The improved electrochemical properties of novel La–Mg–Ni-based hydrogen storage composites

Hai-Liang Chu a,b, Shu-Jun Qiu a,b, Li-Xian Sun a,c,*, Yao Zhang a,*, Fen Xu a,
Tao Jiang a,b, Wei-Xue Li d, Min Zhu e, Wang-Yu Hu f

a Materials and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
b Graduate School of Chinese Academy of Sciences, Beijing 100049, China
c Department of Chemistry, Institute of Nanochemistry, Jinnan University, Guangzhou 510632, China
d State Key Laboratory of Catalysis and Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
e School of Mechanical Engineering, South China University of Technology, Guangzhou 510641, China
f Department of Applied Physics, Hunan University, Changsha 410082, China

Received 9 February 2007; received in revised form 20 April 2007; accepted 21 April 2007
Available online 3 May 2007

Abstract

In the present study, a novel alloy composite has been synthesized by ball milling nonstoichiometric AB₃-type La₀.7Mg₀.3Ni₃.5 alloy with Ti₀.17Zr₀.08V₀.35Cr₀.1Ni₀.3 alloy in order to improve the cyclic stability and other electrochemical properties of La₀.7Mg₀.3Ni₃.5 alloy electrode. The phase structure, morphology and electrochemical performances of the composite have been investigated systematically. From X-ray diffraction (XRD) patterns, it can be found that the La₀.7Mg₀.3Ni₃.5 and Ti₀.17Zr₀.08V₀.35Cr₀.1Ni₀.3 alloys still retain their respective phase structures in the composite. Electrochemical studies show that the cyclic stability of the composite electrode is noticeably improved after 100 charge–discharge cycles in comparison with single La₀.7Mg₀.3Ni₃.5 alloy electrode due to enhanced anti-corrosion performance in the alkaline electrolyte. The discharge capacity retention rate C₁₀₀/Cₘₐₓ of composite electrode is 62.3%, which is much higher than that of the La₀.7Mg₀.3Ni₃.5 alloy electrode, although the maximum discharge capacity of the former decreases moderately. Both electrochemical impedance spectra (EIS) and linear polarization (LP) studies indicate that the electrochemical kinetics of the composite electrode is also improved. The charge-transfer resistance (R_{ct}), the polarization resistance (R_p) and the exchange current density (I_0) of the composite electrode are 160.2 mΩ, 129.5 mΩ and 201.6 mA/g, respectively, which are superior to those of the La₀.7Mg₀.3Ni₃.5 alloy electrode.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Ni/MH batteries; La–Mg–Ni hydrogen storage alloy; Composite; Electrochemical properties; Electrochemical kinetics; Corrosion behaviors

1. Introduction

In recent years, the AB₃-type La–Mg–Ni-based hydrogen storage alloys were extensively studied as negative electrode candidates for Ni–MH secondary batteries due to their higher discharge capacities [1–8]. For example, the investigations on nonstoichiometric La–Mg–(NiCo)ₓ (x = 3–3.5) series alloys by Kohno et al. [1] indicated that the maximum electrochemical discharge capacity of the La₀.7Mg₀.3Ni₂.8Co₀.5 alloy reached 410 mAh/g, which was much higher than that of conventional AB₅-type hydrogen storage alloys. Chen et al. [5] investigated the structural and electrochemical characteristics of the LaCaMg(NiM)ₓ (M = Al, Mn) alloys which reached a maximum discharge capacity of 356 mAh/g. However, these La–Mg–Ni-based hydrogen storage alloy electrodes suffer from serious degradation of discharge capacity during the charge–discharge cycles. In order to improve the cyclic stability of La–Mg–Ni-type hydrogen storage alloy electrodes, the partial substitution of nickel with many transition metals such as cobalt, manganese, iron, copper, aluminum, zinc, etc. [9–11] and the partial substitution of lanthanum with cerium [12,13] or zirconium [14] have been carried out extensively. However,
the cyclic stability of the alloy electrodes is still unsatisfactory.

