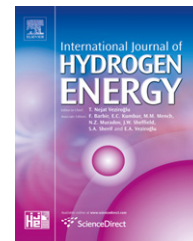


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Electrochemical hydrogen storage of ball-milled MmMg₁₂ alloy–Ni composites

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ABSTRACT

MmMg₁₂–Ni amorphous or nanocrystalline composites (Mm: Ce-rich mischmetal) were prepared through the ball-milling method, and their electrochemical hydrogen storage performance was investigated and compared with that of ball-milled CeMg₁₂–Ni composites. It was found that the ball-milled MmMg₁₂–Ni composites had larger initial discharge capacities and better high rate dischargeability. Analysis of electrochemical impedance spectra (EIS) shows that the reaction resistance and hydrogen diffusion resistance of the ball-milled MmMg₁₂–Ni composites are lower as a result of the decrease in Ce content, and thus can contribute to the larger discharge capacity and better high rate dischargeability. Additionally, the cycle performance of the ball-milled MmMg₁₂–Ni composites is better than those of the ball-milled CeMg₁₂–Ni composites. This may be related to the formation of a Nd oxide or Nd(OH)₃ film on surface of the MmMg₁₂ alloys.

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1. Introduction

Magnesium-based alloys are promising as metal hydride electrode materials in Ni/MH batteries due to their high hydrogen storage capacity and low cost [1–5]. Among these Mg-based alloys, the Mg-rich rare earth–Mg system alloy has drawn much attention due to its hydrogen storage capacity of 3.7–6.0 wt.% [6–8], much higher than that of Mg–Ni alloy. However, pure Mg-rich rare earth–Mg intermetallic compounds are difficult to be charged and discharged electrochemically because they do not contain metallic Ni for high electrocatalytic activity and good corrosion resistance in an alkaline solution. Recently, nanocrystallines or amorphous composites prepared by ball-milling Mg-based alloys with Ni powders have demonstrated to be potential materials for electrochemical hydrogen storage [9–13], because of their

higher hydrogen absorption capacity at low temperature and ambient pressure, and better kinetics of hydriding and dehydriding in comparison to their bulk counterparts.

In our previous work, the ball-milled CeMg₁₂ + 200 wt.% Ni amorphous composite shows an initial discharge capacity of 1040 mAh/g and a little better cycle performance than that of ball-milled PrMg₁₂ + 200 wt.% Ni amorphous composite [14]. It is well known that some hydriding or dehydriding properties of La-rich (Ml) or Ce-rich mischmetal (Mm) AB₅ alloys are better than those of pure La or Ce AB₅ alloys [15,16]. For example, it has been reported [16] that commercial AB₅-type metal hydride electrodes have quite good performance using Mm in place of La, where Mm is a naturally existed mixture of rare earth metals with a composition of (at.%) Ce: 50–55, La: 18–28, Nd: 12–18, and Pr: 4–6. Furthermore, because pure La or Ce is costly, its replacement with the relatively less expensive

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mischmetal is attractive. However, up to date there is no report on the electrochemical hydrogen storage of $MmMg_{12}$ alloys. In this work, we prepared the composites of $MmMg_{12}$ alloys with Ni powders by the ball-milling method, and investigated and compared their electrochemical performance with that of ball-milled composites of $CeMg_{12}$ with Ni powders.

2. Experimental

The Ce-rich mischmetal (Mm) used in this work contains 24 wt.% La, 51 wt.% Ce, 5.2 wt.% Pr and 19 wt.% Nd. $MmMg_{12}$ alloy was synthesized by melting the stoichiometric mixture of metallic Mm and Mg with the melt-salt-cover-melting process. After pulverizing the $MmMg_{12}$ alloy ingot to 200 mesh, the negative electrode materials were prepared by further ball-milling of this alloy with carbonyl nickel powders (255 INCO) at a weight ratio of 1.5 and 2, respectively. All ball-milling processes were performed with a planetary-type ball-mill at a fixed weight ratio of ball to powders of 20:1, a total controlled mass of 6 g and 290 rpm under Ar atmosphere in a cyclohexane solution for 14 h. The microstructure analysis of the alloy powders was performed by X-ray diffraction (XRD, Rigaku D/max-2500).

