Study on AB_5 Hydrogen Storage Alloy Used in Ni/MH Batteries for Electric Vehicles

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Abstract

On the basis of experimental investigation, the electrochemical properties of AB_5 hydrogen storage alloys $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ (x=0.1, 0.2, 0.3) using at -40°-25°C are discussed. The obtained results showed that the discharge capacity at different temperature, the high rate discharge property and the cycling life of the alloy electrode are in close relationship with the x value. When x increases from 0.1 to 0.3, the discharge capacities with discharge current density of 60mA/g are slightly decreased at 25 °C, evidently decreased at -40 °C, and the cycle life was slightly improved. And the element Al is detrimental to the high-rate property of AB_5 alloy.

Keywords

Ni/MH batteries, AB_5 hydrogen storage alloy, electrochemical properties

1. INTRODUCTION

The hydrogen storage alloy is a key negative-electrode material used in MH/Ni battery, and it is crucial for the capacity, cycling life, high-rate discharge, high and low temperature performance, and self-discharge (Sakai et al., 1990). At present, the negative-electrode material used in second MH/Ni battery is mainly the AB_5 hydrogen storage alloy, of which the electrochemical properties are usually stable under a temperature from -10°C to 40°C, but considerably deteriorated when temperature is higher than 45°C or lower than -18°C. However, in order to be used as vehicle power source in some cold places, such as north-east and north-west of china, Russia, etc., the high-rate discharge abilities and low temperature discharge performance for the commercialized AB_5 hydrogen storage alloys still need to be further improved so as to meet the requirement of the extended applications. In this paper, we describe the effect of x on the electrochemical properties of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ alloy. It is of great assistance in producing AB_5-type hydrogen storage alloy with high capacity in wide-range temperature and high rate discharge ability.

2. EXPERIMENTAL METHOD

The raw materials were based on purified metals, of which the purities of the rare earth (RE) are 99.5% and those of Ni, Co, Mn and Al are all greater than 99% (mass fraction). The alloys were prepared by arc melting method under an Ar atmosphere into button forms, which were re-melted 4 times in order to improve the homogeneity. The resulting ingots were pulverized mechanically into powder below 200 mesh. And the average diameter measured by using a laser particle size analyzer is 53 μm. The alloy crystallographic structure was investigated by using X-ray diffraction (XRD) with the diffraction power of 36 kVx20 mA and K_α Cu anticathode. The scan manner was step scanning with a step of 0.02° and a scan rate of 2°/min. The scan scope is from 10° t0 90°.

The electrode pellets were prepared by using the cool-pressure method, that is, 0.4g alloy powder and 1.6g Ni powder were evenly mixed and rapped by Ni foams, and then pressed under a pressure of 12 MPa to be a pellet of $18x18x1.5\ mm^3$. The "sandwich" method was used to examine the electrochemical properties, and the measured temperatures were -40°C and 25°C.

3. RESULTS AND DISCUSSION

3.1 Structure characterization

Figure 1 shows the XRD patterns of $La_{0.54}Ce_{0.28}Pr_{0.18}$-$Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ compounds. The three alloys all have the single $CaCu_5$-type phase. But there are some slight differences between the relative intensities of some Bragg peaks and some slight shifts between the patterns because of the different value of x. The lattice parameters and cell volumes of compounds are listed in Table 1. It can be found that both the lattice parameters and the cell volumes are decreased with the decreasing of x. That's mostly because that the radius of Al is larger than that of Ni.

