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Electrochemical hydrogen storage properties of non-stoichiometric $La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5}$ (x = 0-0.10) electrode alloys

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ABSTRACT

The microstructure and electrochemical hydrogen storage characteristics of $La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5}$ (x = 0, 0.05 and 0.10) alloys prepared by arc-melting and subsequent powder sintering method are investigated. The electrochemical measurement results show that the cycle stability after 100 charge/discharge cycles first increases from 46.4% (x = 0) to 54.3% (x = 0.05), then decreases to 43.2% (x = 0.10), and the high rate dischargeability increases from 64.5% (x = 0) to 68.5% (x = 0.10) at the discharge current density of 1200 mA/g. The electrochemical impedance spectroscopy analysis indicates that the electrochemical kinetics of the alloy electrodes is improved by increasing Ca. The entire results exhibit that a suitable content of Ca (x = 0.05) can improve the overall electrochemical hydrogen storage characteristics of the alloys.

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1. Introduction

Energy and environmental protection have become two major themes in today's world, and development for environment friendly energy materials is the prime objective. Hydrogen storage alloys as negative materials of metal hydride–nickel (MH/Ni) secondary batteries are one kind of environment friendly energy storage materials. In recent years, La–Mg–Ni system hydrogen storage alloys have been paid wide attention and considered as one of the novel candidates for negative electrode materials of AB₅-type alloys due to their larger discharge capacities [1–5].

The main problem for La–Mg–Ni system hydrogen storage alloys to be used for industrialization is the poor cycle stability now. Due to Ca and Mg elements belong to the same group (group IIA) in the periodic table and the electro-negativity of Ca is more negative than Mg, it is significant to study the effect of substituting Mg with Ca in the alloys on microstructure and electrochemical characteristics of AB₃-type hydrogen storage alloys.

In this work, we select the $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$ alloy as a basic alloy and study the microstructure and electrochemical hydrogen storage characteristics of La-Mg-Ni system $La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5}$ (x = 0, 0.05 and 0.10) alloys.

2. Experimental

2.1. Alloy preparation and crystallographic characteristics analysis

The La–Ni–Co alloys were prepared by arc-melting under Ar atmosphere, with the constituent metals (La, Ni and Co; >99.9 wt.% purity) on a water-cooled copper hearth. The alloys were turned over and melted three times to make them homogeneous. Then parts of the alloys were crushed and grinded to powder for composites and powder sintering. Before powder sintering, the La–Ni–Co alloys, CaNi₃, MgNi₂ and Ni powders (200–300 mesh) at a certain molar ratio were pre-mixed using a planetary ball mill QM-1 SP for 10 min under Ar atmosphere. The ball to powder mass ratio was 5:1 and the rotation speed was 200 rpm. After the milling, the mixtures were cold pressed into green compacts under a pressure of 20 MPa. The green compacts were then powder sintered under Ar atmosphere for 12 h at 1273 K.

The La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5} (x=0–0.10) hydrogen storage alloys were mechanically crushed into powders of 200–300 mesh in a glove box under a dry Ar atmosphere. XRD measurements were carried out using a Rigaku D/Max-3B diffractometer with CuK α radiation at 40 kV and 30 mA.

2.2. Electrochemical measurements

The testing electrodes were constructed by mixing the composite powders with carbonyl nickel powders at a weight ratio of 1:5. The powder mixtures were pressed into a small pellet under a pressure of 20 MPa. Electrochemical charge/discharge testing was carried out at 298 K by using a DC-5 battery testing system. The electrolyte was 6 M KOH aqueous solution. In each charge/discharge cycle test, the negative electrodes were charged for 7 h at 60 mA/g and discharged at 60 mA/g to the cut-off potential of -0.6 V (versus Hg/HgO). High rate discharge ability (HRD) was measured by a ratio of the discharge capacity at a given discharge current density (300–1200 mA/g) to the discharge capacity at 60 mA/g. Linear polarization curves were performed on a EG&G PARC's Model 273 Potentiostat/Galvanosta station by scanning the electrode potential at the rate of 0.1 mV/s from -5 to 5 mV (versus open circuit potential) at 50% depth of discharge (DOD), and potential step experiments were performed on the same instrument at 100% charge state. Electro

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Fig. 1. XRD patterns of $La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5}$ (x=0-0.10) hydrogen storage alloys.

chemical impedance spectra (EIS) were obtained in the frequency range from 10 kHz to 1 mHz at 50% DOD.

