[Article ID] 1003 - 6326(2000)05 - 0595 - 04

Surface modification for $La_{1-x}Ce_x(NiCoMnAl)_5$ hydride electrode by hot charging in potassium borohydride solution①

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[Abstract] The $La_{1-x}Ce_x(NiCoMnAl)_5$ alloy electrodes were treated by hot charging in alkaline aqueous solution containing KBH_4. The activation behavior, hydrogen diffusion coefficient and maximum discharging capacity, high rate discharging capability of alloy electrodes were tested. The surface morphology and element content were observed by scanning electron microscope. The results show that the alloy electrode is fully activated after the second charging-discharging cycle and has a high rate discharging capability of 85 % at 900 mA/g. The surface has a lot of micro-cracks and hydrogen diffusion coefficient is about $(2 \sim 3) \times 10^{-9}$ cm^2/s. Therefore, this method can markedly improve activation behavior and high rate charging capacity of the alloy electrode. The mechanism of this surface modification of the alloy electrode is also discussed.

[Key words] hydrogen storage alloy; surface modification; KBH_4 alkaline aqueous solution; hot charging treatment
[CLC number] TG139 **[Document code]** A

1 INTRODUCTION

In recent years, nickel-metalhydride batteries are becoming popularity with developing portable computer, cellular phone and so on. Ni/MH batteries have a lot of advantages over other advanced battery systems because of their high energy density, high charge and discharge ability and environmental compatibility[1,2]. The key to improving the synthetic characteristics of the Ni/MH batteries is how to improve performance of hydrogen storage alloy used in Ni/MH. $LaNi_5$ alloys combined high absorption and desorption of a large amount of hydrogen with fast electrochemical activation and good charge and discharge kinetics, but the storage capacity of this alloy declined rapidly during charge and discharge cycles. Researchers studied a lot of methods to improve synthetic characteristics of Ni/MH batteries. Element substitutions in $LaNi_5$ alloys were introduced to not only improve the cycle life[3~5], but also decrease hydrogen absorption and desorption capacity and kinetics of hydrogen absorption and desorption. However, the surface modification is a good way to improve kinetics of electrode. This method includes hot alkaline treatment[6], F^- solution treatment[7~10], reducing agent treatment[11,12], hot-charging treatment[13,14] and so on. The methods mentioned-above have their advantages and disadvantages respectively. The purpose of this paper is to take advantages of reducing agent and hot-charging treatment to modify the surface of $La_{1-x}Ce_x(NiCoMnAl)_5$ alloy electrodes and study this method that has effects on activated numbers, high rate discharge capability and hydrogen diffusion of $La_{1-x}Ce_x(NiCoMnAl)_5$ alloy electrodes.

2 EXPERIMENTAL

The as-cast pieces were prepared by vacuum induction furnace in the protective argon, and mechanically ground to powders of 74 ~ 100 μm. Preparing total mass of 3.000 g powders of hydrogen storage alloy and nickel with the ratio of 1∶3, the powders were cold-pressed into a 25 mm diameter electrode pellet. The pellet was sandwiched between two $NiOOH/Ni(OH)_2$ electrodes with excessive capacity, and then put into a beaker with 6 mol/L KOH containing 0.02 mol/L KBH_4 solution at 353 K, during treatment, the samples were charged at a current density of 300 mA/g for 8 h, rested for 5 min and cooled, then discharged at 30 mA/g to cut-off voltage of 1 V. After treated, the sample was charged at current density of 60 mA/g for 8 h, rested for 5 min, and then discharged at the same current density to a cut-off voltage of 1 V. The high rate discharge capability is an important parameter for hydride electrode, measured at 300 mA/g, 600 mA/g, and 900 mA/g charge-discharge current density respectively and determined by the following equation:

$$C_h = \frac{C_i}{C_i + C_{0.2C}} \times 100 \quad (1)$$

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① **[Foundation item]** Project (715 - 004 - 0233) supported by the National Advanced Materials Committee of China

[Received date] 1999 - 08 - 03; **[Accepted date]** 1999 - 10 - 06

where C_h is the high rate discharge capability, C_i is the discharge capacity at current density J_d, $C_{0.2C}$ is the residual discharge capacity determined at 0.2 C current density.

