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Enhanced cycling stability and high rate dischargeability of (La,Mg)$_2$Ni$_7$-type hydrogen storage alloys with (La,Mg)$_5$Ni$_{19}$ minor phase

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HIGHLIGHTS

- A_2B_7-type La–Mg–Ni-based alloys with A_5B_{19}-type minor phase are obtained.
- Cell volumes of A_2B_7- and A_5B_{19}-type phases decrease with more A_5B_{19}-type phase.
- A_5B_{19}-type phase enhances the structural stability of the alloys during cycling.
- A_5B_{19}-type phase catalyzes the discharge process of the A_2B_7-type phase.
- *HRD* and cycle stability are improved by the addition of A_5B_{19}-type phase.

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ABSTRACT

The A_2B_7-type lanthanum (La)–magnesium (Mg)–nickel (Ni)-based alloy with single (La,Mg)$_2$Ni$_7$ phase and different amounts of (La,Mg)$_5$Ni$_{19}$ minor phase was obtained by step-wise sintering. The impact of (La,Mg)$_5$Ni$_{19}$ phase on the alloy's microstructure and electrochemical performance was subsequently studied. It was found that the average subunit volume in (La,Mg)$_5$Ni$_{19}$ phase is smaller than that in (La,Mg)$_2$Ni$_7$ phase, resulting in increases of strains inside the alloys and decreases of cell volumes. During battery charge/discharge, the (La,Mg)$_5$Ni$_{19}$ phase network scattered in the alloys relieves internal stress, alleviates pulverization and oxidation of the alloys, stabilizes the stacking structures against amorphization, and finally improves the cycling stability of the alloys. Furthermore, (La,Mg)$_5$Ni$_{19}$ phase with higher Ni content desorbs hydrogen ahead of (La,Mg)$_2$Ni$_7$ phase. The reduced hydrogen pressure in (La,Mg)$_5$Ni$_{19}$ phase can subsequently lead to the fast discharge of (La,Mg)$_2$Ni$_7$ phase, thus making a remarkable improvement in high rate dischargeability at 1500 mA g^{-1} from 46.2% to 58.9% with increasing (La,Mg)$_5$Ni$_{19}$ phase abundance from 0 to 37.4 wt.%. Therefore, it is believed that A_2B_7-type La–Mg–Ni-based alloys with A_5B_{19}-type minor phase are promising prototypes for high-power and long-lifetime nickel/metal hydride battery electrode materials.

1. Introduction

Nickel metal hydride (Ni/MH) batteries are one of the most promising candidates for advanced automotive energy storage due to their high energy density, good environmental compatibility as well as excellent safety features [1–3]. However, this battery system for energy storage still needs further improvement in terms of its overall electrochemical performance.

Novel negative electrode materials have been the key in the development of Ni/MH batteries. Since 2000 when Kohno et al. [4] reported that the discharge capacity of La$_{0.7}$Mg$_{0.3}$Ni$_{2.8}$Co$_{0.5}$ alloy electrode reached as high as 410 mAh g^{-1} (25% higher than that of

