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Crystallographic and electrochemical characteristics of $La_{0.7}Mg_{0.3}Ni_{3-x}(Al_{0.5}Mo_{0.5})_x$ (x = 0–0.4) hydrogen storage alloys

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Abstract

The effect of partial substitution of Al and Mo for Ni on the structure and electrochemical properties of the $La_{0.7}Mg_{0.3}Ni_{3-x}(Al_{0.5}Mo_{0.5})_x$ (x = 0–0.4) hydrogen storage alloys have been investigated systematically. The result of X-ray powder diffraction (XRD) and Rietveld analysis show that all the alloys consist of the $La(La, Mg)_2Ni_9$ phase and the $LaNi_5$ phase. Meanwhile, the lattice parameter and the cell volume of both the $La(La, Mg)_2Ni_9$ phase and the $LaNi_5$ phase increase with increasing Al and Mo contents in the alloys. The pressure composition isotherms curves indicate that the hydrogen storage capacity first increases and then decreases with increasing x. The electrochemical measurements show that the maximum discharge capacity of the alloy electrodes first increases from 343.3 (x = 0) to 377.6 mAh/g (x = 0.3) and then decreases to 350.4 mAh/g (x = 0.4). Moreover, the high rate dischargeability (HRD) and the exchange current density of the alloy electrodes decrease first and then increases with the increase of x in the alloys. The hydrogen diffusion coefficient increases with increasing Al and Mo content and thus increases the low temperature dischargeability (LTD) of the alloy electrodes.

Keywords: Hydrogen storage alloy; Metal hydride electrode; Crystal structure; Electrochemical properties

1. Introduction

Hydrogen is expected to be a promising new energy source to replace conventional fossil for solving shortage of fossil energy resources and global warming in near future. In order for hydrogen to become a viable solution to the energy crisis and the environmental problem the hydrogen storage is one of many important processes. Among different ways to store hydrogen, absorption in solid to form hydride is very attractive since it allows safe storage at pressure and temperature close to ambient conditions [1]. It is the most successful for the metal hydrides to be applied as a negative electrode material in many application fields of metal hydrides. Nickel metal hydride (Ni-MH) secondary battery has been widely adopted in various portable electronic devices, electric hand tools and hybrid electric vehicles [2–6]. To date, almost all commercial Ni-MH batteries are employing AB_5-type alloys as the negative electrode materials [7]. However, the electrochemical capacity of the AB_5-type alloys is limited by the single $CaCu_5$-type hexagonal structure [8], the energy densities of the Ni-MH batteries are not competing favorably with some other advanced secondary batteries. Therefore, it is necessary to search for new type alloys with much high energy density, better rate dischargeability and lower cost, which perhaps may be alternative for the conventional rare earth-based AB_5-type alloys or another choice [9].

Recently, R–Mg–Ni (R = rare earth element, Ca or Y) system hydrogen storage electrode for Ni-MH batteries have attracted considerable attention because of their higher hydrogen storage capacities (absorb–desorb 1.8–1.87 wt.% H_2) than of the $LaNi_5$ alloy (absorb–desorb 1.4 wt.% H_2)

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[10–14]. As to their electrochemical hydrogen storage, Chen et al. [6] found that the maximum discharge capacity of $LaCaMgNi_9$ alloy reached 356 mAh/g. Kohno et al. [15] have studied the structure and electrochemical characteristics of La–Mg–$(NiCo)_x$ ($x = 3$–3.5) system alloys and found that $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$ alloy reached 410 mAh/g. Although the La–Mg–Ni–Co alloy has high hydrogen storage capacity, the cyclic stability is too low to be used as negative material of the Ni-MH secondary batteries [16], and hence their cycling stability has to be upgraded for practical applications. In commercial AB_5-type alloys the presence of 10 wt.% of Co has indeed improved the cycling life of Ni-MH batteries. However, it influences negatively the discharge capacity as well as initial activation and it constitutes about 40% of the material cost [17]. Much effort has been devoted to search for cheaper substitute element with high reliability to improve the cycling life of Ni-MH batteries. It is believed that Al is one of the best candidates for cobalt substitution [18]. However, Al addition is detrimental to hydrogen diffusion from electrode surface to alloy bulk and thus inevitably decrease the high rate dischargeability (HRD) of alloy electrode [19]. It is reported that Mo addition can remarkably increase the kinetic property [20] as well as the electrochemical capacity of alloy electrode [21]. Therefore, it can be expected that the overall electrochemical properties of the La–Mg–Ni type hydrogen storage alloys could be improved by substitution of Al and Mo for Ni in the alloys.