The hydrogen diffusion coefficient can be determined by the following equation[15]:

$$D_H = \frac{r_0^2 J_d}{15(Q_0 - tJ_d)} \quad (2)$$

where Q_0 is the maximum capacity, t is the discharging time to cut off voltage of 1 V, and r_0 is the particle radius.

SEM was finished on the S-360 type Scanning Electron Microscope with EDXA made in the Cambridge Instrument Ltd.

3 RESULTS AND DISCUSSION

3.1 Effects of surface modification on activated behavior and discharge capacity

Fig.1 shows that $La_{1-x}Ce_x(NiCoMnAl)_5$ alloy electrode is fully activated at the second charge-discharge cycle after hot charging treatment in alkaline solution containing potassium borohydride and the high discharge capacity is about 292 mA/g; but the untreated alloy electrode is fully activated at the fifth charge-discharge cycle; therefore, this treatment method can well improve activated behavior of alloy electrode.

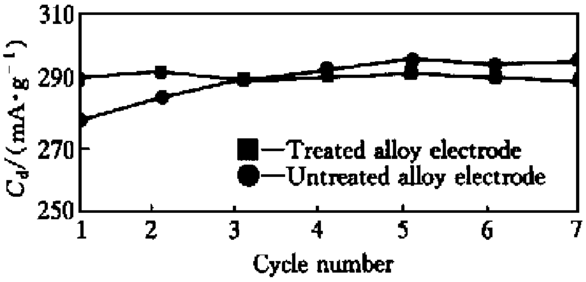

Fig.1 Discharge capacity(C_d) as a function of cycle number

3.2 Effects of treatment on high rate discharge capability(HRDC)

Fig.2 shows that the C_h of alloy electrode after treatment is about 90 % at discharge current density of 600 mA/g and up to 85 % even at 900 mA/g. It can be seen that this treatment method is beneficial to improving the high rate discharge capability of alloy electrode. So, this method lays the ground-work for preparing high power battery.

3.3 Surface morphology and chemical composition

The results of SEM observation are presented in Fig.3. It shows that the surface of treated alloy electrode has a lot of microcracks, which increase the surface-to-volume ratio that is beneficial to hydrogen diffusion. Therefore, the rate of absorbing-desorbing hydrogen can be improved.

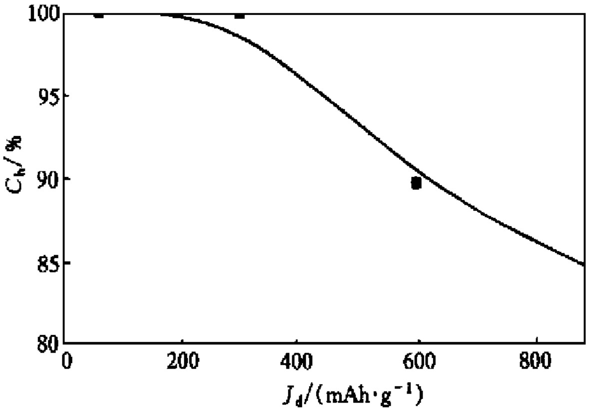

Fig.2 High rate discharge capability (C_h) as a function of discharge current density(J_d)

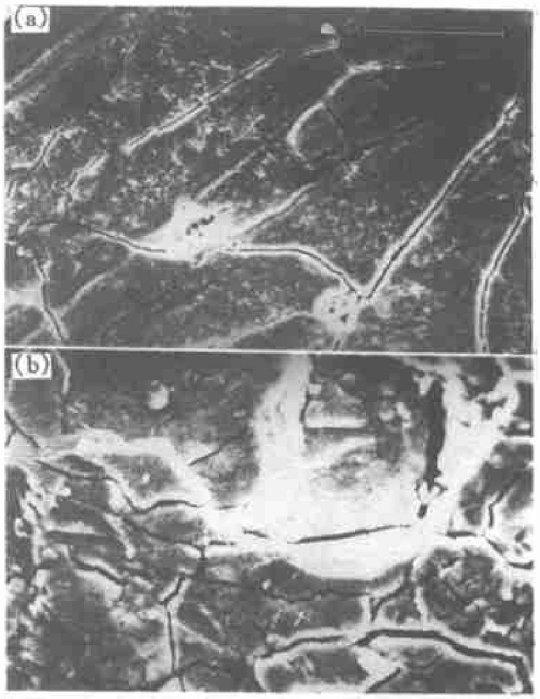

Fig.3 SEM surface morphologies of alloy electrodes

(a) —Untreated; (b) —Treated

It can be seen from Table 1 that the content of lanthanum, cerium on the surface of alloy electrode decreased after treatment. It may be due to the partial dissolution of lanthanum oxide and cerium oxide. At the same time, the content of nickel increases, which makes the electrode surface become nickel rich layer and got catalyst action. So these factors are beneficial to absorbing hydrogen.