Meanwhile, the Ti–V-based multiphase hydrogen storage alloys were paid much attention, which generally consist of a C14 Laves phase and a V-based solid solution phase. The V-based solid solution phase is the major hydrogen-absorbing phase, while the C14 Laves phase is not only a hydrogen-absorbing phase, but also works as a catalyst for the electrochemical hydrogenation and dehydrogenation process of the V-based phase [15–17]. The synergistic effect of the two phases gives the alloy a favorable electrochemical performance, especially the discharge capacity. Moreover, the Ti–V-based alloy electrodes have improved cyclic stability during the charge–discharge cycles. For example, the discharge capacity retention after 50 cycles of Ti0.17Zr0.08V0.35Cr0.1Ni0.3 alloy electrode is 97% and 95% at 303 K and 313 K, respectively [18]. Therefore, it can be expected that the overall electrochemical properties, especially the cyclic stability, of the La–Mg–Ni-type hydrogen storage alloys could be improved through the formation of composite with Ti–V-based multiphase hydrogen storage alloy.

In this paper, the La0.7Mg0.3Ni3.5 and Ti0.17Zr0.08V0.35Cr0.1Ni0.3 alloys were served as parent alloys and the composite was successfully prepared by ball milling the mixture of both alloys powder. The structure, corrosion behaviors and the electrochemical properties of the as-prepared composite were investigated systematically.

2. Experimental

Hydrogen storage alloys of nominal composition La0.7Mg0.3Ni3.5 and Ti0.17Zr0.08V0.35Cr0.1Ni0.3 were prepared by vacuum magnetic levitation melting under high purity argon atmosphere from component metals with the purity all above 99.5%. To assure the homogeneity of these two alloys, the ingots were turned over and remelted three times. The ingot was thus mechanically crushed in air and ground into the powder of 200-mesh size. The composite was prepared by ball milling the homogeneous mixture of La0.7Mg0.3Ni3.5 and Ti0.17Zr0.08V0.35Cr0.1Ni0.3 in the weight ratio of 1:1, which was performed upon QM-1SP planetary ball miller under 0.2–0.3 MPa argon atmosphere for 10 min. In each stainless milling pot, the ball-to-powder weight ratio was 20:1. The crystal structure of the parent alloys and as-prepared composite was characterized by XRD (Rigaku D/max-2500, Cu Kα, 40 kV, 250 mA). The surface morphology of the composite was observed using scanning electron microscopy (SEM, JSM6360LV) linked with energy dispersive X-ray spectrometer (EDS, Oxford INCA).

The tested electrodes for electrochemical measurements were fabricated by mixing 100 mg alloy powder with 300 mg electrolytic Ni powder. The mixture was then pressed into a circular pellet of 10 mm in diameter under a pressure of 30 MPa. The electrode pellet was then pressed with two foam nickel sheets at a pressure of 6 MPa and tightly spot-welded. A nickel lead wire was attached to this pressed foam nickel sheet by spot welding. Electrochemical measurements were performed in a standard open tri-electrode electrolysis cell consisting of a working electrode (the MH pellet electrode for studying), a sintered Ni(OH)2/NiOOH counter electrode, and a Hg/HgO reference electrode. The temperature was controlled at 303 K (±0.5 K) and the electrolyte was 6 M KOH solution. Charge–discharge cycles of alloy electrodes were conducted by an automatic LAND battery test instrument (CT2001A). The electrodes were charged for 3 h at a current density of 300 mA/g, rested for 5 min and then discharged to the cut-off potential of −0.6 V (versus Hg/HgO reference electrode) at a current density of 100 mA/g.

