Short Communication

Effects of yttrium substitution for magnesium on the electrochemical performances of La$_2$Mg$_{1-x}$Y$_x$Ni$_{8.8}$Co$_{0.2}$ hydrogen storage alloys

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A R T I C L E   I N F O

Article history:
Received 14 November 2018
Accepted 15 May 2019

Keywords:
Energy storage and conversion
Elemental substitution
Metals and alloys
Ni/MH battery

A B S T R A C T

The effects of yttrium substitution for magnesium in the La$_2$Mg$_{1-x}$Y$_x$Ni$_{8.8}$Co$_{0.2}$ hydrogen storage alloys on the electrochemical properties are investigated in this paper. Yttrium substitution in the alloys can significantly improve the cycle stability, although the discharge capacity was decreased. The capacity and retention capacity after 20th cycle of the La$_2$Mg$_{0.9}$Y$_{0.1}$Ni$_{8.8}$Co$_{0.2}$ alloys achieved values above 370 mAh/g and 95%, respectively, which already exceed those of most hydrogen storage alloys with A$_2$B$_7$ or A$_3$B$_2$ structure. The charge-transfer resistance also reached the lowest when x was 0.1 in the La$_2$Mg$_{1-x}$Y$_x$Ni$_{8.8}$Co$_{0.2}$ alloy, resulting in the highest charge transfer rate.

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1. Introduction

Hydrogen energy has been considered as one of the most practical methods to solve some serious environment problems related to the increasing use of fossil fuels [1–3]. Rare earth-magnesium based alloys as an important hydrogen storage medium, specially associated with application in the nickel-metal hydride (Ni/MH) battery system, has attracted more attention. However, the relatively high volatility of magnesium can easily cause safety problems in the alloys melting process [4–10].

In order to solve the volatility problem of Mg during the preparation process, the effects of Y substitution for Mg in the La-Mg-Ni based hydrogen storage alloys have recently received recent attentions [11–13]. Baddour-Hadjj et al. [14] studied the La-Y-Ni ternary alloy, which is equivalent to an overall replacement of Mg in the LaMg$_2$Ni$_5$ alloy by the yttrium. A new type of hydrogen storage alloy with La$_2$Y$_2$Ni$_{10}$Mn$_{0.5}$ compositions was reported [12], and the max capacity could reach 391 mAh/g. Yan et al. [13] studied the structure and properties of various types of La-Y-Ni hydrogen storage alloys. Their comprehensive properties had the following order: A$_5$B$_{13}$-type > A$_2$B$_7$-type > AB$_3$-type. Yttrium in the
hydrogen storage alloy could increase the structural stability during the hydrogenation process and delay the hydrogen-induced degradation [15]. Therefore, the effects of yttrium substitution for magnesium in the La2Mg1−xYxNi8.8Co0.2 alloys (x = 0, 0.05, 0.10, 0.15 and 0.20) alloys on the microstructures and electrochemical properties were studied in the work. We expected that some replacements of Mg could be developed to reduce the uncertainty during the preparing process of the Mg-contained hydrogen storage alloys.

2. Experimental and methods

The La2Mg1−xYxNi8.8Co0.2 alloys were prepared through an induction furnace with high-purity La, Mg, Y, Ni and Co metals (99.9 wt.%, GRINM, China) under pure argon atmosphere and followed heat-treatment at 1273 K for 15 days. The alloy particles with (30–40) μm were mixed with carbonyl nickel powder in a mass ratio of 1:4, and then they were cold pressed into the work electrode pellet with diameter of 10 mm and thickness of 1 mm under 15 MPa. The alloy phases were identified by X-ray diffraction (XRD, Rigaku, D/Max-2400, Japan). The diffraction peaks were analyzed using MDI JADE software through the Rietveld method. The surface microstructure is characterized through scanning electron microscope (SEM, JEOL JSM-IT300, Japan). The electrochemical experiments were performed at room temperature with a 6 M KOH electrolyte in a electrochemical workstation (CHINSTR, CHI760E, China) through a three electrodes system. The pellet electrode was the working electrode, the Ni(OH)2/NiOOH electrode was the counter electrode and Hg/HgO electrode was as the reference electrode. The electrode plates were fully charged at 100 mA g−1 for 8 h and discharged at 30 mA g−1 to −0.2 V in charge/discharge test.

