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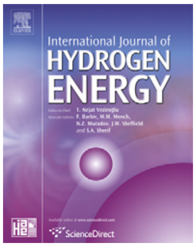

Electrochemical hydrogen storage properties of the ball-milled $PrMg_{12-x}Ni_x$ + 150 wt% Ni (x = 1 and 2) composites

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ABSTRACT

The electrochemical hydrogen storage properties of the ball-milled $PrMg_{12-x}Ni_x$ + 150 wt% Ni ($x = 1$ and 2) composites were investigated, and compared with those of the ball-milled $PrMg_{12}$ + 150 wt% Ni composite. The ball-milled $PrMg_{11}Ni$–Ni composite has the highest initial discharge capacity (973 mAh/g) and high-rate dischargeability (HRD). The cycle life improves with the increase of Ni content, which was confirmed by the XRD results of the ball-milled composites after 10 cycles. By means of electrochemical impedance spectra, linear polarization and anodic polarization measurements, the electrochemical kinetic parameters were studied. It is suggested that the high hydrogen diffusivity and moderate reaction resistance are responsible for the higher discharge capacity and HRD of the $PrMg_{11}Ni$–Ni sample, while the lower discharge capacity and HRD of the $PrMg_{10}Ni_2$–Ni sample is probably due to the excessively high reaction resistance.

1. Introduction

Hydrogen storage alloys have been widely investigated for their application in energy storage media or battery [1,2]. In recent years, nickel-metal hydride batteries using hydrogen storage alloys as negative electrode materials have attracted great attention because they have many advantages over the conventional lead-acid and nickel–cadmium batteries, such as high energy density, less detrimental effect on the environment, high tolerance to overcharge/overdischarge and better low temperature capacity [3–5].

Magnesium-based alloys are regarded as one of the most promising materials for hydrogen storage due to their high hydrogen storage capacity and low material cost [6–8]. However, pure magnesium-based alloys are difficult to be charged and discharged by means of electrochemistry because they have poor hydrogen absorption and desorption kinetics and need relatively high temperature and pressure for hydrogenation [9,10]. A breakthrough in electrochemical hydrogen storage was achieved by preparing nanocrystalline or amorphous hydrogen storage alloys using high-energy ball-milling with Ni powders. These nanocrystalline hydrogen storage alloys show a higher hydrogen absorption capacity at low temperatures and ambient pressure, and better kinetics of hydriding and dehydriding compared with their bulk counterparts [11–15]. Lei et al. [11] reported that amorphous Mg–Ni alloy prepared by mechanical alloying could be charged/discharged in a secondary battery system even at room

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temperature, which offered a new possibility for the application of Mg-based alloys in Ni–MH batteries. Kohno et al. [13] and Nohara et al. [14] also reported that amorphous Mg–Ni prepared by ball-milling of Mg_2Ni and Ni powders exhibits a high discharge capacity. All the improvements in electrochemical characteristics of Mg_2Ni alloy are mainly ascribed to the appearance of a nanocrystalline or amorphous structure by mechanical grinding.

Ln–Mg system alloy is another promising candidate for negative electrode material with a hydrogen storage capacity of 3.7–5.5 wt% [16,17], much higher than that of the Mg–Ni alloy. Besides the strong affinity for hydrogen, it was found that lanthanide elements have a catalytic effect on the hydriding rate of magnesium [18,19], together with other hydrogen storage materials [20,21]. This kind of alloy can display very high discharge capacity after mechanical grinding treatment. In our previous work, the discharge capacity of $LaMg_{12}$ and La_2Mg_{17} alloys after ball-milled with Ni powders has reached over 990 mAh/g, and even higher value (1204 mAh/g) was obtained for the ball-milled $PrMg_{12} + 200$ wt% Ni composite (La_2Mg_{17} or $LnMg_{12}$ alloys as active materials) [22–24]. The inlaid metallic Ni particles with fine crystallites were dispersed throughout the Ln–Mg alloy matrix, which was identified to have a positive effect on the electrochemical hydrogen storage. However, the amount of added Ni in Ln–Mg alloys should be reduced to a minimum value for the practical application as electrode materials.

In the present work, the electrochemical properties of the amorphous composites prepared through ball-milling $PrMg_{12-x}Ni_x$ ($x = 1$ and 2) alloys with Ni powders were investigated in order to decrease the amount of added Ni powders and maintain their high discharge capacity. In addition, it is well known that Ni usually can enhance the corrosion resistance of Mg-based alloys in electrochemical reactions. Hence, the effect of the substitution of Ni for Mg on the cyclic performance was also determined in this study.

