ELSEVIER

Crystal structure and electrochemical characteristics of La$_{0.9}$Mg$_{0.1}$Ni$_{5-x}$Sn$_x$ ($x = 0.1, 0.2, 0.3, 0.4$) alloy electrodes

Xinbo Zhang [a], Danzi Sun [b], Wenya Yin [a], Yujun Chai [a], Minshou Zhao [a,*]

[a] Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Graduate School of Chinese Academy of Sciences, No. 5625 Renming Street, Changchun 130022, PR China
[b] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Graduate School of Chinese Academy of Sciences, Changchun 130022, PR China

Abstract

The crystal structure and electrochemical performance of La$_{0.9}$Mg$_{0.1}$Ni$_{5-x}$Sn$_x$ ($x = 0$–0.4) system compounds have been investigated systematically. It is found that the addition of Sn is beneficial to the dischargeability of the alloy electrodes at low temperature but detrimental to the dischargeability at high temperature. Moreover, addition of Sn is beneficial to both charge retention and high rate dischargeability.
© 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The nickel–metal hydride (Ni–MH) secondary battery has been widely adopted in many fields by virtue of its many advantages: high power density, high resistance to overcharging and overdischarging, capability of performing a high rate charge/discharge, environmental friendliness and interchangeability with nickel–cadmium battery [1–4]. As the most important component in a Ni–MH battery, metal hydride electrodes have attracted significant attention during the last decade [5–8]. However, in order to compete favorably with some other secondary batteries, alloys with higher energy density, faster activation and lower cost are urgently required. Recently, Kadir et al. [9–12] have reported that R–Mg–Ni based alloys can absorb–desorb 1.8–1.87

mass% H$_2$, and are therefore regarded as promising candidates for reversible gas hydrogen storage. As to their electrochemical hydrogen storage, Kohno et al. [13] developed several kinds of La–Mg–Ni–Co hydrogen storage electrodes and showed that the discharge of La$_{0.7}$Mg$_{0.3}$Ni$_{2.8}$Co$_{0.5}$ alloys reaches 410 mAh g^{-1}. Unfortunately, the La–Mg–Ni–Co system hydrogen storage electrode alloys have some disadvantages, such as a high absorption/desorption plateau pressure, and poor cyclic stability. Pan et al. [14] have systematically studied the structure and electrochemical properties of La$_{0.7}$Mg$_{0.3}$(Ni$_{0.85}$Co$_{0.15}$)x ($x = 3.0$–5.0) alloys and pointed out that La$_{0.7}$Mg$_{0.3}$(Ni$_{0.85}$Co$_{0.15}$)$_{3.5}$ suffers the poorest cyclic stability although it has the highest discharge capacity among the alloy electrodes. It is well known that elemental substitution is one of the most effective methods for improving the overall properties of the hydrogen storage alloys and obtaining the desired overall properties, e.g. proper capacity at a favorable hydrogen pressure, favorable high rate dischargeability (HRD) and good cyclic stability [15–18]. Liu et al. [19]

indicated that Co substitution for Ni can obviously improve the cyclic durability of the later charge/discharge cycles of the La–Mg–Ni–Mn–Co system alloy electrodes, while the discharge capacity decay of the starting charge/discharge cycles cannot be effectively prevented. Moreover, the existence of Co in these alloy electrodes increases the price greatly, making it unfavorable for practical applications. Lambert et al. [20] reported that tin substituted compounds have especially attractive properties because they show no line broadening and little capacity decay even after 10,000 cycles. It was found that Sn substitution for Ni in LaNi$_5$ alloy electrodes results in an obvious improvement of discharge capacity and cycle life of the alloy electrodes and improves the kinetics of hydrogen absorption–desorption [21]. Furthermore, Luo et al. [22] observed that the use of Sn as a partial substitute for Ni in LaNi$_5$ leads to a significant decrease in the hysteresis ratio. As to their electrochemical characteristics, Deng et al. [23] indicated that substitution of tin for Ni in LaNi$_5$ can apparently improve the electrochemical performance of the alloys.