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commercialized AB_5-type alloys), considerable effort has been made to develop La–Mg–Ni-based alloys ($AB_{3.0-4.0}$-type) as novel negative electrode materials for Ni/MH batteries, and great progress has been achieved in both structural understanding and electrochemical optimization [4,5]. It is found that La–Mg–Ni-based alloys have super-lattice structure with Laves-type [$(La,Mg)_2Ni_4$] subunits and $CaCu_5$-type [$LaNi_5$] subunits stacking along c axis in various ratios, consisting $(La,Mg)Ni_3$, $(La,Mg)_2Ni_7$, $(La,Mg)_5Ni_{19}$, and $(La,Mg)Ni_4$ phases [6–8]. Each of these phases has two allotropes including hexagonal (2H-) type for $MgZn_2$-type Laves subunits and rhombohedral (3R-) type for $MgCu_2$-type Laves subunits. Among different types of La–Mg–Ni-based alloys, A_2B_7-type alloys are believed to have superior overall electrochemical properties [9,10]. However, the high rate dischargeability (*HRD*) and cycling stability of the alloy electrodes still need to be further improved before practical applications. For this purpose, it would be beneficial to reveal the functions of alloy phases and thus optimize the phase compositions in the alloys. Zhang et al. [11] adjusted the $LaNi_5$ minor phase in the $La_{0.7}Mg_{0.3}Ni_{2.975-x}Co_{0.525}Mn_x$ alloys by increasing Mn content, and found that the electrochemical performances including specific discharge capacity, rate chargeability and dischargeability of the alloys became optimum when the $LaNi_5$ phase abundance reached 35.84% ($x = 0.3$). Jiang et al. [5] annealed $La_{1.8}Ti_{0.2}MgNi_{8.9}Al_{0.1}$ alloy at various temperatures and found that the $LaNi_2$ impurity phase can be eliminated after annealing at 900 °C for 12 h, leading to improvement in the general electrochemical performance of the alloy electrodes. However, in the research work mentioned above, the hydrogen absorption/desorption characteristics of a certain phase in the multiphase alloys and the interactions between different phases in the alloys have not been studied. Moreover, single-phase alloys as check samples were not included in most of the studies, making it hard to accurately analyze the function of secondary phases.

In one of our previous studies, various amounts of $LaNi_5$ minor phase were introduced into the $La_{0.75}Mg_{0.25}Ni_{3.5}$ alloy with only $(La,Mg)_2Ni_7$ phase by step-wise sintering method [12]. Although the discharge capacity and *HRD* of the alloy electrodes were improved by the catalytic $LaNi_5$ minor phase, there still remained a problem that the crystal lattice of the non-stacking-structure $LaNi_5$ phase and the stacking-structure $(La,Mg)_2Ni_7$ phase showed a discrete expansion/contraction during hydrogen absorption/desorption [12], which aggravated the alloy pulverization and jeopardized the cycling stability of the alloy electrodes. In order to further improve the overall electrochemical properties of A_2B_7-type La–Mg–Ni-based alloys, we consider that a secondary phase with both stacking structure and catalytic effect may be a good choice to be used into A_2B_7-type alloys.

The $(La,Mg)_5Ni_{19}$ phase, a neighboring phase of the $(La,Mg)_2Ni_7$ phase, not only possesses super-stacking structure that is similar to the $(La,Mg)_2Ni_7$ phase, but also has high Ni content that acts as catalyst for hydrogen absorption/desorption. Moreover, the $(La,Mg)_5Ni_{19}$ phase itself is believed to have superior *HRD* and cycling stability. Liu et al. [13] reported that $(La,Mg)_5Ni_{19}$ alloy was able to achieve the discharge capacity of 140 mAh g^{-1} even at the discharge current density as high as 3600 mA g^{-1}. The alloy also exhibited good cycling stability in both repeated hydriding/dehydriding and charging/discharging processes. However, the hydrogen storage capacity of the $(La,Mg)_5Ni_{19}$ phase is relatively low, which deteriorates the alloy overall electrochemical performance. One possible solution is to find out the optimal content of the $(La,Mg)_5Ni_{19}$ phase in A_2B_7-type alloys.

In this study, various $(La,Mg)_5Ni_{19}$ phase amounts were introduced into $(La,Mg)_2Ni_7$-phase $La_{0.75}Mg_{0.25}Ni_{3.5}$ alloy with the effect of the $(La,Mg)_5Ni_{19}$ phase on alloy microstructure and electrochemical performance being investigated. Particularly, the impact mechanism of $(La,Mg)_5Ni_{19}$ minor phase on cycling stability and rate dischargeability of the A_2B_7-type alloys are systematically revealed.

