



Short communication

Study on the surface modification of metal hydride electrodes with cobalt

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ARTICLE INFO

Article history:

Received 8 January 2008
 Received in revised form 19 March 2008
 Accepted 19 March 2008
 Available online 8 April 2008

Keywords:

Surface modification
 Vacuum evaporate plating technology
 Electrode
 MH/Ni batteries

ABSTRACT

A novel method has been applied to the surface modification of the metal hydride (MH) electrode of the MH/Ni batteries. Both sides of the electrode were plated with a thin cobalt film about 0.15 μm using vacuum evaporate plating technology and the effect of the electrode on the performance of the MH/Ni batteries was examined. It was found that the surface modification could enhance the electrode conductivity and decrease the battery ohmic resistance. After surface modification, the discharge capacity at 5C (8.5 A) was increased by 115 mAh and discharge voltage was increased by 0.04 V, the resistance of the batteries was also decreased by 18%. The batteries with modified electrode exhibited satisfactory durability. The remaining capacity of the modified batteries was 93% of the initial capacity even after 500 cycles. The inner pressure of the batteries during overcharging was lowered and the charging efficiency of the batteries was improved.

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1. Introduction

The metal hydride MH/Ni batteries has been commercialized and used widely in portable electric applications and electric vehicles because of their advantages such as cleanness, high energy density and no pollution [1,2]. As the active material of the negative electrode, the hydrogen storage alloys have also attracted much attention. So far, many multi-component, mischmetal-based hydrogen storage alloys have been developed [3,4]. In order to improve the performance of hydrogen storage alloys, several kinds of surface modifications have been employed. Microencapsulation of the alloys powder with an electroless coating of copper or nickel has been confirmed to be effective in improving the electrochemical characteristics of the negative electrode and decreasing the inner pressure of the MH/Ni batteries [5–7]. Surface treatment with alkaline and acid leads to the appearance of a Ni-rich surface, which is effective in enhancing the activation performance of alloys [8–11]. Modification by plating the MH electrode with platinum group metals, Co and Ni has been proved to be effective in improving the high-rate dischargeability as well as accelerating the activation process [12–14].

In this work, a novel method has been employed to modify the surface of the MH electrode. The MH electrode was plated with a thin cobalt film using vacuum evaporate plating technology. The electrochemical properties such as the charge–discharge

characteristics, the cycle life and the inner pressure of the batteries were investigated. In addition, the surface structure of the electrode was analyzed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). The crystal structure of the alloy was identified by X-ray diffraction (XRD) and the particle size distribution of the alloy powders was also examined.

2. Experimental

Ingots of $\text{Mn}_{0.3}\text{Co}_{0.7}\text{Ni}_{3.6}\text{Al}_{0.4}$ (MI = La-rich mischmetal, La: 55.4 wt%; Ce: 26.2 wt%; Pr: 5.4 wt%; Nd: 12.6 wt%; other rare earths: 0.4 wt%), were mechanically crushed into a powder of particle size 30–70 μm . MH electrode was constructed by packing the paste of alloy powder, nickel powder and 3 wt% polytetrafluoroethylene (PTFE) as a binder into a foamed nickel substrate and then cold-compressed under a pressure of 20 MPa to 0.3-mm thickness. Both sides of the electrode was subsequently plated with a thin cobalt film about 0.15 μm in vacuum using vacuum evaporate plating technology.

The surface structure of the electrode was determined by XPS with a KRATOS XSAM800 spectrometer with Al K α radiation. Surface morphology of the electrode was examined by SEM (JSM–35C). The crystal structure of the electrode was identified by XRD (Rigaku $D_{\text{max}}-2500$) with Cu K α radiation.