3. Results and discussion

The XRD patterns of the La2Mg1−xYxNi8.8Co0.2 alloys are displayed in Fig. 1a. In these patterns, A8-type (LaNi5), AB2-type (YNi2 and MgNi2) and AB3-type (La2Ni3) phases make up a big part of the samples. Almost all the diffraction peaks of MgNi2 phase moved to the lower angles, the MgNi2 began to transform to YNi2 with the substitution of Y for Mg in the

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**Table 1 – Lattice constants and abundances of the La2Mg1−xYxNi8.8Co0.2 alloys.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Phase type</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>Abundance (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>LaNi5</td>
<td>5.020</td>
<td>3.988</td>
<td>87.02</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>La11.7</td>
<td>5.067</td>
<td>24.474</td>
<td>544.22</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>MgNi2</td>
<td>4.796</td>
<td>15.757</td>
<td>313.81</td>
<td>24</td>
</tr>
<tr>
<td>x = 0.05</td>
<td>LaNi5</td>
<td>4.980</td>
<td>4.050</td>
<td>86.98</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>La11.7</td>
<td>5.053</td>
<td>25.443</td>
<td>562.56</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>MgNi2</td>
<td>4.803</td>
<td>15.923</td>
<td>318.17</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>YNi2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>LaNi5</td>
<td>5.027</td>
<td>4.009</td>
<td>87.72</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>La11.7</td>
<td>5.074</td>
<td>24.521</td>
<td>546.8</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>MgNi2</td>
<td>4.818</td>
<td>15.753</td>
<td>316.66</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>YNi2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>LaNi5</td>
<td>4.991</td>
<td>3.991</td>
<td>86.1</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>La11.7</td>
<td>5.065</td>
<td>24.544</td>
<td>545.45</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>MgNi2</td>
<td>4.821</td>
<td>15.702</td>
<td>316.04</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>YNi2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>12</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>LaNi5</td>
<td>5.013</td>
<td>3.979</td>
<td>86.62</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>La11.7</td>
<td>5.064</td>
<td>24.547</td>
<td>545.23</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>MgNi2</td>
<td>4.826</td>
<td>15.743</td>
<td>317.17</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>YNi2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>14</td>
</tr>
</tbody>
</table>
Alloys. Significant amounts of YNi$_2$ phase appeared with the 2θ value of about 41.7 in the alloys when the $x$ was 0.1. The lattice parameters and phase abundance (wt.%) have been calculated using MDIJADE software through the Rietveld method, as shown in Table 1. The abundance of AB$_5$-type and A$_2$B$_7$-type phases are all decreasing with the increasing of yttrium contents, and the AB$_2$-type are increasing at the same time. However, there is no distinct rule in the distributions of the lattice parameters along with the yttrium contents. How to measure precisely these indexes are the key in the future research work. The SEM-EDS element mapping images of the $x = 0.1$ sample (La$_2$Mg$_{0.9}Y_{0.1}$Ni$_8.8$Co$_{0.2}$) are illustrated in Fig. 1b. The pictures show that all the elements are distributed equally on the alloy surface.

The electrochemical hydrogen capacities of the La$_2$Mg$_{1-x}$Y$_x$Ni$_8.8$Co$_{0.2}$ alloys are shown in Fig. 2a. The highest
discharge capacity was decreased slightly with the increasing of Y content in the alloys, but the capacity cycle stability was effectively improved with the substitution process. The max capacity \((C_{\text{max}})\) and the retention capacity after 20th cycle \((S_{20})\) of the La\(_2\)Mg\(_{0.9}\)Y\(_{0.1}\)Ni\(_{8.8}\)Co\(_{0.2}\) alloys can reach above 370 mAh/g and 95%, respectively. We also summarized the capacity and cyclic stability data of the typical hydrogen storage alloys electrodes with AB\(_3\) or A\(_2\)B\(_7\) types which have been reported in the previous papers, as shown in Fig. 2b. Comparing to these alloys, the comprehensive performances of the La\(_2\)Mg\(_{0.9}\)Y\(_{0.1}\)Ni\(_{8.8}\)Co\(_{0.2}\) alloy has already surpassed the most alloys without Y element, especially in the cyclic stability properties.