2. Experimental

The alloy samples including the single $(La,Mg)_2Ni_7$ phase alloy, the alloys with different amounts of $(La,Mg)_2Ni_7$ and $(La,Mg)_5Ni_{19}$ phases and the single $(La,Mg)_5Ni_{19}$ phase alloy were obtained by step-wise sintering using $La_{0.75}Mg_{0.25}Ni_{3.5}$ and $La_{0.80}Mg_{0.20}Ni_{3.8}$ as-cast alloys as precursors. The detailed preparation methods are as follows: (1) For the single $(La,Mg)_2Ni_7$ phase alloy, $La_{0.75}Mg_{0.25}Ni_{3.5}$ as-cast alloy was firstly crushed and ground to −300 mesh and the alloy powder was ball milled with supplementary Mg powder for 1 h. Then the mixture was squashed into a pellet and sintered in a tube furnace at the temperature ranging from 600 °C to 980 °C, and subsequently annealed for 4 days at 900 °C. (2) For the alloys with various amounts of $(La,Mg)_2Ni_7$ and $(La,Mg)_5Ni_{19}$ phases, the $La_{0.75}Mg_{0.25}Ni_{3.5}$ alloy powder was ball milled individually with 5 wt.%, 10 wt.%, 20 wt.% and 40 wt.% of $La_{0.80}Mg_{0.20}Ni_{3.8}$ alloy powder as well as extra Mg powder for 1 h, and then the mixtures were cold squashed into pellets followed by sintering and annealing. The parameters such as extra Mg amount, pressing pressure and the heating treatment scheme were the same as those for the preparation of single $(La,Mg)_2Ni_7$ phase alloy. (3) For the single $(La,Mg)_5Ni_{19}$ phase alloy, the as-cast $La_{0.80}Mg_{0.20}Ni_{3.8}$ alloy was grounded into powder and ball milled with extra Mg powder. Then the mixture was cold squashed into a pellet and sintered using the same heating scheme in (1) and (2). For convenience, the alloys mixed with 0, 5 wt.%, 10 wt.%, 20 wt.% and 40 wt.% of $La_{0.80}Mg_{0.20}Ni_{3.8}$ alloy powder during preparation process were labeled as #1, #2, #3, #4 and #5. The single $(La,Mg)_5Ni_{19}$ phase alloy was notified as #6. The chemical compositions of the final pellets were examined by inductively coupled plasma (ICP) system. The ICP results of each alloy are listed in Table S-1.

Powders of −300 mesh size were used to carry out XRD measurement on a D/Max-2500/PC X-ray diffractometer with Cu Kα1 radiation. The XRD patterns were analyzed by Rietveld method [14] using Maud software [15]. An S-4800 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability was used to study the phase distribution and elemental compositions of the phases in the alloys.

For electrochemical measurements, a three-electrode system consisting of MH electrode as working electrode, $Ni(OH)_2/NiOOH$ electrode as counter electrode and Hg/HgO electrode as reference electrode was used. To prepare the working electrode, the alloys were crushed and grounded to the powder of 200–400 mesh, and alloy powder was mixed with Ni powder in a weight ratio of 1:5. Then the mixtures were pressed into pellets under 15 MPa. After that, each of the pellets was welded to a nickel stick. The measurements were carried out on an automatic DC-5 battery testing instrument.

For the electrochemical pressure–composition test, the alloy electrodes were charged and discharged at the current density of 60 mA g^{-1} for 0.5 h followed by an interval of 0.5 h. The voltages between every interval were recorded as the equilibrium potential. The equilibrium potential (E_{eq}) was converted into hydrogen equilibrium pressure (P_{eq}) according to Nernst Equation (1) [16], and the charge transfer amount ($I_0 \times t$) was converted into hydrogen storage capacity (C_{abs} and C_{rev}) according to following Equation (2). The experimental temperature was 298 K.

$$E_{eq}\ (\text{versus Hg/HgO}) = -0.925 - 0.03\log(P_{eq}) \qquad (1)$$