In present study, the structure and electrochemical characteristics of the $La_{0.7}Mg_{0.3}Ni_{3-x}(Al_{0.5}Mo_{0.5})_x$ ($x = 0$–0.4) hydrogen storage alloys has been investigated systematically.

2. Experimental details

2.1. Alloy preparation and X-ray diffraction analysis

All alloys were prepared by arc-melting carefully the constituent elements with the purity all above 99.9% on a water-cooled copper hearth under argon atmosphere. A slight excess of Mg over composition was needed to compensate for evaporative loss of Mg under preparation conditions. The alloys were turned over and remelted five times to ensure the good homogeneity. The weight loss of the alloys is less than 1 mass% during melting. Therefore, no chemical analyses were carried out. Thereafter, the alloy samples were crushed in mortar into fine powders of -300 meshes powder.

Crystallographic characteristics of the hydrogen storage alloys were investigated by X-ray diffraction on Rigaku D/Max 2500PC X-ray diffractometer (Cu Kα radiation, Bragg-Brentano geometry, 2θ range 10–100°, step size 0.02°, 4 s per step, backscattered rear graphite monochromator). The lattice constants and cell volume were calculated by Rietica program [22]. Silicon is used as standard reference material to calibrate the instrument before we obtain the XRD data.

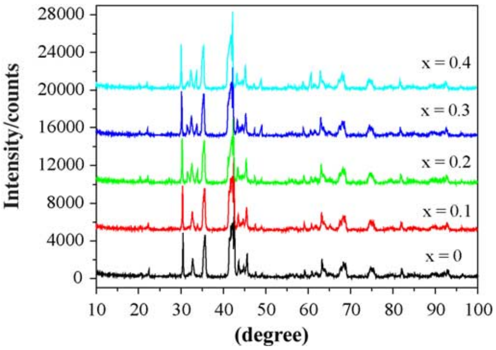

Fig. 1. XRD patterns of the $La_{0.7}Mg_{0.3}Ni_{3-x}(Al_{0.5}Mo_{0.5})_x$ hydrogen storage alloy.

2.2. Electrochemical measurement

The preparation of the disk-type electrodes, the set-up of the electrochemical cell and the measurement of electrochemical properties were similar as described in our previous paper [23]. Pressure–composition isotherms (P–C–T) curves, HRD, linear polarization curves and coefficient of diffusion of the alloy electrodes were measured according to our previous paper [24].

3. Results and discussion

3.1. Crystal structure

The X-ray diffraction patterns of the $La_{0.7}Mg_{0.3}Ni_{3-x}(Al_{0.5}Mo_{0.5})_x$ ($x = 0$–0.4) hydrogen storage alloys are shown in Fig. 1. It can be seen that all alloys have similar diffraction patterns, which indicates that the structure of the alloys almost unchanged with increasing Al and Mo content in the alloys. Moreover, careful examination of the diffraction angle reveals that the diffraction peaks shift to lower angles as a function of the increase of Al and Mo content in the alloys. Fig. 2 shows the XRD pattern and Rietveld analysis pattern of the $La_{0.7}Mg_{0.3}Ni_{2.9}(Al_{0.5}Mo_{0.5})_{0.1}$ hydrogen storage alloy as a representative example of $La_{0.7}Mg_{0.3}Ni_{3-x}(Al_{0.5}Mo_{0.5})_x$

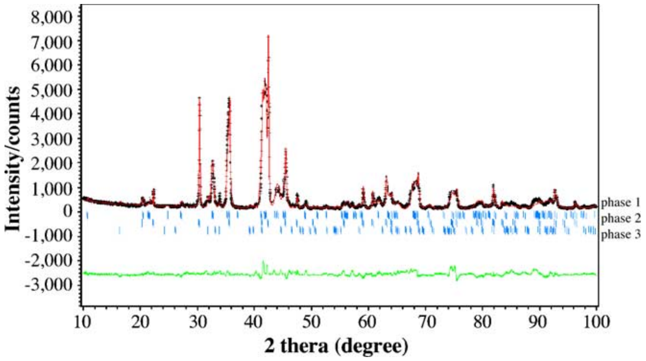

Fig. 2. Rietveld refinement pattern of the XRD profiles for the $La_{0.7}Mg_{0.3}Ni_{2.9}(Al_{0.5}Mo_{0.5})_{0.1}$ hydrogen storage alloy (phase 1: La (La, Mg)$_2$Ni$_9$; phase 2: $LaNi_5$; phase 3: LaNi).