Effects of annealing temperature on structure and the electrochemical properties of La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ hydrogen storage alloy

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Abstract

In our endeavor to improve the cyclic stability of the La–Mg–Ni–Co type alloys, the as-cast and annealed La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ hydrogen storage alloys were prepared and the effects of annealing at 1173, 1273 and 1373 K for 8 h on the crystal structures and the overall electrochemical properties of the alloys are reported in this paper. XRD and Rietveld analyses have revealed that the major phases of all the alloys are the (La,Mg)Ni$_3$ phase and the LaNi$_5$ phase. Both the lattice parameters and cell volumes of the (La,Mg)Ni$_3$ phase and the LaNi$_5$ phase increase with increasing annealing temperature, but the phase abundance of these two phases varies differently. It is found that the discharge capacity and the cycle life of the alloys are improved after annealing treatment owing to the variable phase abundance and composition homogenization, respectively. However, high rate dischargeability (HRD), electrochemical impedance spectra (EIS), linear polarization, anode polarization and potential-step studies indicate that the electrochemical kinetics of the alloy electrodes is deteriorated after annealing treatment. This phenomenon can be ascribed to that the composition homogenization and the suppression of the pulverization due to decreasing of the crystal lattice strain and defect after annealing treatment, which increases the charge-transfer resistance of the alloy electrodes and also reduces the rate of the diffusion of hydrogen from the interior of the bulk to the surface.

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1. Introduction

Recently, R–Mg–Ni (R = rare-earth, Ca or Y element) type hydrogen storage alloys with the general formula RMg$_2$Ni$_9$ (PuNi$_3$-type rhombohedral structure) have attracted attention widely because of their high hydrogen storage capacity and good electrode properties [1–12]. Kadir et al. [2] reported the maximum hydrogen storage capacity of the (La$_{0.65}$Ca$_{0.35}$)(Mg$_{1.32}$Ca$_{0.68}$)Ni$_9$ alloy reached 1.87 wt.%. Chen et al. [3] studied the structure and hydriding properties of LaCaMgNi$_9$, LaCaMgNi$_6$Al$_3$ and LaCaMgNi$_6$Al$_3$ alloys and found all of these alloys can absorb/desorb hydrogen up to 1.8 wt.% under the conditions studied. As to their electrochemical hydrogen storage, Kohno et al. [4] reported the discharge capacity of the La$_0.7$Mg$_{0.3}$Ni$_{2.8}$Co$_{0.5}$ alloy reached 410 mAh/g, with fairly good cyclic stability within 30 cycles. Moreover, our laboratory has also done much research on this topic [5–12]. The study on La$_{0.7}$Mg$_{0.3}$Ni$_{2.8}$Co$_{0.5}$($x$ = 2.5–5.0) hydrogen storage alloys showed that the maximum discharge capacity of a La$_{0.7}$Mg$_{0.3}$Ni$_{3.5}$Co$_{1.5}$ alloy electrode was 396 mAh/g [5,6]. And further studies have revealed that the substitution of Ni by Mn, Co or Al can improve the overall properties of the La–Mg–Ni–Co type alloys [7–12]. For example, the La$_0.7$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ alloy exhibits higher discharge capacity ($C_{max}$ = 370.3 mAh/g) and better cyclic stability ($S_{100}$ = 67.1%) [12]. All of the above results suggest that these types of alloys are promising candidates for electrochemical hydrogen storage.

However, the overall electrochemical properties of the La–Mg–Ni–Co type hydrogen storage electrode alloys should be further improved for their practical application, particularly cyclic stability. It is well known that the annealing
treatment is a very effective way to improve the overall properties of the hydrogen storage alloys, such as the maximum discharge capacity, cyclic stability and high rate discharge-ability and so on [13–15]. Nakamura et al. [13] reported that the plateau regions of the desorption $P$-C isotherm of LaNi$_5$[13] type alloys, and found that the discharge capacity of the La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ alloy annealed at 1173 K reached 44.4 mA h/g, and the cyclic stability was markedly improved [15].

In this paper, in order to improve further the overall properties of the La-Mg-Ni-Co type alloys, La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ alloy was selected and the effects of annealing treatment on the structure and electrochemical properties were studied systematically and are reported.

### 2. Experimental

The La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ alloy sample was prepared by induction levitation melting under argon atmosphere and remelted four times for homogeneity. All starting elemental metals have a purity higher than 99.9%. Some of the alloy was annealed at 1173, 1273 and 1373 K for 8 h in vacuum. Then, all the alloy samples were mechanically crushed and ground into powders of 300 mesh size (<50 μm) and used for both X-ray diffraction (XRD) and electrochemical measurements.

All test electrodes were prepared by cold pressing a mixture of 0.1 g alloy powder and 0.4 g carbonyl nickel powder to pellets of 10 mm in diameter and about 1 mm in thickness under a pressure of 12 MPa. The electrochemical studies were performed in a half-cell consisting of a working electrode (the MH electrode for investigation), a sintered Ni(OH)$_2$/NiOOH counter electrode and a Hg/HgO reference electrode. The electrolyte was a 6 M KOH solution. The discharge capacity, activation and cycle stability of the alloy electrodes were determined by an automatic galvanostatic system. The discharge capacity, activation and cycle stability of the alloy electrodes were conducted in a frequency range from 10 KHz to 5 MHz with AC amplitude of 5 mV under open-circuit condition on a Solartron SI1287 Electrochemical Interface with 1255B Frequency Response Analyzer, fully activated electrodes at 50% depth of discharge (DOD). Linear polarization and anode polarization were measured on a Solartron SI1287 potentiostat by scanning the electrode potential at a rate of 0.1 mV/s from −5 to 5 mV (versus open-circuit potential) and 5 mV/s from 0 to +500 mV (versus open-circuit potential) at 50% depth of discharge, respectively.

### 3. Results and discussion

#### 3.1. Phase structure and metallurgical microstructure

Fig. 1a shows the XRD patterns of the as-cast and annealed La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ hydrogen storage alloy electrodes. The alloy samples were annealed for 8 h at 1173, 1273 and 1373 K, respectively. Fig. 1b shows as an example the Rietveld analyses of the as-cast alloy. As can be seen in the figure, the major phases in all alloys are the (La,Mg)Ni$_3$ phase with rhombohedral PbNi$_3$-type structure and the LaNi$_5$ phase with hexagonal CaCu$_5$-type structure. The phase abundance, lattice parameters and cell volumes of the as-cast and annealed La$_{0.7}$Mg$_{0.3}$Ni$_{2.45}$Co$_{0.75}$Mn$_{0.1}$Al$_{0.2}$ alloys obtained