3.4 Effect of treatment on discharge property

Fig.4 shows that the curves of discharge voltage have almost not changed with increasing cycle number. It can be suggested that electrochemical characteristics of alloy electrode are very stable after treatment.

Table 1 Elements content on surface of alloy electrode

Element	Element content on surface of electrode after treated/ %	Element content on surface of untreated electrode/ %
Al	2.12	2.07
Mn	2.71	2.55
Co	9.32	10.08
Ni	57.25	54.09
La	17.14	17.93
Ce	11.46	12.45

Fig.4 also shows that when the discharge current density J_d is small, such as $J_d = 60$ mA/g ,the voltage initially drops slowly and then changes abruptly at the end of the discharge, which indicates that the determining step changes from charge transfer reaction to the diffusion of hydrogen in electrode, with increasing J_d, the potential initially drops rapidly and changes slowly at the end of the discharge, for example, $J_d = 900$ mA/g, which can be considered that the rate determining step is controlled by electrochemical reaction and diffusion of hydrogen during the whole discharge process.

3.5 Mechanism of surface modification

Table 2 shows that at several discharge current density, hydrogen diffusion coefficient decreases gradually with J_d increasing, but almost at the same order. The results improve one order of magnitude than the result(5.8×10^{-10} cm^2/s) that Pang et al[15] used KBH_4 reducing agent to treat $MnNi_3Co_{0.6}Mn_{0.4}Al_{0.3}$ alloy electrode, and two order of magnitude than the result (about 3.3×10^{-11} cm^2/s) that Zheng[16] used electroless-plating Pd on $LaNi_{4.25}Al_{0.75}$ alloy electrode. It can be suggested that the hydrogen diffusion capability was improved by reducing agent hot charging treated. The above results can be explained satisfactorily as following.

For hydrogen storage alloys, the rate of absorbing-desorbing hydrogen is controlled by the following:

1) the rate of hydrogen dissociation at the solid-liquid surface;

2) the capability of hydrogen penetrating to the surface, which is typically covered by an oxide layer;

3) the rate of hydrogen diffusing into bulk metal

Table 2 Hydrogen diffusion coefficient at different discharge current density

Discharge current density $J_d/(mA \cdot g^{-1})$	Hydrogen diffusion coefficient $D_H/(10^{-9}\ cm^2 \cdot s^{-1})$
60	3.47
300	3.26
600	3.23
900	2.24

