

# Electrode properties of $\text{La}_2\text{Mg}_{17}$ alloy ball-milled with $x$ wt.% cobalt powder ( $x = 50, 100, 150$ and $200$ )

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## Abstract

$\text{La}_2\text{Mg}_{17}$  alloy prepared by induction was ball-milled with different amounts of metallic cobalt powder. The effect of the ball-milling on the alloy microstructure and surface image was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD results showed that the more Co added, the higher amorphization degree could be obtained. Electrochemical characteristics of the composite electrodes were investigated at 303 K. The discharge capacity and high-rate dischargeability increased with the increment of Co amount added because of the changed structure and surface state of the alloy, and the high-rate dischargeability is mainly determined by the charge-transfer process occurring at the metal/electrolyte interface, namely, the exchange current density  $I_0$ . But the cycling stability deteriorated with the increase of Co amount introduced during ball-milling.

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**Keywords:** Hydrogen storage alloy;  $\text{La}_2\text{Mg}_{17}$ ; Amorphous; Electrochemical properties

## 1. Introduction

Mg-based hydrogen storage alloy is a promising candidate for negative electrode material because this alloy is superior to the  $\text{LaNi}_5$ -system or the Zr-based Laves phase alloys in theoretical discharge capacity and materials cost [1]. However, crystalline Mg-based alloy absorbs hydrogen only at high temperatures under high pressure [2].

Recently, many efforts have been made to improve their hydriding–dehydriding and charge–discharge characteristics from a practical point of view. Lei et al. [3,4] and Iwakura et al. [5,6] reported that amorphous MgNi alloys prepared by mechanical alloying (MA) could charge and discharge even at room temperature, which presented a new possibility for the application of Mg-based alloys in nickel-metal hydride batteries. As is the case with Ni, Co is a good catalyst for the electrode property. It was ever reported by

Chen et al. [7] that  $\text{Mg}_2\text{Ni}$  alloy mechanically ground with 3 wt.% Co powder showed markedly increased capacity up to 476 mAh/g( $\text{Mg}_2\text{Ni}$ ), and at the same time the cycle life was also improved.

Ln–Mg (Ln=La, Ce and misch-metal) system alloy is another promising candidate for negative electrode material. Gao et al. [8] ever reported that the first discharge capacity of the  $\text{LaMg}_{12}$  alloy ball-milled with Ni powders in a weight ratio of 1:3 could reach up to 1010 mAh/g( $\text{LaMg}_{12}$ ). In the present work,  $\text{La}_2\text{Mg}_{17}$  alloy was ball-milled with different amounts of metallic cobalt powder, and its effect on the electrode properties was investigated.

## 2. Experimental

The as-cast  $\text{La}_2\text{Mg}_{17}$  alloy was prepared by induction melting method. The ingot was crushed and mechanically pulverized to less than 300 mesh in diameter. The powders were mixed with  $x$  wt.% ( $x = 50, 100, 150$  and  $200$ ) metallic

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cobalt powder, and ball-milled with stainless steel balls in a stainless steel vessel under the protection of argon atmosphere by using planetary ball miller at a speed of 350 rpm for 90 h. The phase structure and surface images of the alloy powders were identified by X-ray diffractometer (XRD) with Cu K $\alpha$  radiation and scanning electron microscopy (SEM).

The test electrode was fabricated as follows. A 100 mg amount of test powders was mixed thoroughly with 400 mg fine nickel powder. The mixture was then pressed at 12 MPa to form circular pellets of 10 mm diameter. Electrochemical measurements were performed in a three-electrode system, in which Ni(OH) $_2$ /NiOOH and Hg/HgO were used as the counter electrode and the reference electrode, respectively. The electrolyte was a 6 mol/L KOH aqueous solution, used for electrochemical measurements of an automatic galvanostatic system (DC-5). In this work, each charging step was conducted at a current density of 300 mA/g for 5 h and discharge at 180 mA/g with a cut-off voltage set at  $-0.6$  V (versus Hg/HgO). The discharge capacity of each electrode was expressed in mAh/g of the alloy. When the capacity was calculated, the weight of the Co powder in the electrode was subtracted. The test for high-rate dischargeability (HRD) was executed at the following current densities: 360, 720 and 1440 mA/g. The testing temperature was fixed at 303 K.

For investigating the electrocatalytic activity of the hydrogen electrode reaction, the linear polarization curves of the electrodes were measured with a Solartron SI 1287 potentiostat by scanning the electrode potential at the rate of 0.1 mV/s from  $-5$  to 5 mV (versus open circuit potential) at full-charge state.