An AA-size MH/Ni battery was assembled with the surface modified MH electrode as the negative electrode. The electrolyte was 6 M KOH + 1 M LiOH solution. The nominal capacity of the batteries was 1700 mAh. The sealed MH/Ni batteries were firstly activated by charge–discharge at a rate of 0.2C (340 mA) for five cycles. Then

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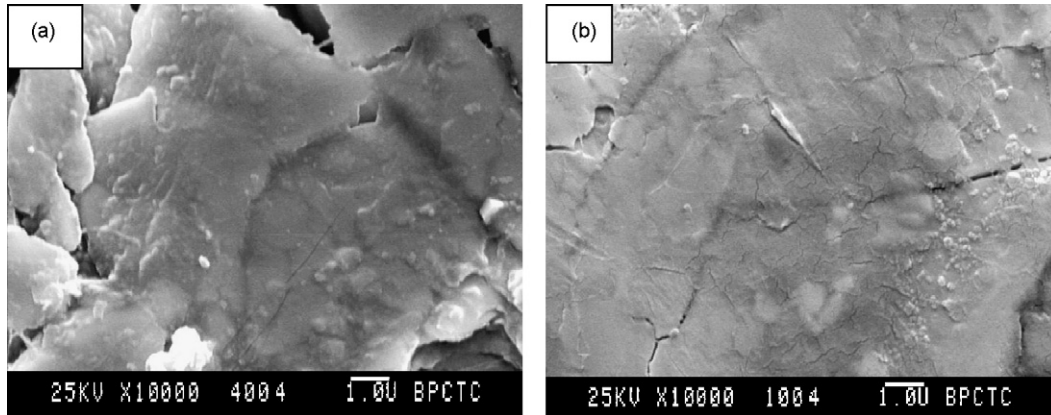


Fig. 1. SEM photographs of the metal hydride electrode: (a) surface modified electrode and (b) surface unmodified electrode.

the discharge capacity of the MH/Ni batteries was determined at 0.2C. The performance of the batteries at high-rate discharging was evaluated from the discharge capacity and the plateau voltage during discharge at 1, 3, and 5C rate, respectively. In the cycle life test, the batteries were charged at 1C by controlling to cut-off at $\Delta V = -10$ mV, discharged at 1C to 1.0V after a rest of 10 min. All the tests above were carried out on an Arbin instrument. The ohmic resistance of the batteries was tested by HIOKI 3551 Batteries HiTester. After the cycle life test, the particle size distribution of the alloy powder was examined by a HORIBA LA-300 laser scattering particle size distribution analyzer.

The inner pressure of the batteries during charging and discharging were measured by a batteries inner pressure test system at 20–25 °C as reported previously [15]. The batteries was placed into a chamber and the gas generated during charging was led out to a pressure sensor through a hole on the top of the batteries.

3. Results and discussion

3.1. Surface and crystal structure analysis of the electrode

The SEM photographs of the electrode surface are shown in Fig. 1. SEM analysis shows that the surface of the unmodified electrode is relatively smooth, and cleavage and the small particles of 200-nm diameter on the surface are alloy debris. As for the modified electrode, the surface appears coarse and the cleavage which appears on the unmodified electrode is covered.

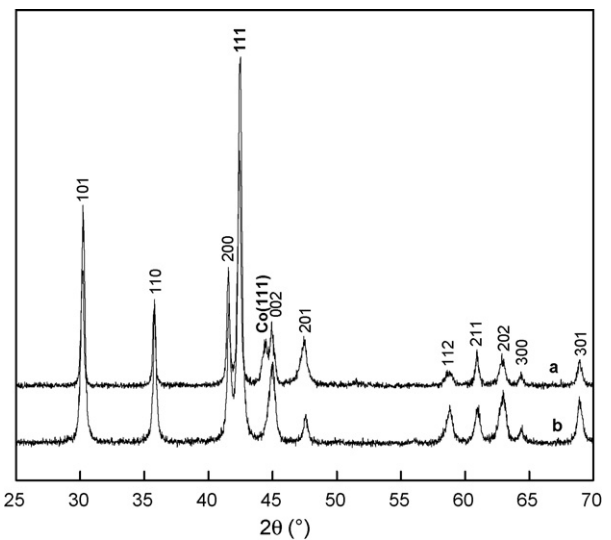


Fig. 3. XRD patterns of the metal hydride electrode: (a) surface modified electrode and (b) surface unmodified electrode.