3.2 Electrochemical properties

Typical detail capacity-potential curves at the third cycle

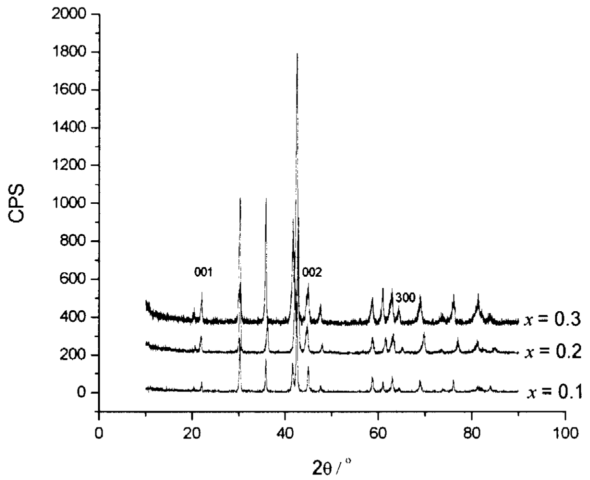

Fig. 1 XRD Spectra of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ Alloy

Table 1 Lattice Parameter and Cell Volume for $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ Alloy

x value	Lattice parameter		Cell volume (nm^3)
	a (nm)	*c* (nm)	
0.1	0.5013	0.4041	0.08795
0.2	0.5018	0.4049	0.08832
0.3	0.5021	0.4056	0.08855

of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Mn_{0.35}Al_x$ alloys at -40°C and 25°C during discharging processes are shown in Figure 2 (a) and (b), respectively. It can be clearly seen that the discharge capacity at room temperature (25°C) have not obvious difference with x varying from 0.1 to 0.3. The maximum discharge capacity emerged at $x = 0.1$. But the discharge capacity at low temperature (-40°C) is intensively influenced by x value. When x is increased from 0.1 to 0.3, the discharge capacity of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ is decreased from 251.5mAh/g to 140.4mAh/g.

To elucidate this phenomenon, the chemical elemental characteristics of Ni and Al must be considered. As the atomic radius and atom volume of Al are larger than that of Ni, the increasing of x will inevitably cause the increasing of the lattice cell and therefore increase the interstitial space of the lattice cell and this will be favorable to the hydrogen-storage process. At the same time, the lattice distortions are also enlarged with the increasing of Al, and this will detrimental to the hydrogen-storage ability of alloys. The comprehensive effects of above two opposing factors make the voltage- capacity dependence curves at 25°C like those of Figure 2 (a). Nevertheless, the discharge capacity of an alloy at low temperatures, especially lower than -20°C, is mainly controlled by dynamic processes of the electrode reaction (Valøen et al., 2000; Iwakura et al., 2002). In this case, the smaller the cell volume the higher the hydrogen-equi-

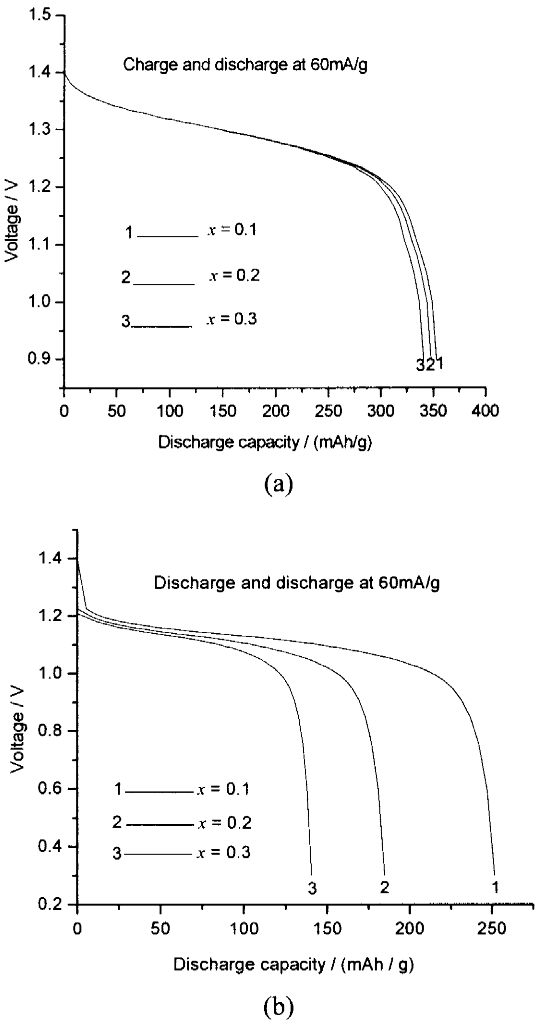

Fig. 2 Discharge Capacities of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ Alloys at 25°C (a) and -40°C (b)

