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Electrochemical Properties and Crystal Structure of Rare Earth $AB_{3.5}$-Type Alloy as Negative Electrode Material in MH-Ni Battery*

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Abstract: The electrochemical characteristics and crystal structure of metal hydride electrode of $AB_{3.5}$-type alloy was studied. The electrochemical properties of the metal hydride electrode were investigated at room temperature and - 30 ℃. The partial substitution of Ni by Al element causes an expansion of the lattice cell and increases the specific capacity and rate discharge ability of the alloy.

Key words: metal hydride electrode; electrochemical properties; MH-Ni battery; lattice cell; rare earths
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Due to high specific energy, environment friend and no memory effect, MH-Ni battery has been widely investigated and applied in portable computers, cellular telephones, new cordless and hybrid electric vehicles[1~3]. Metal hydride electrode is the most important part in MH-Ni battery. AB_5-typed hydrogen storage alloys have been extensively studied and used as metal hydride electrode material in MH-Ni battery[4~6], but rare earth AB_2, AB_3 and AB_4-type hydrogen storage alloys almost have not been paid to attention. This paper, as a part of $AB_{3.5}$-type hydrogen storage alloy research, concerns the electrochemical characteristics of metal hydride electrode of the alloy and the partial substitution of Ni by Al element.

1 Experimental

1.1 Preparation of alloy

All alloys were prepared by arc - melting of the constituent metals on a water-cooled copper hearth under an argon atmosphere. The purity of the metals, i.e., La, Ni, Al, is higher than 99.9% (mass fraction). The samples were then inverted and remelted 5 times to ensure good homogeneity. Thereafter, the alloy samples were crushed into fine powders of 200～300 mesh in mortar.

1.2 X-ray diffraction

Crystallographic characterization of the hydrogen storage alloys were carried out by XRD analysis utilizing Cu Kα radiation on a Ragaku D/max 2500V PC X-ray diffractometer. The cell parameters of the alloys were calculated by Cell program.

1.3 Electrochemical measurements

The metal hydride electrode was prepared by mechanically pressing (6000 kg·cm^{-2}) the well-mixed alloy powder with nickel powder in weight ratio of 1∶5. The weight of whole electrode was 0.9 g. The pellet with a diameter of 13 mm and thickness of 1.5 mm was formed at room temperature. The electrochemical properties were measured in a cell which consists of a working electrode (metal hydride electrode), a counter-electrode ($NiOOH/Ni(OH)_2$ electrode). The electrolyte is 6 mol·L^{-1} KOH aqueous solution. Charge and discharge test was conducted using DC-5 battery testing instrument controlled by computer. The emphasis of these charge/discharge tests was on electrochemical capacity and stability of the negative electrode. The capacity of the positive electrode was designed to be much higher than that of the negative electrode. The experimental cells were charged at a current of 60 mA·g^{-1} for 5.5 h, after 5 min rest, and were discharged at certain currents.

2 Results and Discussion

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2.1 Crystal structure

XRD patterns of $LaNi_{3.5-x}Al_x$ ($0 \leq x \leq 0.3$) compounds shown in Fig. 1 exhibit sharp peaks, indicating a long-rage crystallographic order and excellent crystallinity. The compounds have single phase with La_2Ni_7-type phase, There are some slight offside among the patterns of $LaNi_{3.5-x}Al_x$ ($0 \leq x \leq 0.3$) compounds because of the elemental substitutions. Table 1 lists the lattice parameter and cell volume of compounds. It can be found that cell volume increases with the increases of x in the compounds because of the radius of Al is larger than that of Ni.