XPS analysis of the surfaces of the unmodified and modified electrodes was performed (Fig. 2).

Compared with the unmodified electrode, it is observed on the modified electrode that Co exists in the metallic state, and is

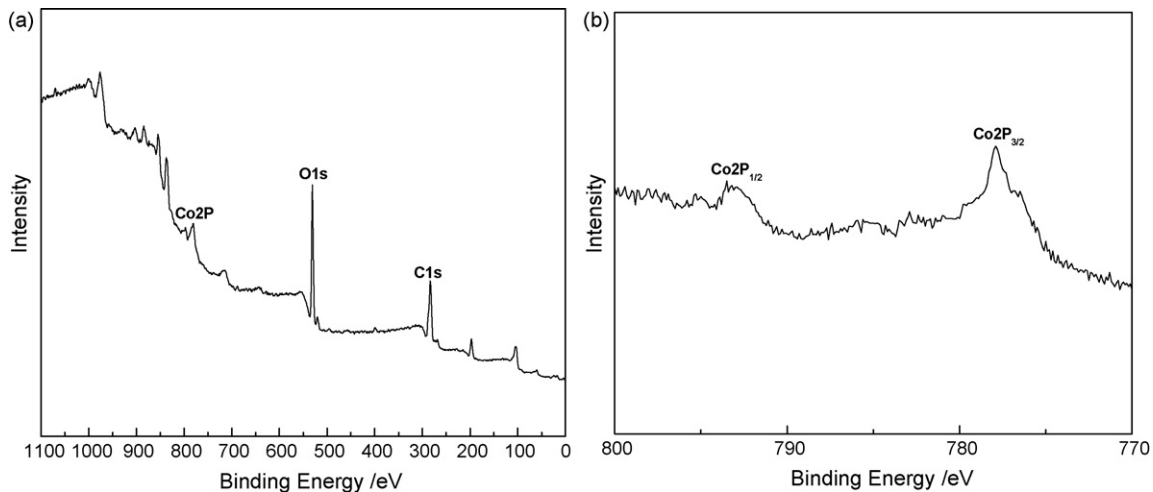


Fig. 2. XPS spectra from the electrode surface: (a) full spectrum and (b) Co2p core level.

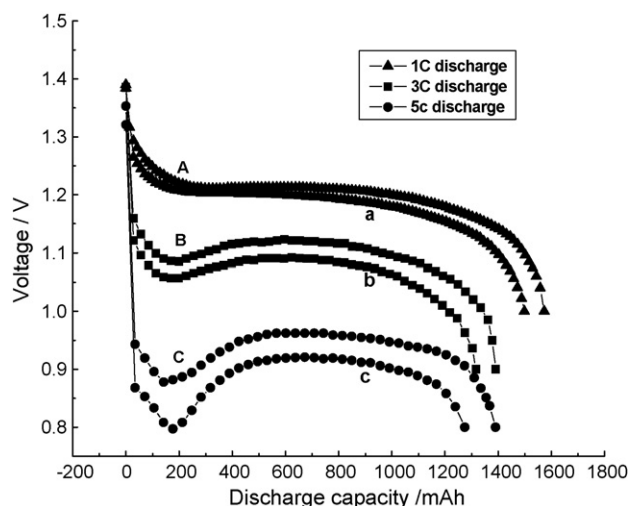


Fig. 4. The discharge curves for the AA-size batteries at 1C (1.7 A), 3C (5.1 A) and 5C (8.5 A): (A–C) with modified electrode and (a–c) with unmodified electrode.

signed by $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ peaks with binding energy 777.9 and 792.9 eV, respectively.

From the result of the XPS analysis, the electrode can be sputtered with cobalt using this method described in this article.

