The electrochemical hydrogen storage performances of $\text{Mg}_x\text{Co}_{100-x}$ ($x = 40, 45, 50, 55, 60, 63$) body-centered cubic alloys and their Pd-doped system

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**Abstract**

In this work, a serial of $\text{Mg}--\text{Co}$ binary alloys with body-centered cubic (BCC) phase were prepared for anode materials of Ni-MH hydrogen storage battery system. TEM/SAED analyses on binary $\text{Mg}--\text{Co}$ alloys demonstrated that their grains were all in nano-size (~5 nm) with BCC structure. Electrochemical tests found that, with increase of the concentration of Mg in alloys, theoretical charge–discharge capacities would increase accordingly, discharge kinetics (exchange current densities and hydrogen diffusion abilities) were improved as well. However, the tested capacity will attain a maximum value (325 mAh g$^{-1}$) at the point of $\text{Mg}_{55}\text{Co}_{45}$ and deteriorate subsequently with continuous increase of Mg content, which was possibly due to the optimized lattice parameter value and Mg corrosion. The increase of Co concentration in the binary alloys effectively inhibited the corrosion of the electrodes. On the basis of $\text{Mg}--\text{Co}$ binary alloys, the Pd-doped ternary alloys with BCC structure were also prepared by means of ball milling. These alloys possess greatly enhanced discharge capacities (280–500 mAh g$^{-1}$) from binary ones. It shows that with increase of the Mg content, the discharge capacities of $\text{Mg}--\text{Co}--\text{Pd}$ ternary alloys will increase monotonously. The additional Pd also improved cycle stabilities, kinetics, and corrosion potentials of the alloys, which was beneficial to improving the properties of $\text{Mg}--\text{Co}$ hydrogen storage electrodes.

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Introduction

The nickel–metal hydride (Ni–MH) battery is an attractive candidate for various applications due to the safety, environmental friendliness and overall charge–discharge performance, even though the Li-ion battery is now a prevailing power source for many portable devices. In emerging electrical vehicle (EV) and hybrid engine vehicle (HEV) market, the nickel-metal hydride battery is competitive with Li-ion battery. However, the high energy density of the Ni–MH battery is urgently required. Using high capacity electrode, for example Mg-based hydrogen storage alloy, seems to be a promising approach to improve the energy density.

Mg-based hydrogen storage electrodes have drawn much attention during last decades due to its large capacity and abundant reserves on earth [1–11]. Among there alloys, Mg–Co BCC alloys are able to absorb hydrogen at very ambient temperature, and the maximum capacity is about 2.7 wt. % H2 at a temperature of 100 °C [12,13]. However, the Mg–Co alloy hardly desorbs hydrogen in the solid–gas reaction system [14–19]. In our recent work, the Mg–Co BCC alloy serves as an anode material of Ni–MH battery system and exhibits high capacity of reversible charge–discharge in the first cycle. Mg50Co50 is capable of discharging 350 mAh g−1 at a rate of 30 mAg−1 [20], while Pd-doped Mg67Co33 is enable to discharge maximum 530 mAh g−1 in the initial cycle [21]. It raised a question that how the variation of the x in Mg50Co50–x alloy affects their discharge capacities and cyclic degradation, therefore it’s reasonable to investigate the effects of the Mg/Co concentration on the electrode’s behavior. Furthermore, the Pd-doped Mg–Co ternary electrodes were also concerned. Their structures were studied by means of XRD and TEM analyses. The electrochemical properties were investigated through cyclic charge–discharge tests, polarization measurements and potential-step tests.

Experimental section

Nanocrystalline Mg50Co50–x (x = 40, 45, 50, 55, 60, 63) alloys were prepared by milling Mg and Co mixture powders with purities over 98% in respective compositions. The jar loading the mixtures was operated in a glove box (Mikrouna Super purities over 98% in respective compositions. The jar loading were prepared by milling Mg and Co mixture powders with Pd-doped Mg through cyclic charge concentration on the electrode therefore it raised a question that how the variation of the x in MgxCo100–x alloy affects their discharge capacities and cyclic degradation, therefore it’s reasonable to investigate the effects of the Mg/Co concentration on the electrode’s behavior. Furthermore, the Pd-doped Mg–Co ternary electrodes were also concerned. Their structures were studied by means of XRD and TEM analyses. The electrochemical properties were investigated through cyclic charge–discharge tests, polarization measurements and potential-step tests.

