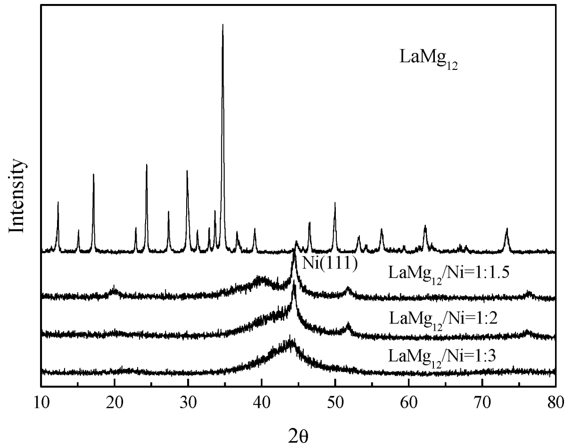

Figure 1. X-ray diffraction patterns of the as-cast $LaMg_{12}$ and the ball-milled $LaMg_{12}$ alloy with Ni powders.

after resting for 5 min at room temperature. When the discharge capacity was calculated, only the weight of $LaMg_{12}$ hydrogen storage alloys was considered as active materials. The electrochemical impedance spectroscopy (EIS) was taken after fully charging using a Solartron 1287 potentiostat and a Solartron 1250 frequency response analyzer. The working electrodes for EIS experiments were constructed from porous nickel with an apparent surface of 1.0 cm^2.

The XRD patterns of the as-cast $LaMg_{12}$ alloy and the ball-milled $LaMg_{12}$ alloys with Ni powders are shown in Figure 1. Earlier, it was shown that all peaks in the pattern of the as-cast $LaMg_{12}$ alloy can be indexed as a body-centered orthorhombic structure with a space group of *Immm*.[14] The calculated lattice parameters of the $LaMg_{12}$ alloy were $a = 10.29 \pm 0.01$ Å, $b = 10.36 \pm 0.01$ Å, and $c = 77.13 \pm 0.03$ Å. The diffraction peaks merged and broadened after mechanical grinding of the as-cast $LaMg_{12}$ alloy with Ni powders, indicating that the crystalline structure has transformed into an amorphous or nanocrystalline structure to a certain extent except for a small amount of residual crystalline metallic Ni. As shown in Figure 1, the diffraction intensity of crystalline metallic Ni decreased with increasing the Ni amount in the samples of the ball-milled $LaMg_{12}$ alloy. This means that the larger content of Ni powders is important to amorphism or nanocrystallization. TEM images of the as-cast $LaMg_{12}$ alloy and the ball-milled samples are shown in Figure 2. As identified from the inserted SAED, the as-cast $LaMg_{12}$ alloy had a perfect single-crystalline structure in agreement with the XRD analysis. The ring patterns were observed from inserted SAED (Figure 2b,c), demonstrating that the $LaMg_{12}$ alloys ball-milled with Ni powders had a polycrystalline or nanocrystalline structure. TEM observation to identify the existence of nanosized metallic Ni particles in the ball-milled alloys is more sensitive as compared to XRD analysis. It was observed that the smaller inlaid metallic Ni particles with fine crystallites of 10−20 nm in diameter were dispersed through a La−Mg amorphous alloy matrix, although XRD peaks of fine metallic Ni crystallites were not observed in the XRD pattern in the case of $LaMg_{12}/Ni = 1/3$. Similarly, metallic Ni particles with smaller sizes in Mg-based nanocrystalline alloys and La_2Mg_{17}−Ni composites can still be identified from TEM observation in the case of the vanishing of all crystalline peaks in the XRD pattern.[15,16] It was worth noting that the addition of metallic Ni powders in a $LaMg_{12}$ alloy was beneficial to the formation of highly dispersed nanocrystalline alloys and decreasing of the hydride stability consequently.

The first charge/discharge curves of all the ball-milled samples are illustrated in Figure 3. The charge acceptance of the $LaMg_{12}$ alloys ball-milled with Ni powders in the first charging under a current density of 1000 mA/g was found to have increased remarkably with increasing the Ni content. The first discharge capacity of the $LaMg_{12}$ alloys ball-milled with Ni powders in a weight ratio of 1:3 was near 1010 mA•h/g, corresponding to a hydrogen storage capacity of 3.77 wt %. The enhanced discharge capability of the samples probably contributed to the formation of the metallic Ni particles highly dispersed through a nanocrystalline alloy matrix. Moreover, it should be noted that the stability of the metal hydride decreased with the increase of instable hydride elements in alloys such as Ni. The larger content of Ni addition can decrease the stability of $LaMg_{12}$ hydride to a large extent and contribute to the enhanced discharge capacity.

