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Effect of B and Fe substitution on structure of AB_3-type Co-free hydrogen storage alloy

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Abstract: A series of hydrogen storage Co-free AB_3-type alloys were directly synthesized with vacuum mid-frequency melting method, within which Ni of $La_{0.7}Mg_{0.3}Ni_3$ alloy was substituted by Fe, B and (FeB) alloy, respectively. Alloys were characterized by XRD, EDS and SEM to investigate the effects of B and Fe substitution for Ni on material structure. The content of $LaMg_2Ni_9$ phase within $La_{0.7}Mg_{0.3}Ni_3$ alloy reaches 37.9% and that of $La_{0.7}Mg_{0.3}Ni_{2.9}(FeB)_{0.1}$ alloys reduces to 23.58%. Among all samples, ground particles with different shapes correspond to different phases. The major substitution occurs in $LaMg_2Ni_9$ phase. Electrochemical tests indicate that substituted alloys have different electrochemical performance, which is affected by phase structures of alloy. The discharge capacity of $La_{0.7}Mg_{0.3}Ni_3$ alloy reaches 337.3 mA·h/g, but $La_{0.7}Mg_{0.3}Ni_{2.9}(FeB)_{0.1}$ alloy gets better high rate discharge (HRD) performance at the discharge rate of 500 mA/g with a high HRD value of 73.19%.

Key words: Ni-MH battery; AB_3-type; B substitution; Co-free hydrogen storage alloy

1 Introduction

Today, batteries with high capacity and small size are demanded as mini-appliances become popular in our life. The demands of hybrid electric vehicle (HEV) and electric vehicle (EV) have promoted the research on high-capacity green power batteries. Battery materials for vehicles should have good cycling performance, high rate discharge capability and high specific discharge capacity.

Nickel/metal hydride (Ni-MH) secondary battery has been widely used due to its high energy density, high rapid charge−discharge ability and considerable safety performance. The potentially high performances of Ni-MH battery will meet the requirements of the power battery.

Hydrogen storage alloy determines the properties of the battery such as plateau potential, maximum discharge capacity, high rate discharge ability and cycling life. AB_5-type and AB_2-type hydrogen storage alloys are regular anode materials of Ni-MH batteries among hydrogen storage alloys[1]. The theoretical discharge capacity of AB_5-type alloys reaches 348 mA·h/g and that of AB_2 alloy is lower. And different methods have been studied extensively to improve the properties including element substitution[2−3]. Element Co is usually added into the alloys to make them have sufficient cycling stability and high discharge capacity. The test discharge capacity of AB_5-type alloys could reach 320−340 mA·h/g according to recent studies[4−5]. However, properties of enhanced AB_5-type alloys are still low for meeting the demands of HEV and EV. HEV and EV require a new kind of hydrogen storage alloy which has higher discharge capacity and outstanding stability under high current density.

AB_3-type hydrogen storage alloy has higher discharge capacity than AB_5-type because of the strong hydrogen storage ability of Mg element within $LaMg_2Ni_9$ phase[6−9]. According to recent studies, the discharge capacity of La-Mg-Ni AB_3-type alloys with Co element could reach 380−400 mA·h/g[10−14]. Element Co could be added into AB_3-type alloys to guarantee the cycling stability and high discharge capacity when it works in

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AB_5-type alloys[6]. Considering that Co element is not environmentally friendly enough and can increase the cost of batteries, there are some work done on low-Co alloys in which Co was substituted by Fe or other elements[15−16]. Co-free hydrogen storage alloy has got attention and there are some studies on it in recent years[17−20].

In this work, a series of Co-free hydrogen storage alloys were directly synthesized with vacuum melting method in which Ni was substituted by Fe, B and FeB alloy, respectively. And $La_{0.7}Mg_{0.3}Ni_3$ alloy was synthesized under the same condition for comparison. The effects of B and Fe substitution on structure and electrochemical performances of hydrogen storage alloy were investigated. Morphologies and phase structure of alloy were deeply discussed, because the electrochemical performances of material mainly depend upon both morphologies and phase structure.