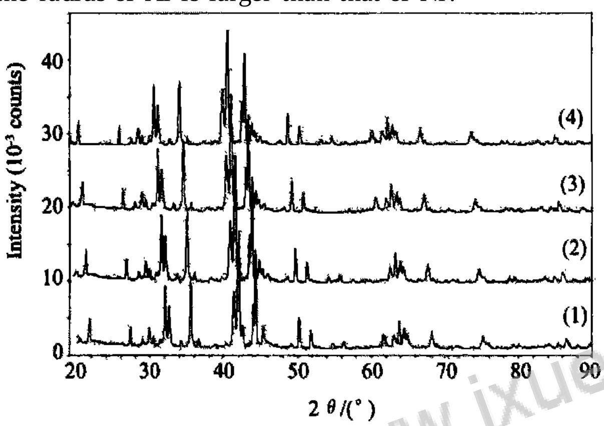

Fig. 1 XRD analyses of alloy compositions of (1) $LaNi_{3.5}$, (2) $LaNi_{3.4}AL_{0.1}$, (3) $LaNi_{3.3}AL_{0.2}$ and (4) $LaNi_{32}AL_{0.3}$

Table 1 Lattice parameter, cell volume for $LaNi_{3.5-x}Al_x$ ($0 \leq x \leq 0.3$) compounds

Al-stochiometry	Lattice parameter		Cell volume/ nm^{-3}
	a/ nm	c/ nm	
0.0	5.05242(665)	24.6371(2)	544.67
0.1	5.0515(928)	24.64871(3)	544.71
0.2	5.05247(475)	24.63729(1)	544.74
0.3	5.05282(696)	24.63941(2)	544.79

2.2 Discharge performance of metal hydride electrodes

The discharge characteristics of the metal hydride electrodes at low current density are shown in Fig. 2.

It can be clearly seen that the $LaNi_{3.5}$ electrode has low discharge capacity. However, the performances of the electrodes are greatly improved on Al addition. The chemical characteristics of Al and Ni may be considered to elucidate this phenomenon. As the atomic radius and atomic volume of Al are greater than that of Ni, the addition of Al with inevitably causes an expansion of the lattice cell and will thus enlarge the interstitial space and accordingly will benefit the processes of hydrogen sorption and desorption.

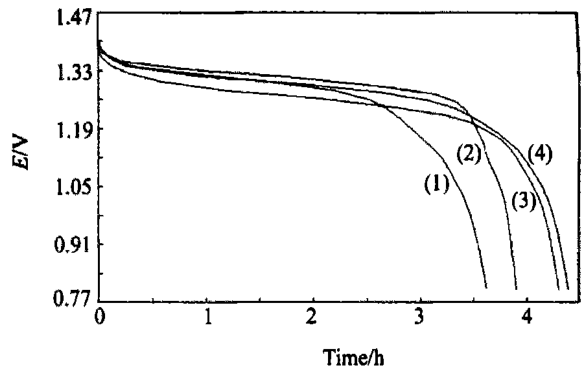

Fig. 2 Discharge characteristics of metallic hydride electrodes (Charge at current of 60 mA $\cdot g^{-1}$ for 5.5 h; Discharge at current of 60 mA $\cdot g^{-1}$ (1) LaNi3.5, (2) $LaNi_{3.4}AL_{0.1}$, (3) $LaNi_{3.3}AL_{0.2}$, (4) $LaNi_{32}AL_{0.3}$)

2.3 Effect of element substitution on activation of electrodes

It is found from Fig. 3 that $LaNi_{3.5}$ electrode shows very low capacity, less than 90 mAh $\cdot g^{-1}$. However, the discharge capacity of $LaNi_{3.4}Al_{0.1}$, $LaNi_{3.3}Al_{0.2}$, and $LaNi_{3.2}Al_{0.3}$ is over 135 mAh $\cdot g^{-1}$ for the first cycle and the discharge capacity is up to 90 % of the maximum capacity in the third cycle. Therefore it is reasonable to conclude that Al addition causes an expansion of the lattice cell and is beneficial to the activity of the electrode.