The open circuit potentials of the electrodes were recorded immediately after immersing the electrode into the KOH solution until the potentials of the electrodes tend to be constant. The anodic polarization curves were measured at 0.1 mV/s from 0 mV to 20 mV (versus open circuit potential) after the electrodes were immersed in KOH solution for 10 h in order to obtain the corrosion current of the electrode. The linear polarization (LP) curves of the alloy electrodes were measured on a Zahner Elektrik IM6e electrochemical workstation by scanning the electrode potential at a rate of 0.1 mV/s from −5 mV to 5 mV (versus open circuit potential) at 50% depth of discharge (DOD). To investigate the alloy electrode kinetics, the electrochemical impedance spectroscopy (EIS) studies were conducted from 10 kHz to 5 mHz with an amplitude of 5 mV versus open circuit potential at 50% DOD using the IM6e electrochemical workstation. Before EIS measurements, the electrodes were first fully activated by charge/discharge for five cycles.

3. Results and discussion

3.1. The phase structure and morphology of the composite

Fig. 1 shows that X-ray diffraction patterns of the La0.7Mg0.3Ni3.5 alloy, Ti0.17Zr0.08V0.35Cr0.1Ni0.3 alloy, and the as-prepared composite. From Fig. 1(a), it is found that the La0.7Mg0.3Ni3.5 alloy mainly consists of the (LaMg)Ni3 phase with the PuNi3-type rhombohedral structure (space group R-3m), the LaNi5 phase with the CaCu5-type hexagonal structure (space group P6/mmm) and the LaNi phase with the orthorhombic CrB-type structure (space group Cmcm). This result is consistent with that reported by Pan et al. [19]. It is also found that the Ti0.17Zr0.08V0.35Cr0.1Ni0.3 alloy is mainly composed of V-based solid solution with BCC phase (space group Im3m) and C14 Laves phase with MgZn2-type structure (space group P63/mmc). After ball milling the powder mixture of La0.7Mg0.3Ni3.5 and Ti0.17Zr0.08V0.35Cr0.1Ni0.3 (weight ratio 1:1) for 10 min, both La0.7Mg0.3Ni3.5 and Ti0.17Zr0.08V0.35Cr0.1Ni0.3 basically maintain their respective original phase structures in the composite. No new phase forms in the composite after ball milling treatment according to the XRD detection.

Fig. 2 shows the SEM images and the corresponding EDS pattern of the composite. It is found that the composite particles are pulverized to the size of less than 50 μm. The EDS pattern of the micro-region in (b) is shown in (c). All elements in the composite are detected in the EDS pattern and their abundances agree with those of as-designed composite very well (see Table 1).
3.2. Discharge capacity and cyclic stability

Fig. 3 presents the discharge potential curves of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy, Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy, and the composite electrodes at the largest discharge capacity at 303 K. The maximum discharge capacities are 362.7 mAh/g and 335.7 mAh/g for La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode and Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy electrode, respectively. Moreover, they have different discharge potentials, i.e., $-0.8969$ V for La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode and $-0.8725$ V for Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy electrode at 50% depth of discharge (DOD). The composite electrode in this work has a maximum discharge capacity of 319.9 mAh/g and a discharge potential of $-0.8969$ V at 50% DOD. The discharge potential of the composite electrode is the same as that of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode and lower than that of Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy electrode ($\Delta E_{50\%\text{DOD}} = 0.0247$ V). This phenomenon indicates that the composite is not the simple mixture of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ and Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloys.

Fig. 4 exhibits cyclic stability curves of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy, and the composite electrodes at 303 K. The electrochemical characteristics of these two electrodes are summarized in

<table>
<thead>
<tr>
<th>Elements</th>
<th>La</th>
<th>Mg</th>
<th>Ni</th>
<th>Ti</th>
<th>Zr</th>
<th>V</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated (wt.%)$^a$</td>
<td>16.34</td>
<td>0.89</td>
<td>48.59</td>
<td>7.71</td>
<td>5.90</td>
<td>16.39</td>
<td>4.20</td>
</tr>
<tr>
<td>Experimental (wt.%)$^b$</td>
<td>15.68</td>
<td>1.17</td>
<td>48.84</td>
<td>7.26</td>
<td>6.50</td>
<td>15.89</td>
<td>4.64</td>
</tr>
</tbody>
</table>

$^a$ The values calculated from the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ and Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloys in the weight ratio of 1:1.