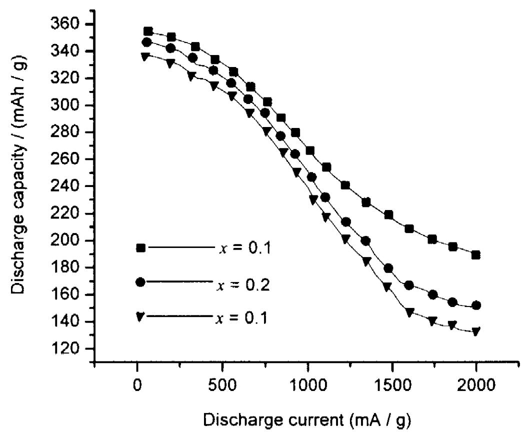

Fig. 3 High-rate Discharge Ability of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ Alloys

librium pressure of the metal hydride, which would accelerate the diffusion rate of hydrogen in the metal matrix, therefore favorite to discharge, besides, element Ni in the alloy can promote its electrocatalytic activation. So, with x increasing, the discharge capacity of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ at -40°C decreased seriously. The effect of elements Al and Ni to the high rate performance of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ is as the same as them to the discharge capacity at low temperature and the results are shown as Figure 3.

Aluminum appears to be present in all commercial AB_5 alloys. It is believed that the incorporation of Al the alloys substantially reduced electrode corrosion and attributed this to the formation of protective surface oxides (Marshall and Dieter, 1977; Reilly et al., 1999). The presence of even a small amount of Al substantially decreases V_H (the molar volume of hydrogen), n (the number of H atoms in the charged electrode) and, consequently, both lattice expansion and corrosion are decreased (Reilly et al., 1999). These are beneficial to the cycling stability. The cycle life of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ at 25°C with deferent x are shown as Figure 4. It can be seen that the cycle life slightly increased with the increasing of x.

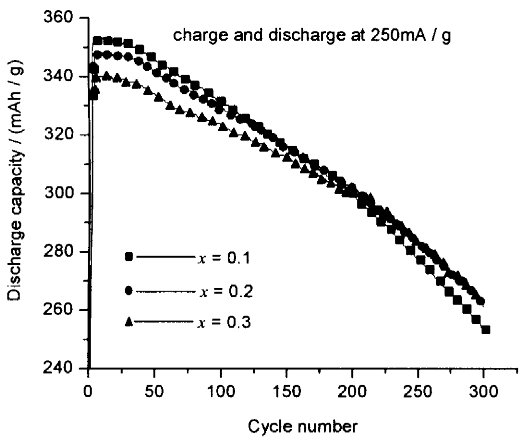

Fig. 4 Cycle Life of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ Alloys

4. CONCLUSIONS

(1) The lattice parameters and cell volume decrease with the decrease of Al content in $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ (x=0.1, 0.2, 0.3).

(2) The discharge capacity of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ at 25°C have not obvious difference with x varying from 0.1 to 0.3. But the discharge capacity at -40°C is intensively influenced by x value. When it increased from 0.1 to 0.3, the discharge capacity of $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{4-x}Co_{0.6}Mn_{0.35}Al_x$ decreased from 251.5 mAh/g to 140.4 mAh/g.

(3) The $La_{0.54}Ce_{0.28}Pr_{0.18}Ni_{3.9}Co_{0.6}Mn_{0.35}Al_{0.1}$ alloy is capable of performing high-rate discharge and has excellent electrochemical properties as negative electrode materials in Ni/MH battery at low temperature, even at -40°C.

Acknowledgements

This research was supported by China "863" Foundation (grant No.: 2001AA322050).

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(Received November 26, 2005; accepted December 20, 2005)