2 Experimental

2.1 Synthesis

La, Ni, Fe, B, $MgNi_2$ alloy and FeB alloy were used as the raw materials to synthesize the hydrogen storage alloys. The purity of La, Ni, Fe and B elements were all above 99.5% (mass fraction). $MgNi_2$ and FeB alloys were industrial products. As, La and Mg elements can easily volatilize, so 10% (mass fraction) extra amounts of them were added into raw materials, respectively. The melted alloy was cooled by water, and its oxidation layer was removed. Then, the products were manually mechanically pulverized to 50 μm. The chemical compositions of alloys were tested by inductively coupled plasma spectrometry (ICP) as shown in Table 1. The ICP results are in agreement with the target compositions.

2.2 Characterization

The XRD measurement of synthesized alloys was carried with Cu K_α radiation (λ=1.540 6 Å) in the scan range of 10º−100º. And the diffraction was performed with the experimental parameters of 40 kV, 150 mA and 2 (º)/min.

The ground powders were observed by SEM and carried out by EDS at the same time to characterize the particle morphologies and phase constitutions of alloys.

2.3 Electrode preparation and battery assembly

Alloy powder and carbonyl nickel (Ni-255) powder were well mixed according to 1:3 mass ratio and pressed into negative electrode disks under a pressure of 15 MPa. The industrial $Ni(OH)_2$-NiOOH positive electrode was used as the counter electrode. The working electrode and counter electrode immersed in 6 mol/L KOH alkaline solution were assembled into an open two-electrode electrolysis cell. The discharge capacities of alloys were tested by LAND test system at a current density of 150 mA/g.

2.4 Electrochemical properties characterization

The charge−discharge cycling performances of alloys were tested by the same test system at a current density of 150 mA/g and the cut-off voltage of 1 V.

High rate discharge (HRD, D) abilities of alloys were tested by following steps: open cell was activated by 3−5 charge−discharge cycles at a current density of 50 mA/g at first, then the cell was fullly charged at 50 mA/g current density. After 10 min rest, the cell was discharged at a certain current density (n) to the cut-off voltage of 1 V and the cell rested for another 10 min to dispel the polarization. The discharge capacity was recorded as C_n. After that, the cell was discharged to the cut-off voltage of 1 V at a current density of 50 mA/g and the discharge capacity was recorded as C_{50}. The D_n could be calculated by equation: $D_n(\%)=C_n/(C_n+C_{50})$.

3 Results and discussion

3.1 XRD results and analysis

The XRD patterns of melted alloys are shown in Fig.1, and cell parameters of different phases of each alloy are shown in Table 2 (the phase content are calculated by JADE software).

As shown in Fig.1, the structure of melted alloy is changed obviously due to the different substitutions. It can be seen that the $La_{0.7}Mg_{0.3}Ni_3$ alloy exhibits parts of the diffraction peaks corresponding to $LaNi_5$ phase

Table 1 Composition of melted alloys by ICP analysis

Sample	Mass fraction/%					Composition formula
	La	Mg	Ni	Fe	B	
$La_{0.7}Mg_{0.3}Ni_{2.9}(FeB)_{0.1}$	34.560	2.850 0	62.59	−	−	$La_{0.7}Mg_{0.3}Ni_{2.95}B_{0.05}$
$La_{0.7}Mg_{0.3}Ni_{2.9}Fe_{0.1}$	35.005	2.515 5	59.51	1.27	−	$La_{0.72}Mg_{0.30}Ni_{2.93}Fe_{0.07}$
$La_{0.7}Mg_{0.3}Ni_{2.9}(FeB)_{0.1}$	34.975	1.987 5	61.94	−	0.108 3	$La_{0.75}Mg_{0.26}Ni_{2.91}(FeB)_{0.09}$
$La_{0.75}Mg_{0.26}Ni_{2.91}(FeB)_{0.09}$	35.805	2.144 5	58.57	1.62	0.437 7	$La_{0.70}Mg_{0.24}Ni_{2.96}B_{0.04}$

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