$^b$ The values from the EDS patterns.
Fig. 3. Discharge potential curves of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$, Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$, and the composite electrodes at the largest discharge capacity at 303 K.

Fig. 4. The cyclic stability curves of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy and the composite electrodes at 303 K.

Table 2. These electrodes can be fully activated within five charge-discharge cycles. It is found that the cyclic stability of the composite electrode is greatly enhanced compared with that of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy, though its maximum discharge capacity is lower than that of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy. For example, after 100 charge-discharge cycles, the discharge capacity retention rate of composite electrode increases significantly to 62.3%, which is much higher than that of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy. It indicates that the Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy in the composite plays an important role in improving cyclic stability of the composite electrode.

3.3. Corrosion behaviors of as-prepared composite electrode

The corrosion potentials of the electrodes were determined by open circuit potential measurements, which started immediately after the alloy electrodes immersed in KOH solution [20,21]. Fig. 5 is the plot of the open circuit potentials $V$ as a function of time $t$ for the electrodes. It can be seen that the open circuit potentials are stabilized after about 2 h. However, the curves of the open circuit potential versus time are totally different from each other, which indicate again that the composite is not the simple mixture of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ and Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloys. The open circuit potential (i.e., the corrosion potential) is $-0.737$ V for the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode. It is obvious that corrosion potential of the composite electrode is $-0.702$ V, which shifts towards more positive direction compared to the former. It is generally accepted that more positive corrosion potential results in the improved anti-corrosion performance of the electrode [20–22]. Therefore, the composite electrode has an enhanced anti-corrosion behavior than that of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode, which enhances the cyclic stability of the composite electrode.

The corrosion currents of La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy and the composite electrodes were investigated by anodic polarization measured after the electrodes were immersed in the 6 M KOH solution for 10 h. The obtained curves are nonlinear fitted with Butler–Volmer equation (Eq. (1)) using Levenberg–Marquardt algorithm. The corrosion current $I_{corr}$ and the Tafel constant $b_a$, $b_c$ are the fitted parameters in the Butler–Volmer equation [23]:

$$I = I_{corr} \left[ \exp \left( \frac{2.303 \Delta E}{b_a} \right) - \exp \left( \frac{-2.303 \Delta E}{b_c} \right) \right]$$

where $I$, $\Delta E$ are experimentally obtained current and overpotential, respectively.
Fig. 6. The anode polarization curves (the dots) and the fitting results (the lines) of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy and composite electrodes at 303 K after immersing in KOH solution for 10 h.

Fig. 6 exhibits the anodic polarization curves and their fitting results of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy and the composite electrodes at 303 K after immersing in KOH solution for 10 h. It can be seen that the fitting results match the experimental data very well. The corrosion current $I_{corr}$ of the composite electrode is 0.0862 A/g, which is much lower than that of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode (0.207 A/g). This indicates once again that the composite electrode has an improved anti-corrosion performance, which is consistent with the result of the corrosion potential measurement.

From the measurements of corrosion potential and corrosion current described above, it can be concluded that the formation of composite after ball milling the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ with Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy enhances the anti-corrosion behaviors of the electrodes, which further leads to the improvement of the cyclic stability of the composite electrode in Fig. 3.