Results and discussion

Features of the Mg–Co binary alloys

Fig. 1(A) exhibits the XRD patterns of all the samples of Mg50Co50–x (x = 40, 45, 50, 55, 60, 63). They are homogeneously formed alloys. A broaden peak located at 2θ = 42° was observed. It means that the major phase in the samples should be in nano-crystallized or even in amorphous. Since it is very hard to characterize the phase structures by means of XRD pattern, the crystal structures need to be sophisticatedly studied by means of TEM analyses. Fig. 2 exhibits the TEM morphologies of the Mg50Co50–x (x = 40, 45, 50, 55, 60, 63) alloys and their SAED images. A serial of co-axis rings can be found in Fig. 2(b), showing that the squares of the rings’ radii (R) agree well with the arithmetic sequence 1:2:3:4 of the BCC structure (see Table 1). It verified the formation of BCC structure in the binary and ternary Mg–Co-based alloys. We also found that the lattice parameter values of the BCC Mg50Co50–x (x = 40, 45, 50, 55, 60, 63) alloys linearly increased with augmentation of Mg concentration in the alloys (see Supplementary Figure 1). All these points (x = 40, 45, 50, 55, 60, 63) are perfectly located in a line, which persuades that the Mg–Co binary BCC alloys prepared in the present work strictly correspond to the Vegard’s law. Since the BCC formation range for Mg–Co binary alloy was determined as 20–63 at.% Co [12], we may deduce the lattice parameters of the Mg50Co50 (0.2956 nm) and Mg50Co50 (0.3059 nm) alloys by means of the
intercepts, which are boundaries of BCC formation range in Mg–Co binary phase diagram according to previous study [12].

The charge–discharge performance

Fig. 3(A) shows the variations of electrode potentials of the Mg<sub>x</sub>Co<sub>100−x</sub> alloys with the discharge capacity in the first cycle. It exhibited that all the electrodes can reversibly discharge after being fully charged. The reversibility of the alloys in electrochemical system seems superior over that in gas–solid reaction system. This phenomenon hints that the force driven by potential difference should be much stronger and more effective than that by pressure difference to draw hydrogen atoms from the lattice interstitial of hydride.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;/nm&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;/nm&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;/nm&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>a/nm</th>
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<td>6.7470</td>
<td>8.2471</td>
<td>0.2965</td>
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<tr>
<td>Mg&lt;sub&gt;45&lt;/sub&gt;Co&lt;sub&gt;55&lt;/sub&gt;</td>
<td>4.7709</td>
<td>6.6676</td>
<td>8.2065</td>
<td>0.2983</td>
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<td>4.7576</td>
<td>6.7012</td>
<td>8.0980</td>
<td>0.2994</td>
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<td>6.6584</td>
<td>8.1249</td>
<td>0.3005</td>
</tr>
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<td>Mg&lt;sub&gt;60&lt;/sub&gt;Co&lt;sub&gt;40&lt;/sub&gt;</td>
<td>4.6963</td>
<td>6.6371</td>
<td>8.1367</td>
<td>0.3012</td>
</tr>
<tr>
<td>Mg&lt;sub&gt;63&lt;/sub&gt;Co&lt;sub&gt;37&lt;/sub&gt;</td>
<td>4.6934</td>
<td>6.6115</td>
<td>8.1304</td>
<td>0.3017</td>
</tr>
</tbody>
</table>

The XRD patterns of (A) Mg<sub>x</sub>Co<sub>100−x</sub> binary alloys ball milled for 120 hrs: (a) x = 40; (b) x = 45; (c) x = 50; (d) x = 55; (e) x = 60; (f) x = 63 and (B) Mg<sub>x</sub>Co<sub>100−x</sub> − 5 at.% Pd ternary alloys: (g) x = 40; (h) x = 45; (i) x = 50; (j) x = 55; (k) x = 60; (l) x = 63.

The TEM image and SAED patterns of Mg<sub>x</sub>Co<sub>100−x</sub> alloys ball milled for 120 hrs. (a) x = 40; (b) x = 45; (c) x = 50; (d) x = 55; (e) x = 60; (f) x = 63.
In Supplementary Figure 1, we can find that the variation of the maximum discharge capacity of Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) alloys with Mg concentration did not exhibit a singly increasing line. It seems that the Mg$_{55}$Co$_{45}$ attains the maximum discharge capacity with 325 mAh g$^{-1}$. We attributed the phenomenon to two aspects:

Firstly, within the range of 40–55 at.% Mg, the capacity was gradually increased with Mg increasing because the expansion of lattice parameter facilitate to hosting the hydrogen atoms. Shao et al. believed that the favorable lattice parameter range for Mg–Co alloy is 0.300–0.308 nm [15], which allows Mg$_x$Co$_{100-x}$ alloys within the range. It means that the gradually expanded lattice parameter may accommodate more and more hydrogen atoms during charge process.

