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SHORT COMMUNICATION

Effect of surface modification on performance of alloy electrodes for hydrogen storage

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1. Introduction

Nickel metal–hydride (Ni–MH) rechargeable batteries employing hydrogen storage alloys have attracted increasing attention in recent years because of their several inherent advantages such as high energy and power density, high-rate charge/discharge capability, high tolerance to overcharge/overdischarge and environmental acceptance (avoidance of Cd) [1]. So far, many multicomponent hydrogen storage alloys based on Mischmetal have been developed to meet the requirements of high storage capacity [2–4]. The performances of hydride electrodes have been improved markedly by replacing part of the nickel by Mn, Co, Al, Sn, etc. The bulk composition of hydrogen storage alloys is an important factor affecting the characteristics of the electrode. However, the surface state of the alloy is another factor of substantial significance. The microencapsulation of alloy powder particles with different kinds of electroless coatings such as copper, nickel and their alloys has been confirmed to be effective in improving the performance of hydride negative electrodes by preventing deactivation of the disintegrated alloy and leading to superior electrical conductivity [5, 6].

In the present paper, the effects of surface modification of metal hydride negative electrodes by chemical treatment and electroless plating of a Ni–P alloy from hypophosphite on the electrocatalytic activity for the hydrogen evolution reaction and capacity for electrochemical H sorption were investigated.

2. Experimental details

A hydrogen storage alloy powder ($Mm(NiMnCoAl)_5$, Mm = mischmetal), having a particle size of about 30–40 μm, was provided by the Xinxian Battery Factory. Metal hydride electrodes were constructed by the following procedure: after mixing the hydrogen storage alloy powder (0.15–0.20 g) with a small amount of 4 wt % polyvinylalcohol solution, the mixture was pasted on to a porous nickel foam support material and then dried in vacuum before compressing it at 200 kg cm^{-2}. The resulting electrodes were modified by immersing them in 6 M KOH + 0.1 M KBH_4 solution at 70 °C for 6 h and then in an electroless Ni–P alloy plating solution ($NiSO_4.6H_2O$ 20–26 g dm^{-3} $Na_3C_6H_5O_7.2H_2O$ 80–100 g dm^{-3}, $NaH_2PO_2.H_2O$ 15–20 g dm^{-3}, $(NH_4)_2SO_4$ 25–30 g dm^{-3}, pH 9.0, temperature 85 °C).

A glass cell with three compartments, separated from each other by sintered glass frits, was employed for the electrochemical measurements. The surface modified metal hydride was placed in the central compartment, with two positive electrodes ($Ni(OH)_2$/NiOOH) in compartments on each side. The electrochemical capacity of the positive electrodes was designed to be sufficiently greater than that of the hydride electrode to avoid cathode limitation. As a reference electrode, a Hg|HgO|6 M KOH half cell was employed. All electrode potentials are recorded with respect to the potential of this Hg|HgO reference electrode. The electrolyte was deaerated 6 M KOH solution. Galvanostatic charge/discharge cycling tests were performed at room temperature (20–30 °C). The metal hydride electrode was charged for 3.5 h and discharged to −0.65 V vs Hg|HgO at a current density of 100 mA g^{-1}.

3. Results and discussion

The nature of the surface and the surface modification of the hydrogen storage alloy electrodes have significant influence on the electrochemical characteristics of hydride electrodes. Usually a thin oxide film exists on the surface of a hydrogen storage alloy which decreases the electrocatalytic activity for the hydrogen electrode reactions, for example, preventing hydrogen atoms being transferred from the surface to the bulk, and decreasing the charge efficiency of the negative electrode. Thus, such metal hydride electrodes must be activated by electrochemical charge/discharge cycling before they have sufficiently high electrochemical capacity and performance.

Figure 1 shows typical discharge curves for the unmodified negative electrode during activation. In the first cycle, the discharge capacity was only about 65 mAh g^{-1}, but after 6–7 charge/discharge cycles, the electrochemical capacity had increased up to 172 mAh g^{-1}. Figures 2 and 3 show typical discharge curves for the surface modified hydride electrodes. In the first cycle, the capacities were 230 mAh g^{-1} and 210 mAh g^{-1}, respectively, and the full charge potential after charging was also quite different. Typical results for the unmodified and modified negative electrodes are shown comparatively in Fig. 4 as a function of the number of cathodic/anodic cycles. A large volume of hydrogen was evolved during charging in the case of the unmodified electrode, but little hydrogen was formed in the charging of the modified electrodes.