The negative electrodes were constructed through mixing as-prepared composites with carbonyl nickel powder in a weight ratio of 1:3, followed by pressing under 30 MPa pressure into a 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 in 6 M KOH solution served as counter and reference electrodes, respectively. The electrodes were charged at a current density of 1000 mA/g for 80 min, and then discharged at a current density of 50 mA/g to -0.6 V (\sim vs. Hg/HgO) after resting for 5 min at room temperature. When the discharge capacity was calculated, only the weight of $MmMg_{12}$

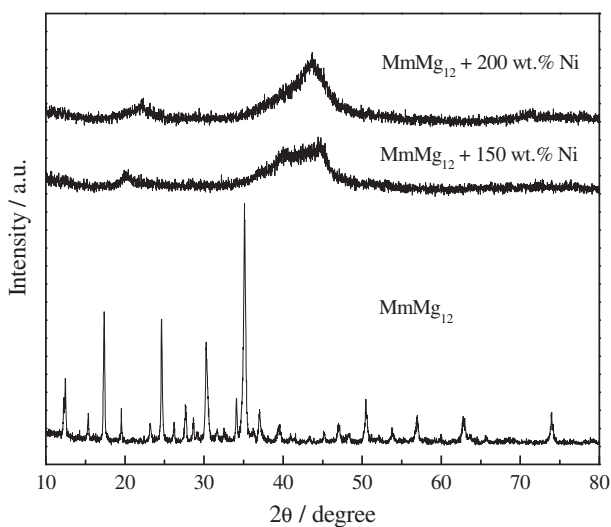


Fig. 1 – The X-ray diffraction patterns of the as-cast $MmMg_{12}$ alloy and the ball-milled $MmMg_{12} + x$ wt.% Ni ($x = 150$ and 200) composites.

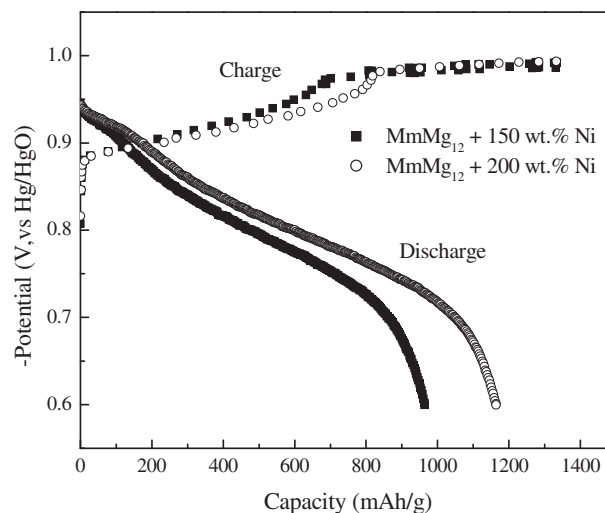


Fig. 2 – The first charge and discharge curves of the ball-milled $MmMg_{12} + x$ wt.% Ni ($x = 150$ and 200) composites.

hydrogen storage alloy was considered as the active material. To determine the high rate dischargeability (HRD) of the alloy electrodes, the discharge capacities at six specific discharge current densities, i.e. 100, 200, 300, 400, 500 and 600 mA/g, were measured. The electrochemical impedance spectra (EIS) were measured in a frequency range over 10 kHz–10 mHz with ac perturbation amplitude of 5 mV after fully charging using Autolab PGSTAT30 potentiostat (Eco Chemie). The working electrodes for EIS and steady-state polarization (SSP) experiments were constructed from an apparent surface of 1.0 cm² porous nickel without addition of the carbonyl nickel powder.

3. Results and discussion

The XRD patterns of the as-cast $MmMg_{12}$ alloy and ball-milled $MmMg_{12}$ alloys with Ni powders are shown in Fig. 1. It can be

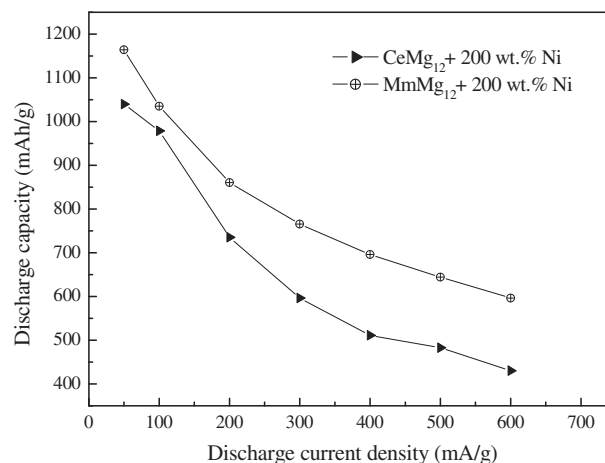


Fig. 3 – Relation between the discharge capacity and the discharge current density for the ball-milled $CeMg_{12} + 200$ wt.% Ni [reference 14] and $MmMg_{12} + 200$ wt.% Ni composites.

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