### 3. Results and discussion

#### 3.1. Microstructures

The XRD patterns for the La $_2$ Mg $_{17}$  +  $x$  wt.% Co ( $x = 50, 100, 150$  and 200) composites after ball-milling 90 h are shown in Fig. 1. For the ball-milled La $_2$ Mg $_{17}$  + 50 wt.% Co composite, all of the peaks corresponding to La $_2$ Mg $_{17}$  almost disappeared, which indicated that there was a phase transformation from polycrystalline La $_2$ Mg $_{17}$  to amorphous or nanocrystalline state. But there were two small peaks corresponding to metallic Co still remaining, suggesting the presence of fine Co particles in/on amorphous La $_2$ Mg $_{17}$ . From Fig. 1 we can also see that the diffraction intensity of metallic Co decreased with increasing the Co amount in the samples of ball-milled La $_2$ Mg $_{17}$  composites, that is to say, the more Co powders added, the more advantageous for the complete amorphization of the composites within certain ball-milling duration.

The surface image of the as-cast La $_2$ Mg $_{17}$  alloy and ball-milled La $_2$ Mg $_{17}$  +  $x$  wt.% Co ( $x = 50, 150$  and 200) composites was examined by SEM as shown in Fig. 2. The as-cast La $_2$ Mg $_{17}$  alloy before ball-milling (Fig. 2(a)) exhibits an irregular morphology, and the size distribution is very inho-

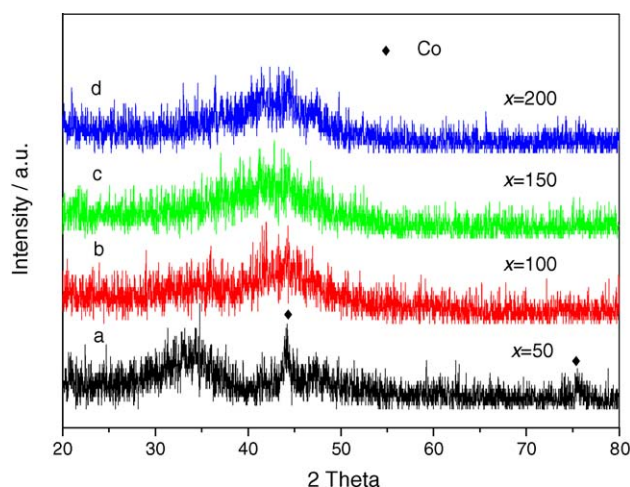


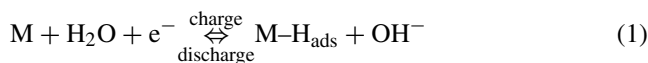
Fig. 1. The XRD patterns for the La $_2$ Mg $_{17}$  +  $x$  wt.% Co ( $x = 50, 100, 150$  and 200) composites after ball-milling 90 h.

mogeneous. After ball-milling with 50 wt.% Co for 90 h, the alloy particle became rounded with a roughly homogeneous size distribution. With more Co addition, as shown in Fig. 2(c) and (d), the particle size decreased to a greater extent. But with Co amount increasing from 150 to 200 wt.%, the particle size decreased a little. In a word, with the increase of Co amount, the particle size decreased to different extent, which greatly increased the surface area of the alloy. Therefore, the ball-milling changes the surface properties of the alloy.

#### 3.2. Electrochemical properties

##### 3.2.1. Discharge capacities and cyclic behavior

The discharge curves of the ball-milled La $_2$ Mg $_{17}$  +  $x$  wt.% Co ( $x = 50, 100, 150$  and 200) composites at their respective maximum discharge capacity are shown in Fig. 3. The as-cast La $_2$ Mg $_{17}$  before ball-milling only has a discharge capacity of  $\sim 9$  mAh/g (not shown here). But from Fig. 3 we can see that the obtained discharge capacities of La $_2$ Mg $_{17}$  ball-milled with Co powder are greater than that of the as-cast alloy. It is well known that the electrochemical reactions taking place at the metal hydride electrode in KOH electrolyte during charging and discharging is the following [9]:



in which, M is the hydrogen storage alloy, M-H $_{\text{ads}}$  denotes the adsorbed hydrogen on the surface of the metal hydride and M-H $_{\text{abs}}$  refers to the absorbed hydrogen in the bulk of the metal hydride. It can be seen from Eqs. (1) and (2) that the discharge kinetics of the alloy electrode is controlled not only by the charge-transfer kinetics occurring at the alloy/electrolyte interface, but also by the hydrogen diffusion rate within the bulk of the alloy particles.

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