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Effect and mechanism of Mg on crystal structures and electrochemical cyclic stability of Ce₂Ni₇-type La–Mg–Ni-based hydrogen storage alloys

Juan Cao ^{a,b,1}, Yumeng Zhao ^{a,b,1}, Lu Zhang ^b, Zeru Jia ^a, Wenfeng Wang ^a, Zhentao Dong ^a, Shumin Han ^{a,b,*}, Yuan Li ^{a,**}

^a College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, PR China

^b State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China

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ABSTRACT

LaNi_{3.50} and La_{0.80}Mg_{0.20}Ni_{3.50} hydrogen storage alloys with single-phase Ce₂Ni₇-type structure are prepared, respectively. It is found that the expansion of [A₂B₄] subunits volumes of Mg-containing alloy is bigger than that of Mg-free alloy, while the expansion of [AB₅] subunits volumes of the two alloys are almost the same, hence the deviation value of [A₂B₄] and [AB₅] subunits volumes and strain value of super stacking structure for Mg-containing alloy are obviously higher than those of Mg-free alloy, and Mg-containing alloy is easier to be pulverized during charge/discharge cycles. Mg-containing alloy has more apparent cracks on the surface of alloy at the same cycle numbers, which demonstrate that Mg-containing alloy has poorer anti-pulverization. Besides, the presence of Mg hydroxides with a regular hexagon shape makes the surface of Mg-containing alloy become loose enough to be easily oxidized after charge/discharge cycles. The corrosion current density of Mg-containing alloy is larger than that of Mg-free alloy, so Mg-containing alloy is easier to be oxidized. Therefore, reducing the deviation value of [A₂B₄] and [AB₅] subunits of super stacking structure and the corrosion of alloying element Mg is the basic solution to enhance the electrochemical cycling stability of La–Mg–Ni alloy.

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Introduction

RE–Mg–Ni-based hydrogen storage alloy is a new type negative material of metal hydride batteries (Ni/MH) with excellent

electrochemical properties, and shows good application prospect [1–5]. Compared with RE–Ni-based binary alloys, RE–Mg–Ni-based ternary alloys have good comprehensive electrochemical properties, in which Mg plays a unique role. Accordingly, the study about the effect and mechanism of Mg

* Corresponding author. State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China.

** Corresponding author.

E-mail addresses: hanshm@ysu.edu.cn (S. Han), liyuan@ysu.edu.cn (Y. Li).

¹ These authors contributed equally to this work.

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on crystal structures and electrochemical properties of RE–Mg–Ni-based alloys become more and more attractive [6–9]. As reported by Ma et al. [5], the $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.8}$ alloy electrode showed a more excellent activation capability, and a higher discharge capacity (373.1 mAh g^{-1}) than the $\text{LaNi}_{3.8}$ alloy electrode (184.0 mAh g^{-1}). In addition, the $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.8}$ alloy electrode owned better cycle stability compared with $\text{LaNi}_{3.8}$. Férey et al. [6] reported that the $\text{LaNi}_{3.8}$ alloy exhibited a much lower reversible hydrogen capacity than that of the $\text{La}_4\text{MgNi}_{19}$ alloy. However, despite the higher capacity, the $\text{LaNi}_{3.8}$ alloy remained to be optimized in term of cycle life.

Furthermore, RE–Mg–Ni-based A_2B_7 -type alloys have been considered to be the most promising candidates as the negative electrode materials of the Ni/MH batteries, and in recent years, there have been many reports about the crystal structures and electrochemical performances of A_2B_7 -type alloys [10–16]. Liu et al. [10] found that when the phase abundance of the main A_2B_7 -type phase was 37.6 wt%, the alloy exhibited optimum comprehensive electrochemical properties. However, most of the previous studies are regarding to multiphase structure alloys which make the investigation more complicated. Therefore, the single-phase structure on the alloys can realize the effect of controlling single variable, which is benefit for the study. Zhang et al. [11] reported the Ce_2Ni_7 -type single-phase alloy showed a superior discharge capacity, close to 394 mAh g^{-1} , and high electrochemical cycling stability, which could achieve 413 cycles as its discharge capacity reduced to 60% of the maximum value.