Table 2

Summary of electrochemical characteristics for the alloy electrodes.

x	N ^a	$C_{\rm max}~({\rm mAh/g})$	$C_{100} ({\rm mAh/g})$	$S_{100}~(\%)$	HRD ₁₂₀₀ (%)
x = 0	3	387.3	179.6	46.4	60.5
x = 0.05	3	384.2	208.6	54.3	65.1
x = 0.10	3	345.4	149.3	43.2	68.5

^a The cycle numbers needed to activate the alloy electrodes.



Fig. 2. Evolution of discharge potential for the alloy electrodes at 298 K.

3. Results and discussion

3.1. Microstructures

The XRD patterns of $La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5}$ (x=0-0.10) hydrogen storage alloys are shown in Fig. 1. It can be seen that the patterns exhibit similar diffraction peaks, and all alloys mainly consist of (La, Mg)Ni₃ and LaNi₅ phases, which indicates that the microstructures are almost unchanged by increasing *x*.

The lattice parameters and unit cell volumes of (La, Mg)Ni₃ and LaNi₅ phases in the alloys are listed in Table 1. As increasing *x*, the *a*, *c* and *v* of (La, Mg)Ni₃ phase increase, which is ascribed to that the atomic radius of Ca (1.74 Å) is larger than that of Mg (1.60 Å), whereas the *a*, *c* and *v* of LaNi₅ phase decrease, which is ascribed to that of Ca can exist in (La, Mg)Ni₃ or LaNi₅ phases unlike Mg [6], thus the lattice parameters of LaNi₅ phase decrease when Ca adds into LaNi₅ phase to replace La (1.88 Å). The abundances of the phases are calculated by Rietveld refinement and also listed in Table 1. It can be found the abundance of (La, Mg)Ni₃ phase decreases while the abundance of LaNi₅ phase increases, which is ascribed to that Ca can exist randomly in AB₅ or AB₂ structural units and Mg can only exist in AB₂ structural unit [6], thus the abundance of (La, Mg)Ni₃ phase increases.

3.2. Discharge capacity and cycle stability

The cycle numbers for activating $La_{0.7}Mg_{0.3-x}Ca_xNi_{2.8}Co_{0.5}$ (x=0-0.10) alloy electrodes are listed in Table 2. It can be seen that the alloy electrodes can be activated to maximum discharge capacities within three cycles. Fig. 2 shows the discharge potential curves of the alloy electrodes for the third cycle. It can be obviously noted that the discharge plateau shifts towards a more positive potential with the increase of Ca, which indicates that Ca leads to an increase in discharge potential for the alloy electrodes due to its more negative electro-negativity.

The maximum discharge capacities (C_{max}) decrease from 387.3 mAh/g (x=0) to 345.4 mAh/g (x=0.10), which is ascribed to that the abundance of (La, Mg)Ni₃ phase decreases and the abundance of LaNi₅ phase increases, and it is believed that the discharge capacity of (La, Mg)Ni₃ phase is larger than that of LaNi₅ phase. Therefore, the maximum discharge capacities of the alloy electrodes decrease by increasing Ca content.

The relationship between discharge capacity and cycle number for the alloy electrodes is represented in Fig. 3. The cycle stability after 100 charge/discharge cycles (S_{100}) at 60 mA/g is listed in Table 2. It can be seen that the S_{100} of the alloy

Table 1

x	Phase	Phase type	Lattice parameter (Å)		Cell volume (Å ³)	Phase abundance ^a (wt.%)
			a	С		
x = 0	(La, Mg)Ni₃	PuNi₃	5.055	24.635	550.1	83.17
	LaNi ₅	CaCu ₅	5.021	3.983	87.1	16.83
x = 0.05	(La, Mg)Ni₃	PuNi₃	5.059	24.711	553.7	81.52
	LaNi ₅	CaCu ₅	5.015	3.971	86.6	18.48
x = 0.10	(La, Mg)Ni ₃	PuNi ₃	5.077	24.843	556.2	77.81
	LaNi ₅	CaCu ₅	5.011	3.962	86.1	22.19

^a Phase abundances of the phases are calculated by Rietveld refinement.

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