The XRD pattern of the modified and unmodified electrode is shown in Fig. 3. The same structure can be observed in the two cases except that the peaks belonging to the Co can be found in the pattern of the modified electrode. The result indicates that the surface modification method used in this work has no influence on the crystal structure of the alloy.

3.2. Charge–discharge characteristics of the MH/Ni batteries

Fig. 4 shows the typical discharge curves at different rates for the MH/Ni batteries with modified and unmodified electrodes, respectively. The discharge capacity of the batteries with unmodified electrode is 1499 mAh at 1C, 1316 mAh at 3C and 1275 mAh at 5C. The plateau voltage during discharge is 1.202 V at 1C, 1.101 V at 3C and 0.918 V at 5C. For the batteries with modified electrode the capacity is 1573 mAh at 1C, 1391 mAh at 3C and 1390 mAh at 5C, the plateau voltage is 1.209 V at 1C, 1.118 V at 3C and 0.957 V at 5C. It is obvious that the discharge capacity and plateau voltage of the batteries with modified electrode are much higher than the unmodified one. Moreover, with the increasing discharge current, the differences on the discharge capacity and plateau voltage between the two batteries become obvious large. Clearly, the electrode modification improved the high-rate dischargeability remarkably. The ohmic resistances of the two batteries were measured to be 23.4 and 19.2 m Ω for unmodified and modified electrodes, respectively. Obviously, the modification of the negative electrode can effectively decrease the inner resistance of the batteries. This result can be ascribed to the role of the cobalt film plated on the electrode. The presence of cobalt enhances the effectiveness of the current collection processes, and further improves the charge transfer process on the interface between the electrode and electrolyte interface.

3.3. Charge–discharge cycle test

The discharge capacity of the MH/Ni batteries as a function of cycle number is shown in Fig. 5. The initial discharge capacity of both batteries is all about 1720 mAh. The discharge capacity of both batteries decays progressively after 120 cycles. This can be ascribed to the continuous oxidation and disintegration of the

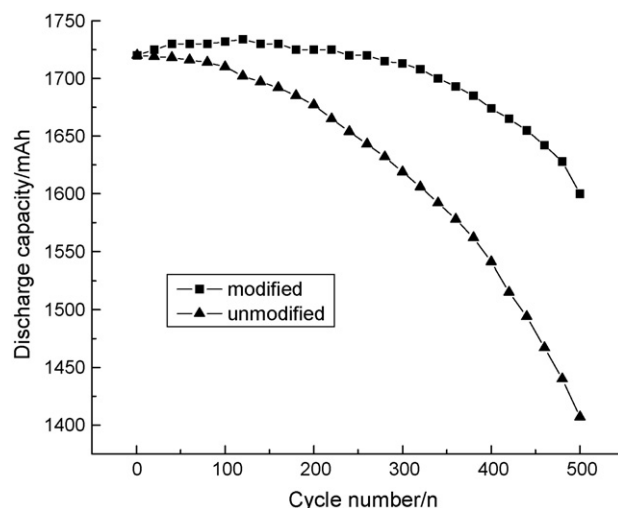


Fig. 5. The cycle durability for the AA-size batteries.

alloy during cycling. Conspicuously, the capacity loss of the batteries with unmodified electrode is larger than the batteries with modified electrode. After 500 cycles, the batteries with modified and unmodified electrode have the capacities of 1600 and 1407 mAh, respectively. The discharge performance of the batteries is significantly stabilized after electrode modification and exhibits satisfactory durability.

The surface XPS analysis of the modified electrode after 500 cycles was performed and the atomic relative ratio of Co, O, Ni on the modified electrode by XPS analysis is shown in Table 1.

Though high level of oxygen was observed on the outer layer, which can be attributed to the rare earth oxides that form readily on the surfaces of intermetallic hydrides, as reported by Schlappbach, it drops greatly after sputtering for 2 min. This suggests that the cobalt film on the electrode restrains the oxidation of the alloy. Since the overcharge of the batteries accelerates its capacity decay, the oxidation should be caused mainly by the oxygen evolved on the nickel cathode during the charging process and then transferred to the anode across the thin separator. The longer cycle life of the batteries using the modified electrode can be partly ascribed to the role of cobalt film as an oxygen barrier, which protects the alloy surface from the oxidation.