Secondly, however, with the increase of Mg content in the alloy, the corrosion of the alloy in alkaline solution would be more serious. With the loss of hydrogen-absorbable element in the alloy, the discharge capacity would be deteriorated. The Mg$_{55}$Co$_{45}$ should be the critical point of the increasing due to lattice parameter increase and decreasing due to Mg loss.

Moreover, the discharge capacity of Mg$_{50}$Co$_{50}$ alloy (310 mAh g$^{-1}$) was slightly lower than that of our previous work (355 mAh g$^{-1}$) [20]. It might be due to the different purchased batches of Mg and Co powders with a little bit difference in purities.

Fig. 4(A) describes the dependency of discharge retention rate of Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) upon cycle number. For these alloys, the initial discharge capacities were usually the maximum capacities. However, it decreases drastically within several cycles. Its discharge capacity of the 20th cycle was reduced by 93% from the first cycle. It is obvious that the discharge capacity retention rate of the Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) was gradually improved due to the loss of Co amount in the alloys.

The charge–discharge kinetics

Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) electrode alloys were implemented linear polarization (LP) measurements at 50% DOD and 303 K. Fig. 5(A) shows a linear dependence between the current and over-potential within a small over-potential range (±5 mV). Butler–Volmer equation (1) and its transformation in weak polarization zone equation (2) can be available to describe the relationship between polarization resistance $R_p$ and current density $i$ [22],

$$i = i^0 \left[ \exp \left( - \frac{a n F}{RT} \eta \right) - \exp \left( \frac{b n F}{RT} \eta \right) \right]$$  \hspace{1cm} (1)

$$i^0 = \frac{RT}{a F R_p}$$  \hspace{1cm} (2)

In these equations, $F$ represents Faraday constant 26.8 A h$^{-1}$, $R$ stands for gas constant, $T$ is absolute temperature. Table 2 tabulates the $i^0$ values of the binary Mg–Co electrode alloys at 50% DOD and 303 K, which were determined from equation (2). It can be found that the $i^0$ values of the electrode alloys increased from 28.8 mAg$^{-1}$ (Mg$_{50}$Co$_{50}$) to 150.7 mAg$^{-1}$ (Mg$_{53}$Co$_{47}$). It is obvious that the Mg helps to increase the exchange current density.

During the electrode process, the rate-dominated step will be usually transformed to hydrogen diffusion with the increase of depth of charge or discharge [7,8]. The hydrogen diffusion coefficient $D$ in one electrode was usually estimated by the potential-step method as reported by equations (3) and (4) [23]. In Fig. 6(A), it was found that the semilogarithmic curves of the current–time response of the Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) alloys being fully charged will finally become a straight line when the rate-determining step changed from electro-oxidation to hydrogen diffusion in the alloy. By fitting the linear section of the current–time response curves as shown in Fig. 6(A), the hydrogen diffusion ability represented by $D/a^2$ of the electrode can be determined:

$$\log i = \log \left[ \frac{a F T}{d^2} (c_0 - c_t) \right] - \frac{\pi^2 D}{2.303 a^2} t$$  \hspace{1cm} (3)

$$D/a^2 = \text{Slope} \times 2.303/a^2$$  \hspace{1cm} (4)

In Supplementary Table 1, we can find that the diffusion ability $D/a^2$ was obtained from $0.50 \times 10^{-5}$ s$^{-1}$ (Mg$_{50}$Co$_{50}$) to 3.53 $\times 10^{-5}$ s$^{-1}$ (Mg$_{53}$Co$_{47}$).
Corrosion behaviors of the binary electrodes

The Tafel polarization curves of the \( \text{Mg}_x\text{Co}_{100-x} \) (\( x = 40, 45, 50, 55, 60, 63 \)) are shown in Supplementary Figure 2, which were tested for the purpose of evaluating the corrosive potentials and corrosive current densities of electrodes. Fig. 2(b) reflects that the corrosive potential decreased with the augmentation of Mg (absolute value increased with Mg content), while the corrosive current density increased with it. Both curves evidenced that Mg dominated the corrosion of the electrode alloys and Co in the alloys effectively inhibit their corrosion. For further enhance the corrosion resistance as well as the discharge capacity, the third element Pd was introduced in the alloys.