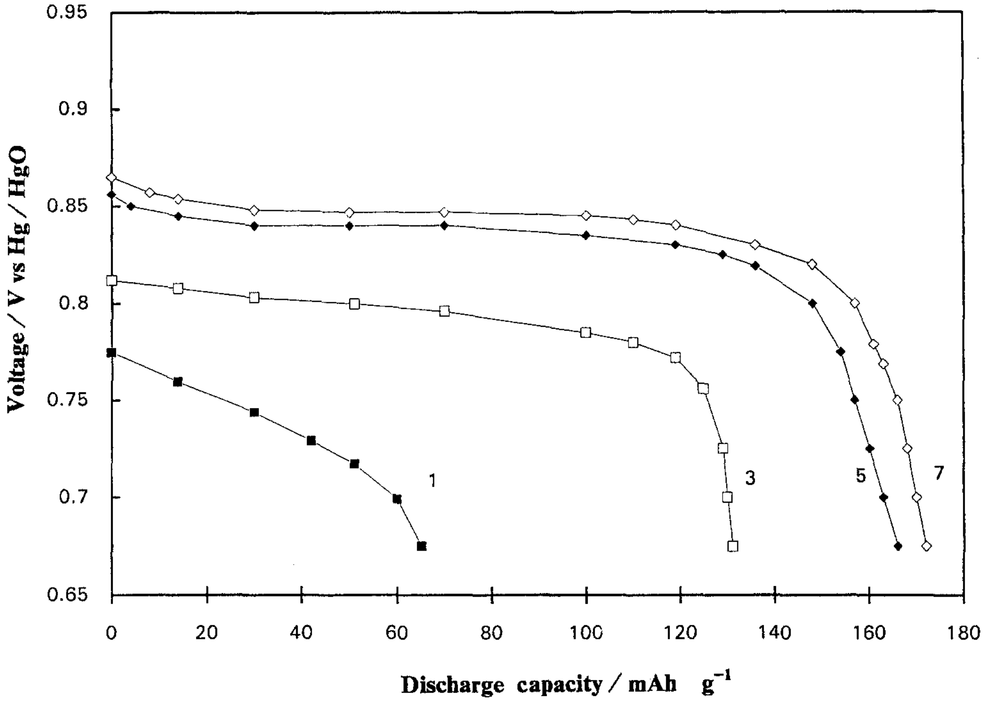

Fig. 1. Typical discharge curves during activation unmodified MH electrodes, discharge current density was 100 mA g^{-1}, the numbers near curves indicate numbers of cycles.

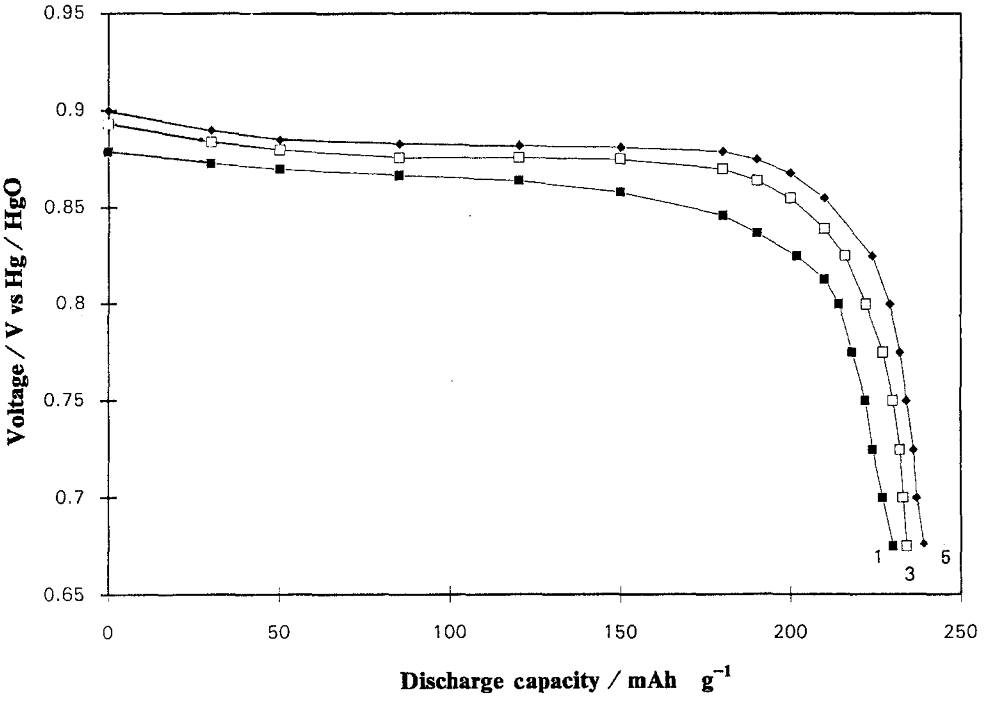

Fig. 2. Typical discharge curves during activation. MH electrodes immersing in 6 M KOH + 0.1 M KBH_4 at 70 °C for 6 h.