Fig. 6 displays the granularity distribution curves of the alloy powders that were stripped out from the MH electrode after 500 cycles using ultrasonic vibrations. The granularity distribution curve of the alloy powders from the unmodified electrode shifts to lower granularity region than that of the alloy powders from the modified electrode. The mean particle sizes of the modified and unmodified electrode are 20.33 and 5.65 μm , respectively. Obviously, the disintegration of the alloy is reduced due to the cobalt film plated on the electrode.

Combining the results of cycle life, XPS analysis and particle distribution, it is clearly proved that the cobalt plated on the electrode acts as a protective layer, which effectively restrains the alloy from oxidation and pulverization, which are known as the main causes

Table 1
Surface components analyzed by XPS for the modified electrode

	Co	O	Ni
Outer layer	29.87	48.66	19.79
Sputtering for 2 min	54.44	18.86	11.66
Sputtering for 10 min	64.79	11.71	13.66

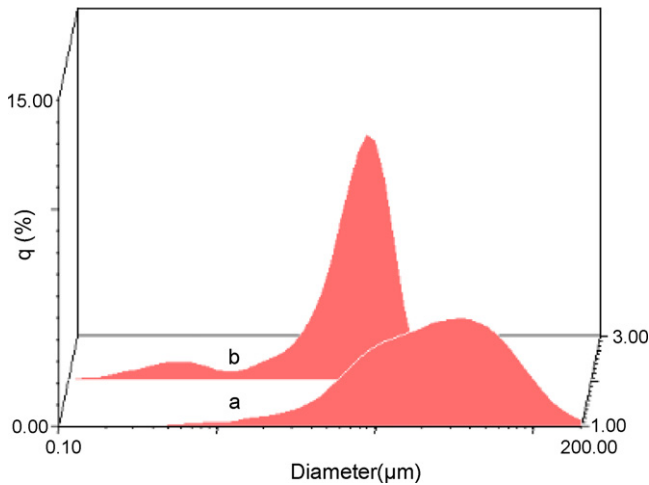


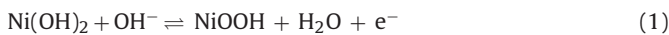
Fig. 6. Particle size distribution curves of the alloy powders of the MH electrode: (a) surface modified electrode and (b) surface unmodified electrode.

that lead to the degradation of the batteries. Therefore, the decay of the capacity is decreased and the cycle life is prolonged.

3.4. Inner pressure of the batteries

In the sealed-type MH/Ni batteries, the charge–discharge reactions can be written as

Positive electrode



Negative electrode



When the battery is overcharged, oxygen gas is generated at the positive electrode according to Eq. (3). The oxygen gas passes through the separator and diffuses onto the negative electrode, and is reduced to water by chemical reaction according to Eq. (4). By the oxygen-consuming reaction (Eq. (4)), elevation of batteries internal pressure owing to the generated oxygen gas is suppressed.

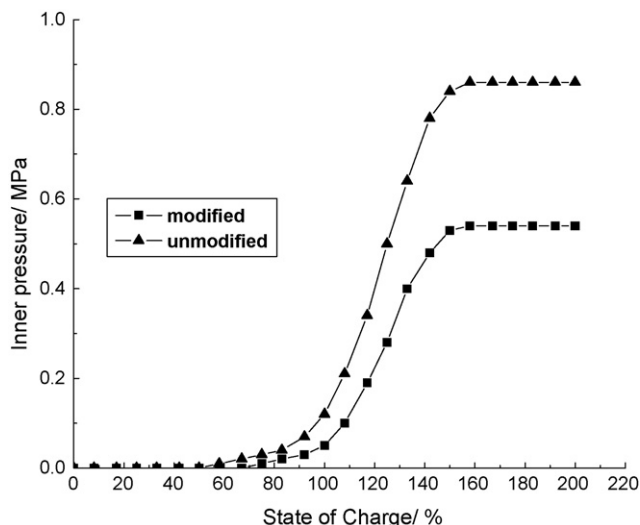


Fig. 7. Inner pressure of the MH/Ni batteries at 0.5C charge.

