Effect of Al on the cycling behavior of the AB5-type La-Ni-Co-Mn alloy electrodes

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Abstract. The AB_5-type hydrogen storage alloys $La_{0.7}Ni_{2.5}Co_{0.9-x}Mn_{0.1}Al_x$ were prepared by magnetic induction melting. The structure and the electrochemical properties of alloys were also investigated using X-ray powder diffraction technique and various electrochemical measurements. All the alloys are mainly composed of the $LaNi_5$ phase with a $CaCu_5$-type hexagonal structure. The alloy electrodes deliver good electrochemical hydrogen storage properties. The maximum discharge capacities of $La_{0.7}Ni_{2.5}Co_{0.9}Mn_{0.1}$ alloy at room temperature and low temperature are 355.2 and 378.3 mAh/g, respectively. Although the discharge capacities the alloy electrodes decrease with the increasing Al content, the cycling stabilities are improved.

1. Introduction

In recent years, Ni-MH secondary batteries have been widely applied in electric vehicle because of their high capacity, better environmental compatibility and high rate performance [1-3]. The AB_5-type hydrogen storage alloy as one of the most common hydrogen storage alloys was employed widely for the negative electrode of the Ni-MH batteries [4-8].

The content of Co in the AB_5-type hydrogen storage alloys have significant effects on the electrochemical performance. Liu [9, 10] et al. have reported that the discharge capacity of the electrode alloys reduced with the increasing of Co content, but the cyclic stability was obviously improved. Because of the high cost of hydrogen storage alloys containing Co, researchers have been exploring the substitution of Co by inexpensive metal elements to reduce the costs of alloys [11]. Al element reported by Luo [12] et al was a suitable candidate to satisfy the low cost and good performance of the alloys.

In this work we have tried the substitution of Al element for Co in $La_{0.7}Ni_{2.5}Co_{0.9}Mn_{0.1}$ to reduce the costs and improve the cycle stability of the alloys. The impact of Al content on the electrochemical properties of the alloys was also investigated in details.

2. Experimental

The AB_5-type hydrogen storage alloys $La_{0.7}Ni_{2.5}Co_{0.9-x}Mn_{0.1}Al_x$ were prepared by magnetic induction melting and post annealing under argon atmosphere at 850 ℃ for 10 hours. The purity of all the component metals is at least 99.9%. Alloy samples were mechanically pulverized to powders of 200 mesh size for electrochemical measurements and X-ray diffraction (XRD) analysis. The crystal structure and lattice parameters of the alloy powders were determined by X-ray diffraction (XRD) using Cu Kα radiation. The experimental electrode pellets (d = 15mm) were prepared by mixing 0.1g alloy powders with carbonyl nickel powders in a weight ratio of 1:4 and then compressed under a pressure of 15 MPa for 5 min. The Ni $(OH)_2$ electrode was used as the counter electrode. The electrochemical measurements were performed in a 6 M KOH electrolyte at room temperature and low temperature (-20 ℃) .

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3. Results and discussion

3.1 Microstructures of alloys

Fig. 1 shows the XRD patterns of the $La_{0.7}Ni_{2.5}Co_{0.9-x}Mn_{0.1}Al_x$ alloys. The patterns were analyzed using the Rietveld refinement. The main phase of the alloys is LaNi5 phase. The lattice parameters of the alloys are listed in table 1. With the increasing Al content, the cell volume and c/a increase. The partial substitution of Al for Co lead to Al element enter into the cell structure of the alloys and replace the position occupied of the Co element, then result in the increase of the cell volume of the alloys, due to the larger atomic radius of Al than that of Co. The addition of Al also has an impact o the lattice parameters of the alloys, leading to the increase of c/a.

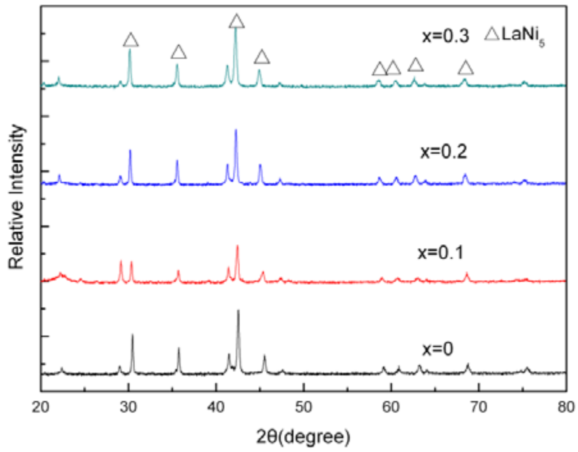

Fig. 1. XRD patterns of the hydrogen storage alloys La0.7Ni2.5Co0.9-xMn0.1Alx.

Table.1Lattice parameters of the La0.7Ni2.5Co0.9-xMn0.1Alx alloys.