This observation indicates that the oxide film on the surface of the hydrogen storage electrodes can be reduced or eliminated. Therefore, the absence of an oxide film on the surface and the resulting more facile penetration of atomic hydrogen into the lattice, are the main causes for the observed high electrocatalytic activity for the HER.

Figure 5 shows a comparison of the electrochemical capacities of unmodified and modified negative electrodes as a function of the number of cycles. The saturation capacity of the unmodified electrode was only 171 mAh g^{-1}. The electrochemical capacities increased markedly up to 240–291 mAh g^{-1} with surface modification by chemical reduction and electroless plating. Significantly, the modified electrodes did not require conditioning activation by electrochemical charge/discharge cycling. Not only was the oxide film on the electrode surface reduced by the

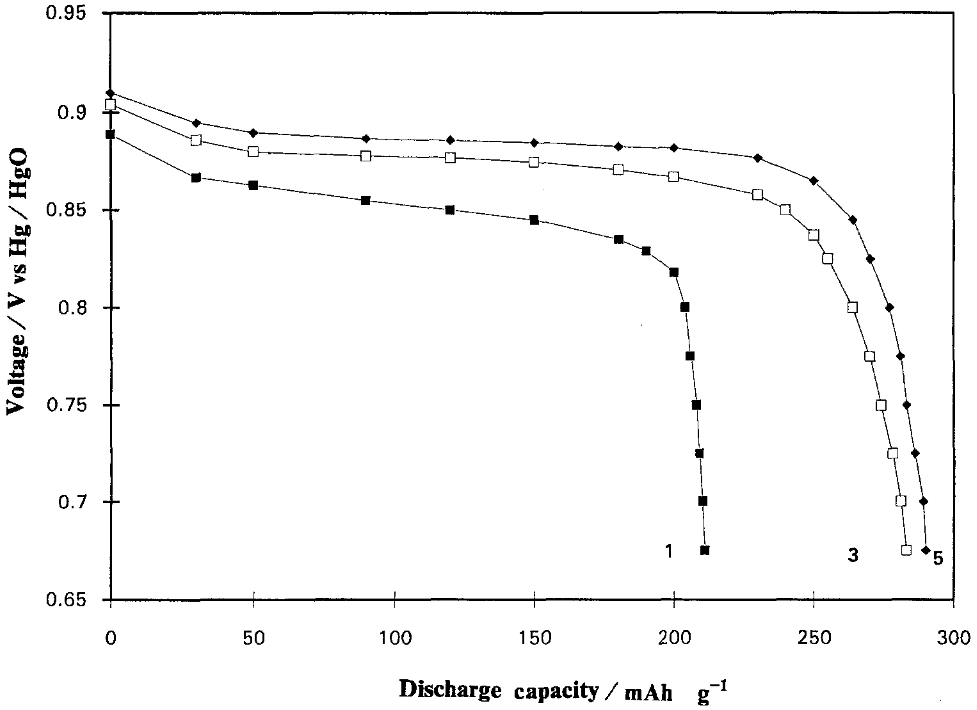

Fig. 3. Typical discharge curves during activation (hydride electrode after electroless plating of Ni–P alloy).