With regard to the criteria of high discharge capacity and low cost of raw materials, in the present study the influence of partial substitution for Ni with Sn on the structural and electrochemical properties of the La$_{0.9}$Mg$_{0.1}$Ni$_{5-x}$Sn$_x$ ($x = 0.1$, 0.2, 0.3, 0.4) hydrogen storage alloys were studied in order to improve the overall properties of the La–Mg–Ni system alloy.

2. Experimental details

2.1. Alloy preparation, X-ray diffraction

All samples were prepared by arc melting the constituent metals or master alloy on a water-cooled copper hearth under an argon atmosphere. The purity of all the metals, i.e., La, Mg, Ni, and Sn, was higher than 99.9 mass%. A slight excess of Mg over stoichiometric composition was needed in order to compensate for evaporative loss of Mg during synthesis. Several attempts were made until the optimum preparative conditions were found. The alloys were turned over and remelted five times to ensure good homogeneity. The weight loss of the alloys was less than 1 mass% during melting. Therefore, no chemical analyses were carried out. Thereafter, the alloy samples were crushed in a mortar and pestle into fine powders of −300 mesh size.

Crystallographic characteristics of the hydrogen storage alloys were investigated using a Rigaku D/Max 2500PC X-ray diffractometer (CuK$_\alpha$ radiation, Bragg–Brentano geometry, 2θ range 20–110°, step size 0.02°, backscattered rear graphite monochromator). The lattice constants and cell volume were calculated by a cell program [24] after internal theta calibration using silicon as standard reference materials.

2.2. Electrochemical measurements

The preparation of the disk-type electrodes, the setup of the electrochemical cell and the measurement of electrochemical properties were similar to those described in our previous paper [25]. The charge efficiency was obtained according to Senoh's previous paper [26]. Both the HRD and the linear polarization curves of the alloy electrodes were measured according to our previous paper [27].

The charge retention (CR) of the negative electrode could be evaluated using the following equation [28]

$$CR = \{1 - 2C_2/(C_1 + C_3)\} \times 100/\text{day} \ (\%\text{day})$$

where C_1 represented the discharge capacity measured after the activation (by repeated charge–discharge cycling), C_2 was the discharge capacity measured after the storage on open-circuit conditions for a given period of time, and C_3, the discharge capacity measured in the charge–discharge cycle immediately after the measurement of C_2.

3. Results and discussion

3.1. Structure characteristic

Fig. 1 shows XRD patterns of La$_{0.9}$Mg$_{0.1}$Ni$_{5-x}$Sn$_x$ ($x = 0.1$, 0.2, 0.3, 0.4) alloys synthesized by arc melting. The sharp diffraction peaks indicate a long-range crystallographic order and excellent crystallinity of the alloy. It can be found that all the alloys have single CaCu$_5$-type phase. Careful examination of the diffraction angle reveals some slight shifts between these patterns, which depend on Sn content in the alloys. The lattice parameter, cell volume and density of the alloys are listed in Table 1. It can be clearly seen that both the lattice
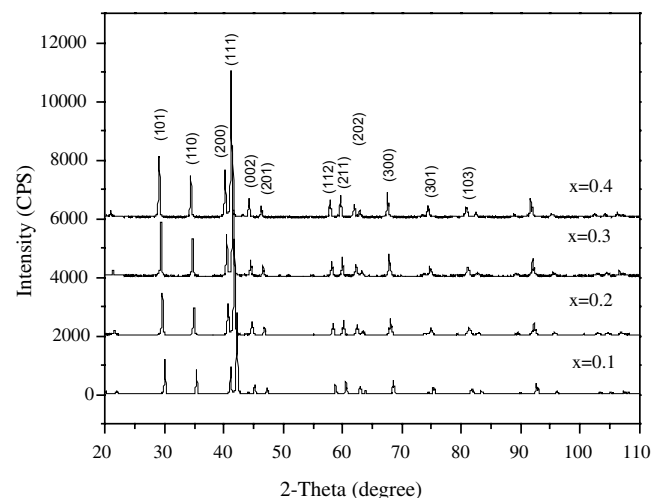

Fig. 1. XRD patterns of La$_{0.9}$Mg$_{0.1}$Ni$_{5-x}$Sn$_x$ ($x = 0.1$, 0.2, 0.3, 0.4).