2. Experimental

$PrMg_{12-x}Ni_x$ ($x = 1$ and 2) alloys were synthesized by melting the stoichiometric mixture of metallic Pr, Mg and Ni with the melt-salt-cover-melting process. After pulverizing the $PrMg_{12-x}Ni_x$ alloy ingots to 200 mesh, the negative electrode materials were prepared by further ball-milling of these alloys with carbonyl nickel powders (255 INCO) at a weight ratio of 1.5. All ball-milling processes were performed at 290 rpm under Ar atmosphere in a cyclohexane solution in a planetary-type ball-mill (Pulverisette 5, Fritsch), where stainless steel grinding bowls with volume of 250 ml and stainless steel balls with diameter of 10 mm were used. The weight ratio of ball to powders was fixed at 20:1 and total mass was controlled at 6 g. The microstructure analysis of the alloy powders was performed by X-ray diffraction (XRD, Rigaku D/max-2500).

The negative electrodes were then constructed by mixing the as-prepared composites with carbonyl nickel powder at a weight ratio of 1:3 and subsequently pressing the mixture powder under 30 MPa pressure into a small pellet of 10 mm diameter and 1.5 mm thickness. The 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 served as counter and reference electrode, respectively. 6 M KOH was used as electrolyte. The working electrodes were charged at a current density of 1000 mA/g for 80 min, and then discharged at current density of 50 mA/g until the cut-off potential of −0.6 V (vs. Hg/HgO) after resting for 5 min at room temperature. When calculating the discharge capacity, only the weight of hydrogen storage alloys was considered as active materials. To determine the high-rate dischargeability (HRD) of the alloy electrodes, the discharge capacities at three specific discharge current densities, i.e., 400, 800 and 1200 mA/g, were measured. The electrochemical impedance spectra (EIS) were measured in the frequency range of 10 kHz–10 mHz with ac perturbation amplitude of 5 mV after fully charging the working electrode using Autolab potentiostat. The linear polarization curves and anodic polarization curves of the electrodes were also measured on Autolab potentiostat by scanning the electrode potential at the rate of 0.1 mV/s from −5 to 5 mV (vs. open circuit potential) and 5 mV/s from 0 to 1200 mV (vs. open circuit potential) at fully-charged state, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the as-cast $PrMg_{12-x}Ni_x$ ($x = 1$ and 2) alloys. It is clear that both these alloys consist of $PrMg_{12}$ phase and Mg_2Ni phase, with the former one as the main phase. Moreover, it is found that the content of Mg_2Ni phase in $PrMg_{10}Ni_2$ alloy is slightly higher than that of $PrMg_{11}Ni$ alloy, due to higher Ni content in $PrMg_{10}Ni_2$ alloy.

XRD patterns of two ball-milled alloys and 150 wt% Ni powders are presented in Fig. 2. It was reported that the activation energy of the phase transformation from the crystalline to amorphous phase becomes lower with the increase of the Ni content in alloys [25], therefore the required

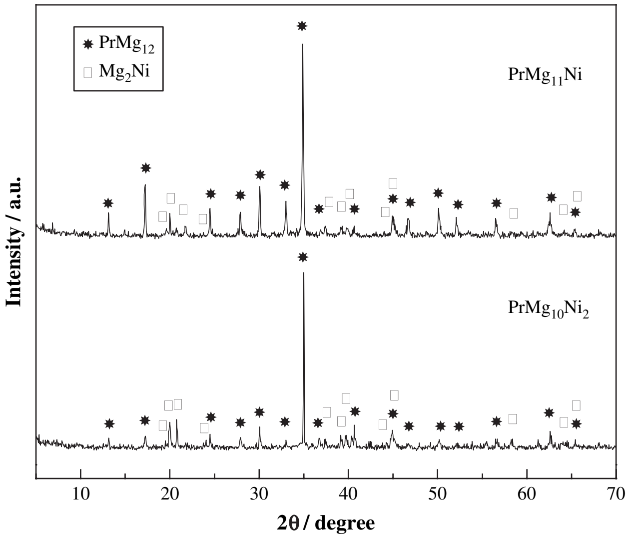

Fig. 1 – The X-ray diffraction patterns of the as-cast $PrMg_{12-x}Ni_x$ ($x = 1$and 2) alloys.