Samples	Phase	a(Å)	c(Å)	c/a	Cell volume($Å^3$)
x=0	$LaNi_5$	5.0248	3.9800	0.7921	87.03
x=0.1	$LaNi_5$	5.0352	3.9951	0.7934	87.72
x=0.2	$LaNi_5$	5.0467	4.0179	0.7962	88.62
x=0.3	$LaNi_5$	5.0482	4.0324	0.7988	89.00

3.2 Electrochemical properties

Electrochemical properties at room temperature

As shown in Fig.3, the capacity retention of the $La_{0.7}Ni_{2.5}Co_{0.9-x}Mn_{0.1}Al_x$ alloys is improved with the increase of Al content from x=0 to x=0.3. The maximum discharge capacity of the alloys is listed in table 2. The maximum discharge capacity reduces from 355.2 mAh/g (x=0) to 326.1mAh/g (x=0.3), implying the addition of Al have an adverse effect on the capacity of the alloys. While the capacity retention is enhanced obviously from 53.3% to 76.6% after 60 charge-discharge cycles, which is ascribed to the formation of the compact oxide film Al_2O_3 on the surface of the hydrogen storage alloy particles [13,14] during the charging and discharging processes. This Al_2O_3 film can reduce continuous oxidation of La, Ni, Co and Mn atoms.

Table.2 The electrochemical data of the sample alloys

Samples	C_{max}(mAh/g)	N_a	S_{60}(%)
x=0	355.2	2	53.3
x=0.1	356.0	1	59.4
x=0.2	348.3	1	71.1
x=0.3	326.1	1	76.6

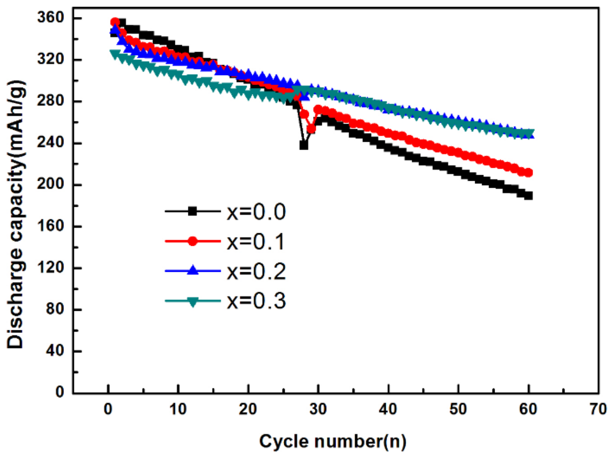

Fig.2. The discharge capacities and cycling performance of the La0.7Ni2.5Co0.9-xMn0.1Alx alloy electrodes.

Electrochemical properties at low temperature

In this study, we have tried to investigate the electrochemical properties of the $La_{0.7}Ni_{2.5}Co_{0.9}Mn_{0.1}$ alloy electrodes at low temperature (-20℃). The results show the alloy electrodes exhibit favorable performance. The alloy electrodes were activated under 0.2C rate at room temperature before the charge-discharge measurements at low temperature. The cycling performance of the $La_{0.7}Ni_{2.5}Co_{0.9}Mn_{0.1}$ alloy electrodes is displayed in Fig.3 and table 3 . The discharge capacity of the alloy electrodes reaches its maximum value of 378.3 mAh/g tested at 0.2 C rate. The capacity retention is 90.0 % after 65 cycles, superior to that of the alloys electrodes at room temperature. It is noted that the alloy electrodes show inferior activation properties, which are activated in 8 cycles, due to the slow transport of hydrogen atoms and charged species in alloy particles at low temperature. In addition, the electrolyte corrosion and the pulverization of the alloy powders are inhibited, resulting in good capacity retention at low temperature.

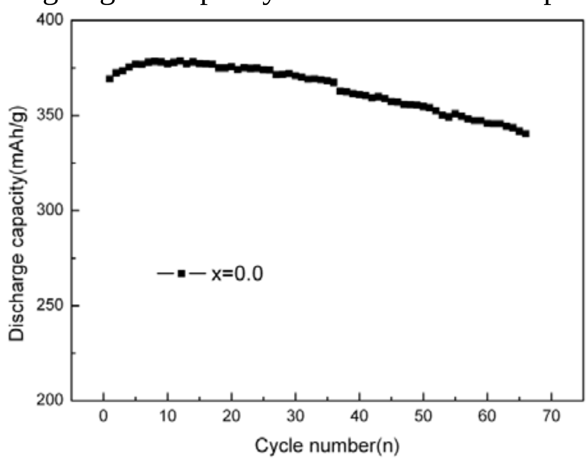

Fig.3 The cycle performance of the La0.7Ni2.5Co0.9Mn0.1 alloy electrodes at -20℃.

Table.3 The electrochemical properties of the La0.7Ni2.5Co0.9Mn0.1 alloy electrodes at -20℃.

Sample	C_{max}(mAh/g)	N_a	S_{65}(%)
x=0	378.3	8	89.95

4. Conclusions

$LaNi_5$ phase is a main phase in the $La_{0.7}Ni_{2.5}Co_{0.9-x}Mn_{0.1}Al_x$ alloys. Partial substitution of Al for Co enlarges the cell volume of the alloys. The addition of Al can improve the capacity fading and prolong the cycling lifetime of the alloys. At low temperature the $La_{0.7}Ni_{2.5}Co_{0.9}Mn_{0.1}$ alloy shows high discharge capacity and good cyclic stability.

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