Besides, it is well known that the Ce_2Ni_7 -type single-phase alloys can be described as the growth along the *c* axis of two different $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ subunits with 1:2 proportion [17]. In La–Ni hydride, only $[\text{AB}_5]$ subunits can be occupied by hydrogen atoms. When Mg atoms substitute La atoms of the $[\text{A}_2\text{B}_4]$ subunit [6], it makes the $[\text{A}_2\text{B}_4]$ subunits begin to absorb hydrogen. Hence the substitution of Mg improves the discharge capacity of La–Mg–Ni-based alloys, but reduces the cycling stability. Therefore, it is an important step to understand the effect and mechanism of Mg on the structure and electrochemical properties of the La–Mg–Ni-based alloy into subunits level. In the present work, we prepare the two alloys of $\text{LaNi}_{3.50}$ and $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{3.50}$ with Ce_2Ni_7 -type single-phase structure in this work, and comparatively study the crystal structure and electrochemical cycling stability of $\text{LaNi}_{3.50}$ and $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{3.50}$ alloys.

Experimental

Ce_2Ni_7 -type single-phase $\text{LaNi}_{3.50}$ and $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{3.50}$ alloys were gained by step-wise sintering. LaNi_5 and LaNi_2 were precursors for $\text{LaNi}_{3.50}$ alloy's preparation, while LaNi_5 and LaMgNi_4 were precursors for $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{3.50}$ alloy's preparation. All of precursors were obtained by induction melting in argon atmosphere of 0.05 MPa [18]. The precursors were ground into powders below 300 meshes separately and mixed together with designed molar ratios. Then the mixtures were cold pressed into tablets (2.5 g) of 10 mm in diameter, 8 mm in thickness under 10 MPa, and wrapped in Ni foils. Finally the tablets were sintered in a tube furnace at the temperature

ranging from 873 K to 1173 K, and subsequently annealed for 4.5 d at 1173 K.

The sintered samples were ground into powders under 400 meshes for XRD measurement on a D/Max-2500/PC X-ray diffractometer with Cu K_α radiation. And the XRD data were analyzed by Rietveld method using Rietica software [19]. The chemical compositions of the final tablets were test by inductively coupled plasma (ICP) system. The results are listed in Table 1. An S-4800 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) was performed to determine the phase distribution and composition of the sintered alloys.

The electrochemical properties were studied by a standard three-electrode system at 298 K, which was composed of MH electrode (working electrode), $\text{NiOOH}/\text{Ni}(\text{OH})_2$ electrode (counter electrode) and Hg/HgO electrode (reference electrode) [20]. The working electrode was prepared of nickel carbonyl powder in a weight of 0.75 g mixed with the sintered samples of 200–400 meshes in a weight of 0.15 g. After that, the mixture was cold pressed into a pellet, sandwiched between two Ni foams, and then welded to a nickel stick. To activate the alloy electrodes, the alloy electrodes were soaked in KOH solution for 24 h, then the batteries were respectively overcharged twenty percent at a current density of 60 mA g^{-1} for 2.5 h and 8 h of Mg-free and Mg-containing alloy electrodes and discharged at the same current density. The Tafel tests were conducted followed our previous reports [21].

To study the capacity degradation mechanism of single-phase Ce_2Ni_7 -type of $\text{LaNi}_{3.50}$ and $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{3.50}$ alloys during charge/discharge process, alloy electrodes with nickel carbonyl powder were made for SEM tests, while particular pure alloy electrodes without nickel carbonyl powder were made for XRD measurements after 5, 10 and 20 charge/discharge cycles. The preparation flow of the particular pure alloy electrodes is similar to that of the normal electrodes except that the special electrodes is only made from 0.4 g alloy powder and contains no nickel carbonyl powder. The alloy powders of 200–400 meshes with a weight of 0.4 g was cold-pressed into a pellet of 10 mm in diameter, 1 mm in thickness under 15 MPa. The pellet was wrapped by a piece of foaming nickel metal mesh and then welded to a nickel stick. Electrode particles after different charge/discharge cycles were separated from the foaming nickel metal mesh and submitted to XRD measurements.

Selected area electron diffraction (SAED) was tested by JEM-2010 transmission electron microscopy (TEM) to study the amorphization of the alloy powders after 5 charge/discharge cycles [22]. Firstly, the alloy samples before and after cycling were grounded into power under 400 meshes. Then, the sample powders were milled in anhydrous ethanol and dispersed in anhydrous ethanol by ultrasonic vibration for 30 min. Finally, a few drops of the suspensions were added onto the copper grids coated with a layer of holey carbon film. In order to study the element distribution profiles on the electrode surface after cycling, X-ray photoelectron spectrometry (XPS) analysis was performed on a PHI-550 type spectrometer at 10^{-8} Torr with monochromatic Al K_α radiation.

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