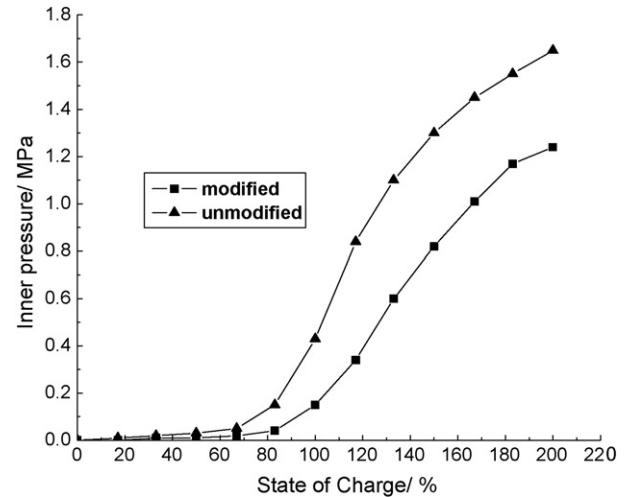
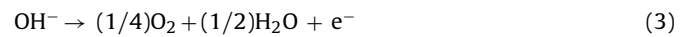


Fig. 8. Inner pressures of the MH/Ni batteries at 1C charge.

Positive electrode



Negative electrode

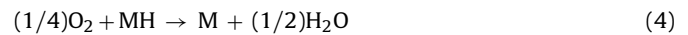


Fig. 7 shows the inner pressure change of AA-size MH/Ni batteries when charging at 0.5C rate.

It can be seen that the inner pressure of the batteries remains unchanged before being charged up to 50% of nominal capacity. After being charged up to 60%, the inner pressure begins to increase, but the rate of the increase is low. After being charged up to 100%, the inner pressure increases sharply. When charged up to about 150%, the inner pressure reaches equilibrium and up to 200% of nominal capacity, the inner pressure remains constant. It indicates that, in this period, the rate of gas evolution equals the rate of gas consumption. It can be seen that the batteries with the modified electrode displays the slower increase of inner pressure, which reaches equilibrium at 0.54 MPa. For the batteries with unmodified electrode, the inner pressure at equilibrium is 0.86 MPa, which is higher than that of the batteries with modified electrode.

The inner pressure change at 1C rate is illustrated in Fig. 8.

The inner pressure of the unmodified batteries increases rapidly when approaching 80% of nominal capacity and reaches 1.65 MPa when charged up to 200% of nominal capacity. For the modified batteries, the inner pressure increases when charged up to 100% and reaches 1.24 MPa at 200% of the nominal capacity.

The above results indicate that the inner pressure of the batteries decreases remarkably after surface modification. The decrease is due to the cobalt film on the electrode have a role in preventing the release of hydrogen gas from the alloy surface, suppressing the recombination of hydrogen atoms.

4. Conclusion

The MH electrode of the MH/Ni batteries can be plated with a thin cobalt film by a surface modification method using vacuum evaporate plating technology and the crystal bulk structure of the alloy remains unchanged. The cobalt film plated on the electrode can play at least three important roles: (i) the microcurrent collector for facilitating the charge transfer on the electrode. The high-rate dischargeability of the batteries after the surface modification is improved, resulting from the enhancement of the

electrode conductivity and the decrease of the batteries ohmic resistance. The plateau voltage increases by 0.04 V at the 5C discharge rate. (ii) The cobalt plated on the electrode surface also acts as a protective layer, which restrains the alloy from oxidation and pulverization. Therefore, the cycle life of the batteries is prolonged. (iii) The inner pressure of the batteries can be decreased and the charging efficiency is improved.

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