The discharge voltage curves of the alloy electrodes for the max capacity are displayed in Fig. 2c. The results showed that the alloy electrodes have the higher platform voltages and remain almost constant when the x value is below 0.15 \((x<0.15)\). At the beginning, Y-based compounds can be existed evenly and independently in the alloys, and they may be used as "the intermediate catalyst" to improve the hydrogenation reactions. With the further increasing of the Y content in the alloys the voltage reduced sharply due to the excess generation of Y-based compounds. Comparing to the commercial AB\(_5\) type alloy, the La\(_2\)Mg\(_{0.9}\)Y\(_{0.1}\)Ni\(_{8.8}\)Co\(_{0.2}\) hydrogen storage alloy exhibited the much higher discharge capacity (by about 15%) and platform voltage (Fig. 2d).

The XRD images of the alloy electrode after the 1st charging and discharging process for the La\(_2\)Mg\(_{0.9}\)Y\(_{0.1}\)Ni\(_{8.8}\)Co\(_{0.2}\) sample are also investigated in Fig. 2e. The diffraction peaks of some hydrides with low intensity, such as LaH\(_{2.3}\), MgH\(_2\) and Mg\(_2\)NiH\(_4\), will be formed after charging, and they have almost disappeared after the discharging process. However, the diffraction peaks after the discharging process became weakened and broadened, and shifted toward to the left, this shows that some hydrogen atoms are still in the alloy electrode.

Cyclic voltammograms are shown in Fig. 3a. The oxidation current density of the Y substitution samples comparing to the original is getting smaller with the increase of Y content. Tafel polarization curves of the alloys are displayed in Fig. 3b. The corrosion potential of the alloy electrodes has a more positive value with the Y substitution for Mg in the system, which illustrated that the Y-contained alloy electrode has a much better anti-corrosion abilities. This is an important reason for the improvement of the capacity cycle stability. The similar results were also obtained in some previous studies [27]. The electrochemical impedance spectra (EIS) for the different samples at 50% discharge depth are shown in Fig. 3c. As shown in this figure, the charge-transfer resistance \((R_{\text{ct}})\) first decreases and then increases with the Y content increasing in the alloys. The lowest \(R_{\text{ct}}\) values will be achieved when \(x\) was 0.1, resulting in the highest hydrogen diffusion rate. The alloys after moderate substitution process can show a much lower \(R_{\text{ct}}\) owning to their higher electrical conductivity and catalytic activity. These results will be associated with the comprehensive properties for the La\(_2\)Mg\(_{0.9}\)Y\(_{0.1}\)Ni\(_{8.8}\)Co\(_{0.2}\) alloys.

![Fig. 3](image-url) - Electrochemical performances of the La\(_2\)Mg\(_{1-x}\)Y\(_x\)Ni\(_{8.8}\)Co\(_{0.2}\) samples. (a) Cyclic voltammetry curves; (b) Tafel curves; (c) EIS curves.
4. Summary and conclusions

In conclusion, the effects of yttrium substitution for magnesium in the La$_3$Mg$_{1-x}$Y$_x$Ni$_8$Co$_{0.2}$ were investigated in the paper. The YNi$_2$ phase begins to precipitate in the alloys when x = 0.1. The maximum capacity and the retention capacity after 20th cycle of the La$_2$Mg$_{0.9}$Y$_{0.1}$Ni$_8$Co$_{0.2}$ alloys can reach values above 370 mAh/g and 95%, respectively. Comparing to the typical A$_2$B$_7$- and A$_2$B$_5$-type hydrogen storage alloys, the main properties of the present investigated alloys have, by far, exceeded the corresponding ones of the typical alloys. The present alloys after moderate substitution can show a much lower charge-transfer resistance owing to the catalytic activity and higher electrical conductivity.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgment

The research funded by the Zhejiang Provincial Natural Science Foundation (LY19E010008 and LQ18E010001).

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