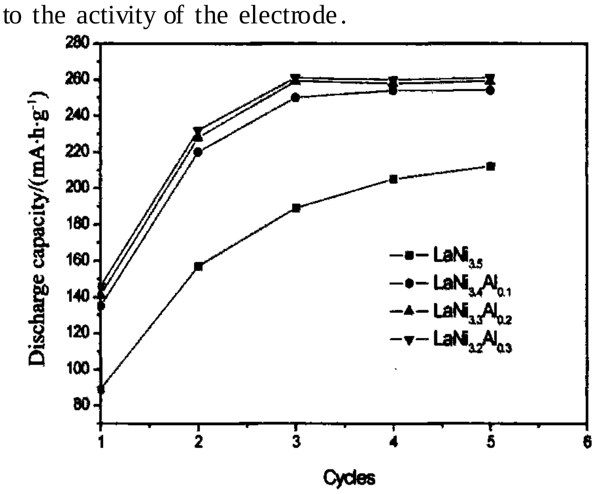

Fig. 3 Dependence of discharge capacity on Al contents

2.4 Effects of Al on rate discharge ability of electrodes

High rate discharge ability (HRD) is an important property for MH-Ni battery. HRD is obtained from discharge capacity at different discharge ability using the following equation.

$HRD(\%) = C_x / C_{60}$

where C_x is discharge capacity at different discharge current, and C_{60} is the discharge ability at the discharge current of 60 mA $\cdot g^{-1}$. The HRD of the metallic hydride electrodes under different discharge current density is shown in Fig. 4. It is clearly seen that the HRD of electrodes increases with the increase of amount of the Al addition. At the discharge current of 2500 mA $\cdot g^{-1}$, HRD of $LaNi_{3.5}$ is only 24 %, which is more than 14 % lower than that of $LaNi_{3.2}Al_{0.3}$. This can also be attributed to the greater interstitial space of alloy with Al addition that make the hydrogen diffuse easily, thus improve the high rate discharge ability.

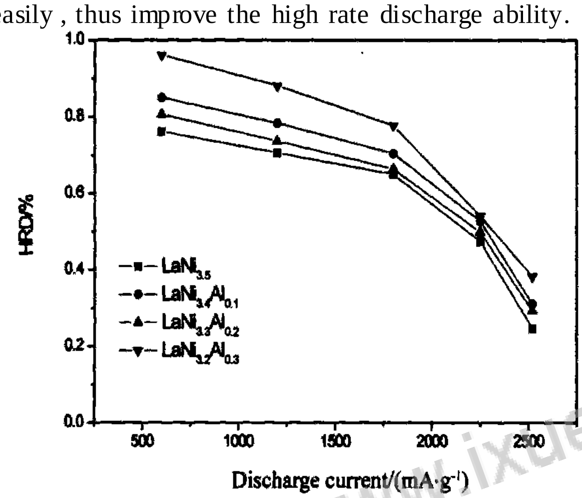

Fig. 4 HRD at different discharge current

2.5 Specific capacity at - 30 ℃

The specific capacity at low temperature is very important for an MH-Ni battery, especially for the MH-Ni battery used in the northeast of china in winter. It is noted from Fig. 5 that Al addition is detrimental to the specific capacity at low temperature. The reason of the phenomenon is not very clear and we will find it in our following research work.

3 Conclusion

Al is found to be benefit not only to the specific

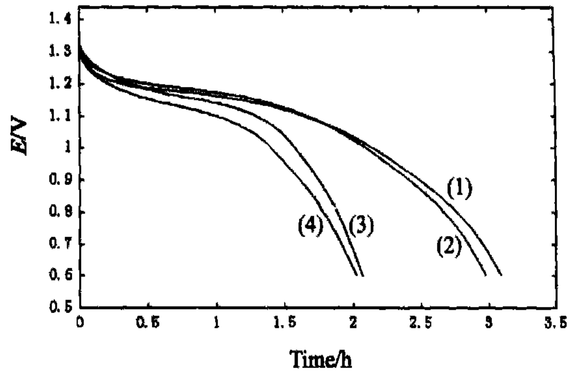

Fig. 5 Discharge characteristics of metallic hydride electrodes at - 30 ℃ (Charge current: 60 mA ·g⁻¹ for 5.5 h; Discharge current: 60 mA ·g⁻¹; (1) $LaNi_{3.5}$, (2) $LaNi_{3.4}AL_{0.1}$, (3) $LaNi_{3.3}AL_{0.2}$, 4. $LaNi_{32}AL_{0.3}$)

capacity, but also to the high rate dischargeability for the alloy. On the other hand it is detrimental to the discharge performance at low temperature.

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