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The microstructures and electrochemical performances of $La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.5-x}Al_x$ (x=0–0.5) hydrogen storage alloys as negative electrodes for nickel/metal hydride secondary batteries

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HIGHLIGHTS

- The substitution Al for Co for A_2B_7-type alloy electrodes was scarcely reported.
- The cooperation of Al and Co yield alloys with superior electrochemical performances.
- The mechanism of capacity degradation for alloy electrodes after Al substitution was provided.

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ABSTRACT

$La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.5-x}Al_x$ ($x = 0$–0.5) hydrogen storage alloys were prepared by induction melting followed by annealing treatment at 1173 K for 8 h. The effects of substitution Al for Co on the microstructures and electrochemical performances were studied systematically. The structure analyses show that all alloys consist of multiphase structures such as $(La, Mg)_2Ni_7$ phase, (La, Mg) Ni_3 phase and $LaNi_5$ phase. The abundance of $(La, Mg)_2Ni_7$ phase decreases while the abundance of $LaNi_5$ phase and (La, Mg) Ni_3 phase increases directly as the Al content increasing. The electrochemical tests show that the maximum discharge capacity of alloy electrodes are almost unchanged when $x \leq 0.2$ while the cyclic stability of the alloy electrode are improved significantly after proper amount of Al substitution for Co. The alloy electrode with $x = 0.1$ exhibits the better balance between discharge capacity and cycling life than any others. Moreover, at the discharge current density of 900 mA g^{-1}, the high rate dischargeability (HRD) of the alloy electrodes decreases with increasing Al substitution and the relative analyses reveal that the charge transfer on alloy surface is more important than the hydrogen diffusion in alloy bulk for the kinetic properties of the alloy electrodes.

1. Introduction

Because of many advantages such as high energy density, perfect activation properties and environmentally friendliness, Ni/MH batteries have been occupying a large market share in secondary battery filed. As negative electrode material of Ni/MH batteries, the conventional rare earth-based AB_5-type hydrogen storage alloys which have been commercialized suffer from low discharge capacity (320 mAh g^{-1}) due to its $CaCu_5$-type crystal structure. The newly La–Mg–Ni system hydrogen storage alloys such as A_2B_7-type and AB_3-type alloys are considered to be the most promising candidates to replace AB_5-type alloys because of the higher discharge capacity (400 mAh/g) [1–3]. However, it is necessary to improve the cyclic durability of this kind of alloy in the alkaline electrolyte for the practical application. Element substitution has been proved to be an effective way to improve the overall electrochemical properties of hydrogen storage alloys. Among the substitution elements, Co is thought to play an important role to improve the cycle life of La–Mg–Ni system hydrogen storage alloys because it can increase the corrosion resistance of the electrodes in the alkaline electrolyte [4,5]. Notten [6] confirmed that Co addition can effectively improve cycle life of MH/Ni secondary batteries. Liu [7] reported that the cycling stability of $La_{0.7}Mg_{0.3}Ni_{3.4-x}Mn_{0.1}Co_x$ ($x = 0$–1.3) alloy electrodes was markedly improved from 25.5% ($x = 0$) to 61.3% ($x = 1.3$) after 90 cycles because of the lower oxidation/corrosion rate with Co addition. Actually, the effects of Co substitution for Ni on electrochemical properties of La–Mg–Ni

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system hydrogen storage alloys have been studied extensively. However, the cycle life of this kind of alloy still not meets the demands of the market by simply Co substitution. Moreover, Co is the most expensive element in such alloys which resists the further commercial application. Consequently, for La–Mg–Ni system alloys, it is important to find an effective way to improve the cycle life further and decrease Co content. Al is another key substitution element to improve the cyclic stability of hydrogen storage alloys which is much more cheaper than Co. Partially substituting Ni with Al can prolong the cycling life of the hydrogen storage alloy electrodes because of forming a dense oxide film which can prevent alloys from further corrosion in KOH electrolyte, however, the discharge capacity of the alloy electrodes decreases too much after Al substitution [8–10]. Dong [11] revealed that Al substitution could prolong the cyclic lifetime of the La–Mg–Ni system alloy electrodes from 55.45% to 70.08% after 100 cycles while the maximum discharge capacity decreased from 401.8 mAh/g to 373.7 mAh/g. Liao [12] found that the cycling stability of the La–Mg–Ni system alloy electrodes could be improved further by Al substitution than by some other elements such as Co, Cu, Fe, Mn and Sn while the alloy electrode with Al substitution showed the minimum discharge capacity which was only 185.4 mAh/g. Based on the effects of Al and Co substitution for Ni on the electrochemical properties for La–Mg–Ni-system hydrogen storage alloys respectively, it is expected that the combination of Al and Co which are used as a group of substitution elements may yield alloys with superior electrochemical performances. As a result, it is essential and important to study the correlations of Co and Al on microstructures and electrochemical performances of La–Mg–Ni system alloys for the further commercial applications.

In our previous research, we found that the addition of Gd with proper content can improve the overall electrochemical properties of the alloy electrodes effectively and the alloy with chemical composition of $La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.5}$ possesses good electrochemical performances such as discharge capacity and cyclic stability. So in this paper, $La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.5-x}Al_x$ ($x = 0–0.5$) alloys were prepared and the effects of substituting Al for Co on microstructures and electrochemical properties were investigated systematically.