Table 2 – The polarization resistances, exchange current densities, and hydrogen diffusion ability of \( \text{Mg}_x\text{Co}_{100-x} \) (\( x = 40, 45, 50, 55, 60, 63 \)) BCC electrodes.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Exchange current density ( I_0 ) ( \text{mA g}^{-1} )</th>
<th>Polarization resistance ( \Omega )</th>
<th>Hydrogen diffusion ability ( D/\Omega^{2} \times 10^{-5} \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}<em>{40}\text{Co}</em>{60} )</td>
<td>28.80</td>
<td>18.03</td>
<td>0.50</td>
</tr>
<tr>
<td>( \text{Mg}<em>{45}\text{Co}</em>{55} )</td>
<td>33.82</td>
<td>15.63</td>
<td>1.13</td>
</tr>
<tr>
<td>( \text{Mg}<em>{50}\text{Co}</em>{50} )</td>
<td>56.87</td>
<td>9.32</td>
<td>2.02</td>
</tr>
<tr>
<td>( \text{Mg}<em>{55}\text{Co}</em>{45} )</td>
<td>60.69</td>
<td>8.95</td>
<td>2.38</td>
</tr>
<tr>
<td>( \text{Mg}<em>{60}\text{Co}</em>{40} )</td>
<td>80.63</td>
<td>6.13</td>
<td>3.08</td>
</tr>
<tr>
<td>( \text{Mg}<em>{63}\text{Co}</em>{37} )</td>
<td>150.70</td>
<td>3.52</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Corrosion behaviors of the binary electrodes

The Tafel polarization curves of the \( \text{Mg}_x\text{Co}_{100-x} \) (\( x = 40, 45, 50, 55, 60, 63 \)) are shown in Supplementary Figure 2, which were tested for the purpose of evaluating the corrosive potentials and corrosive current densities of electrodes. Fig. 2(b) reflects that the corrosive potential decreased with the augmentation of Mg (absolute value increased with Mg content), while the corrosive current density increased with it. Both curves evidenced that Mg dominated the corrosion of the electrode alloys and Co in the alloys effectively inhibit their corrosion. For further enhance the corrosion resistance as well as the discharge capacity, the third element Pd was introduced in the alloys.
The effects of additive Pd on the Mg$_x$Co$_{100-x}$ alloys

Features of the alloys’ surfaces

Fig. 1(B) exhibits the XRD patterns of all the samples of Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63). These alloys are also homogeneously formed when Pd was doped into the binary alloys. A broaden peak was located at 2θ = 42°. It seems as binary alloys that the major phase in the samples should be in nano-crystallized or even in amorphous. Fig. 7 exhibits the TEM morphologies of the Mg$_{40}$Co$_{60}$, Mg$_{55}$Co$_{45}$ and Mg$_{63}$Co$_{37}$ alloys and their SAED images, respectively. A serial of co-axis rings can be found in Fig. 7, showing that the squares of the rings’ radii (R) agree well with the arithmetic sequence 1:2:3 of the BCC structure (see Table 3). It verified the formation of BCC structure in the binary and ternary Mg$_x$Co$_{100-x}$Pd ternary alloys. We also found that the lattice parameter values of the BCC Mg$_x$Co$_{100-x}$Pd (x = 40, 55, 63) alloys simply increased with augmentation of Mg concentration in the alloys. In comparison with Mg$_x$Co$_{100-x}$ binary alloys in Table 1, we found that the ternary alloys possess slightly larger lattice parameters. It suggests that the introduction of Pd may expand the lattice volume of Mg–Co BCC phase.

Mg$_{40}$Co$_{60}$, Mg$_{55}$Co$_{45}$ and Mg$_{63}$Co$_{37}$ alloys were studied on their morphologies and chemical distributions on their surfaces by means of SEM observations and EDS elemental mappings (Supplementary Figure 3 to Supplementary Figure 8). All these alloys achieved homogeneous distributions of Mg, Co and Pd over the surface without any agglomeration. According to the EDS results, Co concentration was generally higher than the designed one suggesting there were concentration gradient from surface to the inner of the particles. On the contrary, Mg was lowly distributed in the surface layer of the alloys, which should be abundantly in the inner bulk.

The charge–discharge performances

The variations of electrode potentials of the Pd doped Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) ternary alloys with the discharge capacity were exhibited in Fig. 2(B) for their first charge–discharge cycle. It can be found that all the electrodes drastically improve their discharge capacities. Fig. 2(B) clearly shows that with the increase of Mg concentration in the ternary alloy, the initial discharge capacity will be improved accordingly. Mg$_{63}$Co$_{37}$ possesses the maximum capacity among these alloys. It might be due to the reason that doping Pd in the binary alloys led to more defects in the BCC lattice. It may slope the hydrogen release curve from that of binary alloy’s phase with relatively perfect lattice. Therefore, a more slanting discharge voltage plateau was observed.