To evaluate electrochemical kinetics of the $LaMg_{12}$ alloy ball-milled with Ni powders, electrochemical impedance spectra are measured and indicated in Figure 4. Clearly from the impedance spectra, the electrochemical reaction kinetics was varied with increasing the Ni content in ball-milled $LaMg_{12}$ alloys. For the $LaMg_{12}$ alloy ball-milled with Ni powders in a weight ratio of 1:1.5, there were a semicircle and a slope related to the Warburg impedance in the low-frequency region, which meant that there was an obvious hydrogen diffusion process. The electrochemical reaction was under the control of both surface charge transfer and a hydrogen diffusion process. In the case of $LaMg_{12}/Ni = 1:3$, however, only a semicircle was observed in the low-frequency region in the case of $LaMg_{12}/Ni = 1:3$. This suggested that the rate-determining step should be dominated by the surface charge transfer. It was

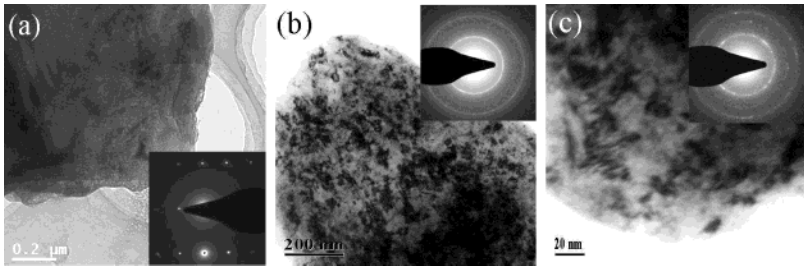

Figure 2. TEM image of the as-cast $LaMg_{12}$ (a) and ball-milled $LaMg_{12}$ alloy with Ni powders in the bright field with selected area electron diffraction (SAED) (weight ratio, $LaMg_{12}/Ni = 1/2$ (b); $LaMg_{12}/Ni = 1/3$ (c)).

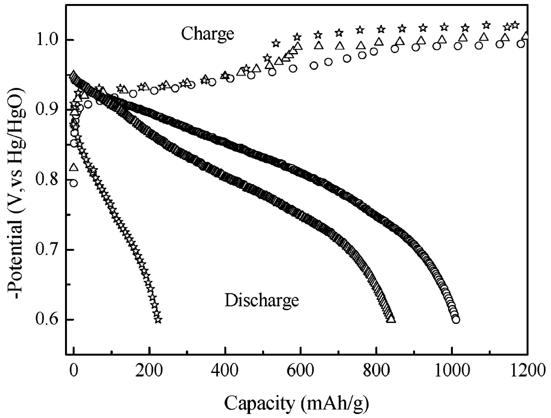

Figure 3. The first charge and discharge curves of ball-milled $LaMg_{12}$ alloy with Ni powders (weight ratio: ☆, $LaMg_{12}/Ni = 1/1.5$; △, $LaMg_{12}/Ni = 1/2$; ○, $LaMg_{12}/Ni = 1/3$).

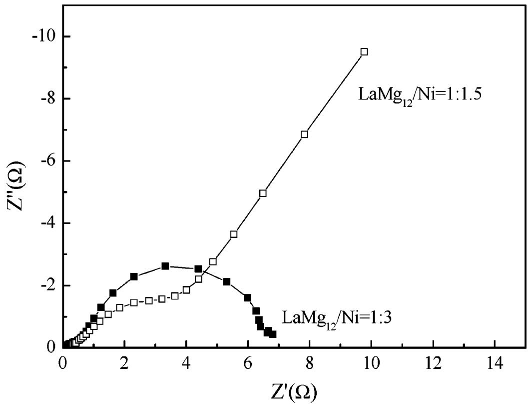

Figure 4. Electrochemical impedance spectra of ball-milled $LaMg_{12}$ alloy with Ni powders.