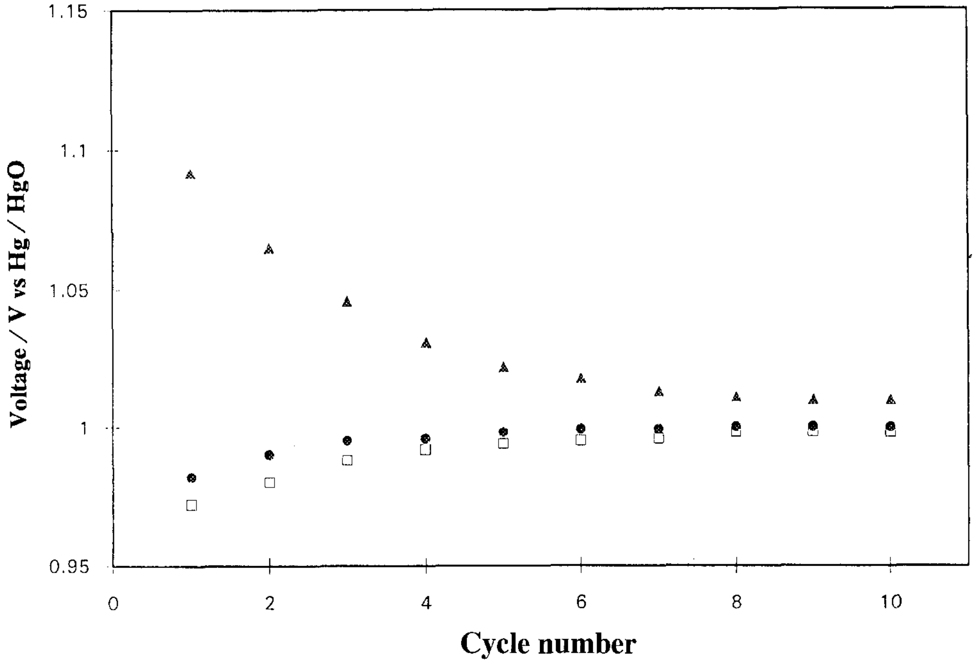

Fig. 4. Full-charge potential in the closed as a function the number of cycles: (▲) unmodified; (●) immersing in 6 M KOH + KBH_4 at 70 °C for 6 h; (□) after electroless plating Ni–P alloy following immersing.

chemical treatment but also the resistances across the current collector and the hydrogen storage alloy powder were eliminated.

As to the effects of surface modification of hydride electrodes on self-discharge and cycle life, further experiments are in progress.

4. Conclusion

Alloy hydrogen storage electrodes of the Mm $(NiMnCoAl)_5$, modified simply by chemical reduction and electroless plating by Ni–P, exhibit much improved performance. Both the electrocatalytic activity on cycling and the electrochemical charge capacity are increased markedly by this kind of surface modification.

Acknowledgement

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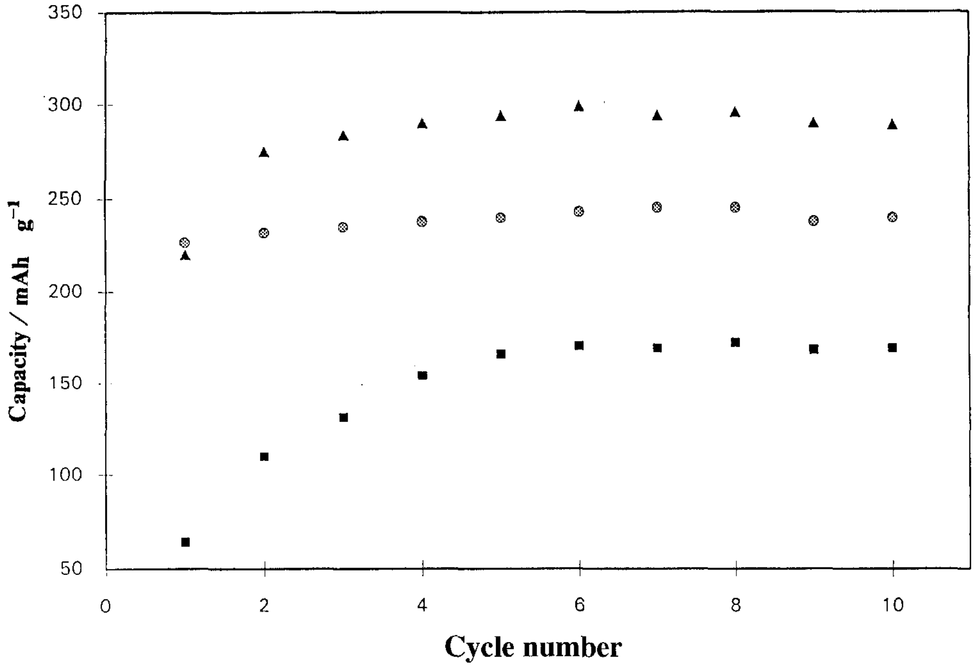

Fig. 5. Discharge capacity as a function of the number of cycles: (■) unmodified; (●) immersing in 6 M KOH + KBH_4 at 70 °C for 6 h; (▲) after electroless plating Ni–P alloy following immersing.

References

[1] J. J. G. Willems, *Philips J. Res.* **39** (1984) 1.

[2] J. C. Sun and Y. Q. Lei, *Xitu* **14**(5) (1993) 61 (in Chinese).

[3] C. N. Park and R. Kirchheim, *Alloy and Compounds* **182** (1992) 321.

[4] C. Iwakura and M. Matsuoka, *Prog. Batts. Batt. Mat.* **10** (1992) 81.

[5] T. Sakai, A. Yuasa, H. Ishikawa, H. Miyamura and N. Kuriyama, *J. Less-Common Metals* **172–174** (1991) 1194.

[6] T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura and H. Yoneyama, *J. Electrochem. Soc.* **134** (1987) 558.