2. Experimental

$La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.5-x}Al_x$ ($x = 0–0.5$) hydrogen storage alloys were prepared by vacuum induction melting on a water-cooled cooper crucible under 0.2 MPa argon atmosphere followed by annealing treatment at 1173 K for 8 h. Due to the high vapor pressure of Mg element, an appropriate excess (10 wt.%) of Mg element was necessary. The purity of all elements was above 99.9 wt.%.

The annealed alloys were mechanically crushed and ground into powders of 400 mesh size for X-ray diffraction (XRD) measurements and into powders of 300–400 mesh size for electrode test. The crystal structures were determined by XRD analyses which were carried out by a Rigaku D/max-2500 diffractometer. The diffraction was performed with Cu Kα1 radiation filtered by graphite. The experimental parameters were 40 kV, 200 mA, and 4° min^{-1}. Then the collected data were analyzed by the Rietveld method using Fullprof 2K software to get the lattice parameters and phase abundance.

All the test electrodes were prepared by cold pressing the mixture of 0.1 g alloy powder and 0.3 g carbonyl nickel powder under 15 MPa pressure to form a pellet of 10 mm in diameter. The additive carbonyl nickel powder was used to increase the electrocatalytic activity and decrease the electrochemical reaction resistance of the alloy electrodes. Then the pellet was sandwiched within two foamed Ni plates with a Ni wire soldered on to form a negative electrode. The electrodes were immersed in 6 M KOH solution for 6 h in order to wet thoroughly before electrochemical measurements. Electrochemical measurements were performed at 298 K in a standard open tri-electrode electrolysis cell consisting of a working electrode (the MH electrode for studying), a sintered $Ni(OH)_2$/NiOOH counter electrode with excess capacity and a Hg/HgO reference electrode, immersed in the electrolyte of 6 M KOH solution. For activation, each electrode was charged at 60 mA g^{-1} for 7.5 h followed by a 10 min rest and then discharged at 60 mA g^{-1} to the cut off potential of −0.6 V (vs. Hg/HgO reference electrode). For cycling test, the activated electrode was charged at 100 mA g^{-1} for 4.5 h followed by a 10 min rest and then discharged at 300 mA g^{-1} to the cut off potential of −0.6 V (vs. Hg/HgO reference electrode). The high rate dischargeablity (HRD) of the alloy electrodes was determined by examining the discharge capacity at various discharge current densities and defined as the following equation:

$$HRD_i = \frac{C_i}{C_i + C_{100}} \times 100\% \tag{1}$$

where C_i is the discharge capacity with a cut-off potential of −0.6 V (vs. Hg/HgO reference electrode) at i current density, C_{100} is the residual discharge capacity to the same cut-off potential at current density $i = 100$ mA g^{-1} after the alloy electrode is discharged at current density i. The data were collected in an automatic Arbin MSTAT battery testing instrument.

To investigate the mechanism of discharge capacity degradation and the kinetics character of alloy electrodes, linear polarization, Tafel polarization, and potential-step discharge method were performed on Princeton VersaSTAT MC electrochemical work station after alloy electrodes were fully activated. The linear polarization curves and the Tafel polarization curves were measured by scanning the electrode potential at a rate of 0.1 mV s^{-1} from −5 to 5 mV (vs. open circuit potential) and 5 mV s^{-1} from −1.2 V to −0.2 V (vs. Hg/HgO reference electrode), respectively, at 50% depth of discharge (DOD). The hydrogen diffusion coefficient was estimated by the potential-step discharge method. The experiment was carried out on Princeton VersaSTAT MC electrochemical work station. The full-charged electrodes were discharged at an overpotential of +600 mV for 4000 s. In addition, the microstructure evolution of the alloy particles after certain charge/discharge cycles was observed by scanning electron microscope (SEM) on a CS3400 instrument.

3. Results and discussion

3.1. Crystal structures

Fig. 1 shows the XRD patterns of $La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.5-x}Al_x$ ($x = 0–0.5$) hydrogen storage alloys. As shown in Fig. 1, the phase structures of the alloys were changed with Al substitution for Co. Fig. 2 illustrates the example of XRD pattern and Rietveld analysis pattern of the $La_{0.6}Gd_{0.2}Mg_{0.2}Ni_{3.0}Co_{0.4}Al_{0.1}$ alloy. Fig. 3 shows the phase structure of the alloys. Phase abundance, lattice parameters and unit cell volumes are listed in Table 1, which were calculated from the data of Fig. 1 with Rietveld method. As seen from Fig. 1 and Table 1, all alloys have multiphase structures including $(La, Mg)_2Ni_7$ phase, (La, Mg) Ni_3 phase and $LaNi_5$ phase. From Table 1 and Fig. 3, it can be found that as Al content increasing, the abundance of $(La, Mg)_2Ni_7$ phase decreases from 91.09% ($x = 0$) to 89.31% ($x = 0.1$) slightly and then decreases to 37.98% ($x = 0.5$) while the abundances of $LaNi_5$ phase and $(La, Mg)Ni_3$ phase increase directly from 3.11% ($x = 0$) to 46.76% ($x = 0.5$) and from 5.80% ($x = 0$) to 15.26% ($x = 0.5$), respectively. The results of structure analyses show that Al