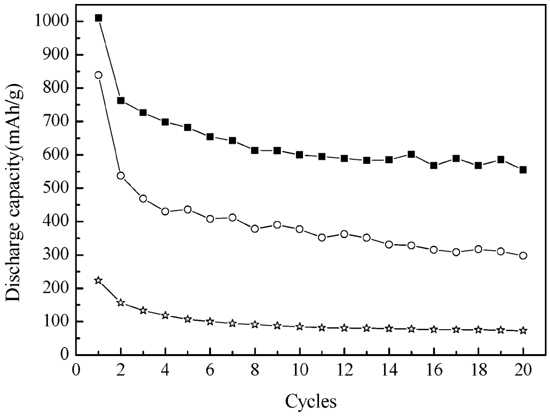

Figure 5. Cycle performance of ball-milled $LaMg_{12}$ alloy with Ni powders (weight ratio: ☆, $LaMg_{12}/Ni = 1/1.5$; ○, $LaMg_{12}/Ni = 1/2$; ■, $LaMg_{12}/Ni = 1/3$).

reported that the hydrogen diffusion rate was significantly enhanced at the grain–boundary interface in nanocrystalline nickel, where the electron density is the lowest.[17] The larger content of Ni addition could create a large amount of grain boundary and crystalline defects distributed through the La–Mg alloy matrix. Therefore, the hydrogen diffusion impedance in the electrode of $LaMg_{12}/Ni = 1:3$ became negligible.

The cycle performance of the $LaMg_{12}$ alloy ball-milled with Ni powders is shown in Figure 5. The capacity decay was serious before five cycles due to the corrosion of Mg in the electrolyte. This phenomenon was also observed in other amorphous or nanocrystalline Mg–Ni-based alloy and La_2Mg_{17}–Ni composite electrodes.[15,16,18] After five cycles, the slower deterioration of cycle stability could be explained by the existence of La,[19] where a La oxide layer restrained the fast corrosion of Mg in the electrolyte. On the other hand, the higher Ni content inlaid into the alloy surface layer also restricted the corrosion of Mg to a certain extent, thus enhancing the cycle stability of the composite electrode. Nevertheless, the cycle performances of the $LaMg_{12}$ alloy ball-milled with Ni powders need to be further improved to fulfill requirements as electrode materials in the practical application of Ni/MH batteries. In this work, the metallic Ni particles highly dispersed through a nanocrystalline alloy matrix still could not effectively maintain the stabilization of the electrode capacity due to further generation of a new interface and corrosion as well as oxidation of active constituent Mg during cycling in the electrolyte. Therefore, further investigations to stabilize the $LaMg_{12}$ alloy with multicomponent composition and surface modification are ongoing at our laboratory.

In summary, the $LaMg_{12}$-based nanocrystalline alloys were prepared by ball-milling $LaMg_{12}$ alloy with Ni powders. The inlaid metallic Ni particles with fine crystallites were dispersed through a La–Mg alloy matrix, which was identified to have a positive effect on improving the electrochemical hydrogen storage on account of the high electrocatalytic activity of active metallic Ni particles. The first discharge capacity of the $LaMg_{12}$ alloy ball-milled with Ni powders in a weight ratio of 1:3 reached up to 1010 mA·h/g, although the cycle performance of the nanocrystalline alloy electrode at present has to be further improved for practical application in Ni/MH batteries. It is concluded that the nanocrystalline alloys prepared through mechanical alloying of intermetallic compounds with a high hydrogen storage capacity would be interesting and new negative materials for Ni/MH batteries.

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(15) Cui, N.; He, P.; Luo, J. L. *Electrochim. Acta* **1999**, *44*, 3549.

(16) Gao, X. P.; Lu, Z. W.; Wang, Y.; Wu, F.; Song, D. Y.; Shen, P. W. *Electrochem. Solid-State Lett.* **2004**, *7* (5), A102.

(17) Szpunar, B.; Lewis, L. J.; Swainson, I.; Erb, U. *Phys. Rev. B* **1999**, *60*, 10107.

(18) Sun, L.; Liu, H. K.; Bradhurst, D. H.; Dou, S. X. *Electrochem. Solid-State Lett.* **1999**, *2*, 164

(19) Vogt, T.; Reilly, J. J.; Johnson, J. R.; Adzic, G. D.; McBreen, J. *J. Electrochem. Soc.* **1999**, *146*, 15.