Fig. 3(B) describes the dependency of discharge capacities retention rate of the Pd doped Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) with cycle number. For these alloys, the initial discharge capacities were also the maximum capacities as those binary ones, and their retention rates after 20 cycles were all higher than the later. It suggests that the additional Pd effectively enhances the cyclic stability possibly due to the improvement in corrosion resistance over the particles surfaces. Mg$_{40}$Co$_{60}$–5 at.% Pd alloy owes the highest discharge retention rate of 41% after the 20th cycle. It is obvious that the discharge capacity retention rates of the Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) were gradually improved with the increase of Co amount in the alloy, which agree well with those of binary alloys.

The charge–discharge kinetics

Linear polarization (LP) measurements were implemented on Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63)–5 at.% Pd electrode alloys at 50% DOD and 303 K. Fig. 4(B) shows a linear dependence between the current and over-potential within a small over-potential range (±3 mV). They are all in accordance with the equation (2). Table 4 tabulates the i$^0$ values of the ternary...
Mg–Co–Pd electrode alloys at 50% DOD and 303 K obtained from equation (2). It can be found that the $I_0$ values of the electrode alloys increase from 71 mA g$^{-1}$ (Mg$_{40}$Co$_{60}$ePd) to 189.6 mA g$^{-1}$ (Mg$_{63}$Co$_{37}$ePd). They are all higher than their binary alloys in comparison with Table 2. It is obvious that Pd facilitates the increase of the exchange current density.

Fig. 5(B) presents the semilogarithmic curves of the current–time response of the Mg$_x$Co$_{100-x}$ (x = 40, 45, 50, 55, 60, 63) alloys being fully charged. The hydrogen diffusion abilities of the alloys represented by $D/a^2$ were calculated according to the equations (3) and (4), and were summarized in Table 4. It shows that additional Pd in the Mg–Co–Pd ternary alloys improves the hydrogen diffusion ability ($D/a^2$) significantly from binary alloys compared with Table 2, demonstrating again that Pd improves the discharge kinetics of the ternary alloys electrodes. Furthermore, the variation of the $D/a^2$ values for Mg$_{63}$Co$_{37}$ePd and Mg$_{63}$Co$_{37}$ePd alloys is shown in Fig. 5(C).
Corrosion behaviors of the ternary electrodes

Supplementary Figure 9 presents the polarization curves of Mg₅₀Co₁₀₀₋ₓPdₓ (x = 40, 45, 50, 55, 60, 63) BCC electrodes, and achieved variations of corrosion potential and corrosion current density with Mg concentration in these electrodes. Fig. 8 exhibits the corrosion current densities of the ternary MgₓCo₁₀₀₋₅Pdₓ (x = 40, 45, 50, 55, 60, 63) electrodes with those of binary MgₓCo electrodes. It obviously shows that the former possesses much lower corrosion current density than the latter, suggesting that the additional Pd benefits to inhibit the corrosion of the alloys in 6 M KOH solution. Both curves evidenced that Mg dominated the corrosion of the electrode alloys and Co in the alloys may alleviate their corrosion.

Conclusions

In the present work we presented Mg–Co and Mg–Co–Pd hydrogen storage electrodes with BCC phase. They were investigated by XRD, TEM, SEM, SAED and EDS analyses in order to observe the phase structures, grain sizes/lattice parameters, morphologies/concentration and distributions of the alloys. Their electrochemical performances were studied including the tests of cyclic charge–discharge, linear polarization, potential step, and Tafel polarization. We thereby drew several conclusions as follows.

1) TEM/SAED demonstrated that all Mg–Co binary alloys possess nano-crystalline with BCC structure. Their lattice parameters increased monotonously with the augmentation of Mg content in the alloy, which were beneficial to storing hydrogen atoms. These binary alloys possessed a maximum capacity value (325 mAh g⁻¹) at the point of Mg₅₅Co₄₅.

2) The discharge capacity of binary alloy electrodes would turn decreasing when Mg content exceeds 55 at.%. Two reasons may lead to the decrease. One can be attributed to the unfavorable lattice parameter exceeding 0.308 nm; the other reason might be the serious corrosion of Mg in the 6 M KOH solution when its concentration was over 55 at.%. On the basis of Mg–Co binary alloys, the Pd-doped ternary alloys with BCC structure were also prepared. These alloys possess greatly enhanced discharge capacities (280–500 mAh g⁻¹) from binary ones. It shows that with increase of the Mg content, the discharge capacities of Mg–Co–Pd ternary alloys will increase monotonously. The additional Pd also improved cycle stabilities, kinetics, and corrosion potentials of the alloys, and was beneficial to improving the properties of Mg–Co hydrogen storage electrodes.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2015.10.040.
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