3.4. The kinetics of the electrochemical reaction

Fig. 7 illustrates the electrochemical impedance spectra of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy and composite electrodes at 50% DOD and 303 K. Both the EIS spectra of these two electrodes consist of a smaller semicircle in the high-frequency region and a larger semicircle in the low-frequency region followed by a straight line. The EIS data were analyzed using an equivalent circuit as that proposed by Kuriyama et al. [24] and used by Tian et al. [25] (see the inset in Fig. 7). The capacitive components labeled by $C$ are modeled as constant-phase elements (CPE) to describe the depressed nature of the semicircles. $R_{ct}$ is ascribed to the electrolyte resistance between the MH electrode and the reference electrode. The semicircle in the high-frequency region, modeled by $R_{cp}$ and $C_{cp}$, results from the contact resistance between the alloy particles and the current collector. The contact resistance and capacitance between the alloy particles generate the parameters $R_{pp}$ and $C_{pp}$, respectively. $R_{ct}$ and $C_{ct}$, representing the semicircle in the low-frequency region, contribute to the charge-transfer reaction resistance and the double-layer capacitance, respectively. $R_{w}$ is the Warburg impedance.

The parameters in the equivalent circuit were calculated by a nonlinear least squares fit using the simulation software of IM6e workstation. The contact resistance $R_{pp}$ between alloy particles and charge-transfer reaction resistance $R_{ct}$ of the electrodes are summarized in Table 3. The $R_{pp}$ and $R_{ct}$ are 747.1 mΩ and 327.8 mΩ for the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode, respectively. However, when the Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy is ball milled with La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy for 10 min, the electrochemical reaction kinetics of the composite electrode is improved, which behaves in two respects according to EIS. On the one hand, the introduction of the Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy into the composite decreases the contact resistance $R_{pp}$ between alloy particles to 334.2 mΩ. On the other hand, the charge-transfer reaction resistance $R_{ct}$ of the composite electrode is decreased to 160.2 mΩ, which indicates that the reaction rate on the surface of the alloy electrode increases resulting from formation of the composite after the addition of Ti$_{0.17}$Zr$_{0.08}$V$_{0.35}$Cr$_{0.1}$Ni$_{0.3}$ alloy.

The exchange current density $I_0$ can be calculated by the following formula supposing that the surface status of the electrode is not changed:

$$I_0 = \frac{Z_{ref}}{Z_{real}}$$

Table 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact resistance between alloy particles, $R_{pp}$ (mΩ)</th>
<th>Charge-transfer reaction resistance, $R_{ct}$ (mΩ)</th>
<th>Polarization resistance, $R_{p}$ (mΩ)</th>
<th>Exchange current density, $I_0$ (mA/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>747.1</td>
<td>327.8</td>
<td>211.5</td>
<td>79.6</td>
</tr>
<tr>
<td>Composite</td>
<td>334.2</td>
<td>160.2</td>
<td>129.5</td>
<td>201.6</td>
</tr>
</tbody>
</table>
electrodes at 50% DOD and 303 K.

It is found that the charge-transfer reaction of metal hydride electrode in KOH electrolyte because it was a Ni-rich phase. Further investigations on the Ti-based hydrogen storage alloy, C14 Laves phase could improve the electrocatalyst in the Ti-based hydrogen reaction in the composite electrode. The other can be ascribed to the enhanced anti-corrosion behaviors of the composite in alkaline solution, in which the corrosion potential and current of the composite electrode are −0.702 V and 0.0862 A/g, respectively. Furthermore, the kinetics of the electrochemical hydrogen reaction is also improved for the composite electrode.

According to the EIS and linear polarization measurement, the charge-transfer resistance $R_{ct}$, the polarization resistance $R_p$, and the exchange current density $I_0$ of the composite electrode are 160.2 mΩ, 129.5 mΩ and 201.6 mA/g, respectively, which are superior to those of the La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$ alloy electrode (327.8 mΩ, 211.5 mΩ and 79.6 mA/g). These improvements can be attributed to the intrinsic synergetic effect between two alloys and the improved electrocatalytic activity of C14 Laves phase in the composite alloy.

### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (nos. 50671098, 20473091 and 20573112) and the project sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

### References