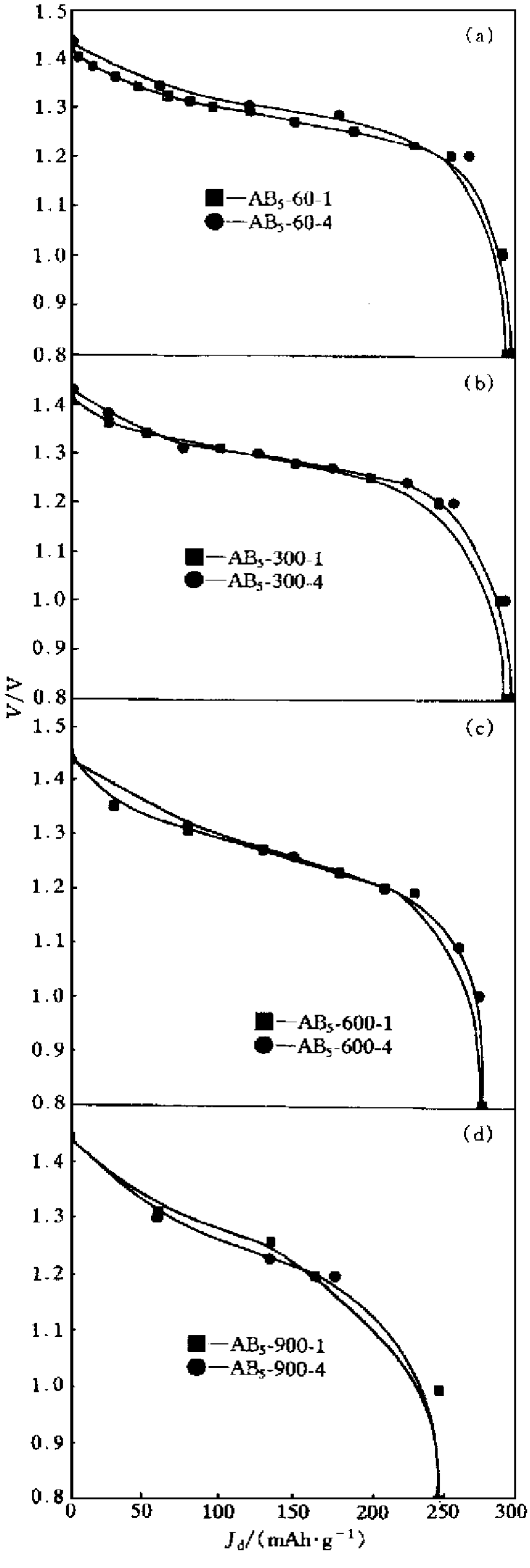

Fig.4 Discharge curves at different discharge current density (J_d)

(a) —Discharge current density is 60 mA/g, cycle number is 1,4; (b) —Discharge current density is 300 mA/g, cycle number is 1, 4; (c) —Discharge current density is 600 mA/g, cycle number is 1, 4; (d) —Discharge current density is 900 mA/g, cycle number is 1, 4 and through the hydride already formed.

There are some reactions of reducing agent KBH_4 in alkaline solution as following[12]:

$$BH_4^- \rightarrow BH_3^- + H \quad (3)$$

$$BH_3^- + OH^- \rightarrow BH_3OH^- + e \quad (4)$$

$$BH_3OH^- \rightarrow BH_2OH^- + H \quad (5)$$

$$BH_2OH^- + OH^- \rightarrow BH_2(OH)_2^- + e \quad (6)$$

$$BH_2(OH)_2^- \rightarrow BH(OH)_2^- + H \quad (7)$$

$$BH(OH)_2^- + OH^- \rightarrow BH(OH)_3^- + e \quad (8)$$

$$BH(OH)_3^- \rightarrow B(OH)_3^- + H \quad (9)$$

$$B(OH)_3^- + OH^- \rightarrow B(OH)_4^- + e \quad (10)$$

$$M + H \rightarrow MH \quad (11)$$

$$H + H \rightarrow H_2 \quad (12)$$

$$H + OH^- \rightarrow H_2O + e \quad (13)$$

The above reactions show reducing agent KBH_4 produces atomic hydrogen, which can reduce oxide on the surface of alloy electrode, so that it decreases obstacle when hydrogen penetrates to the surface. At the same time, reducing agent and charging double actions provide a lot of hydrogen and the unit cell volume expands after absorbing hydrogen, which results in the pulverization of the alloy particles and forms a new nickel rich clean surface having a high catalytic activity that made hydrogen from by-reaction separate into atom. At the same time, high temperature(353 K) accelerates electrode reaction and made surface oxide dissolve rapidly; the several actions mentioned-above promote the absorbing-desorbing of hydrogen. Therefore activated behavior and high rate discharge capability of alloy electrode is improved.

4 CONCLUSIONS

1) The $La_{1-x}Ce_x(NiCoMnAl)_5$ alloy electrode which is treated with KBH_4 reducing agent-hot charging has the maximum capacity about 292 mAh/g at the second cycle number, and HRDC up to 85 % at the charge-discharge current density of 900 mA/g. These results can be suggested that this method is beneficial to the activated behavior and HRDC of the alloy electrode.

2) Hydrogen diffusion coefficient D_H in alloy electrode is about $(2 \sim 3) \times 10^{-9}$ cm^2/s after treatment. The controlling step changes from electrochemical reaction to hydrogen diffusion during discharging process.

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(Edited by HUANG Jin-song)