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Influence of surface pretreatment and charge–discharge mode on cycle performance of metal hydride electrodes

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Abstract

The influence of surface pretreatment and charge–discharge mode on the cycle performance of metal hydride (MH) electrodes is studied by using stable, AB_5-type, hydrogen-storage, alloy particles. The initial electrochemical performance of MH electrodes, which use copper-coated and electroless nickel-plated hydrogen-storage alloy particles, respectively, is improved, but the cycle lives are the same as that of a bare MH electrode. It is considered that the cycle lives of MH electrodes depend primarily on the bulk properties of hydrogen-storage alloy particles. The pulverization of these particles is the main cause of the degradation in electrode life. In addition, it is found that overcharging accelerates the decline in the capacity of the MH electrode. The decreasing charge efficiency of the MH electrode during the course of charge–discharge cycling is due partly to the declining charge–discharge coulombic efficiency of the MH electrode, and its accumulated effect is an important cause of performance degradation of sealed MH/Ni batteries. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pretreatment method; Metal hydride electrode; Cycle performance; Charge capacity; Degradation

1. Introduction

The nickel/metal hydride (Ni/MH) battery which uses an AB_5-type metal hydride (MH) electrode has attracted much interest because of its higher electrochemical performance than the nickel/cadmium battery [1,2]. The MH electrode plays an important role in the Ni/MH battery, and its performance is affected by many factors such as the bulk and surface properties of hydrogen-storage alloy particles, the preparation method and the charge–discharge mode of electrode, etc. [3]. To date, copper-coating, electroless nickel-plating and other surface pretreatment methods have been investigated extensively and even some of these methods have been applied to the production of Ni/MH batteries [4–13]. Nevertheless, the effects of different pretreatment method on the cycle life and other performances characteristics of the electrode are usually ignored. Moreover, it is necessary to investigate the change in the characteristics of the MH electrode under different working conditions, particular the charge–discharge mode of the MH electrode, in order to increase the performance of the MH/Ni battery.

In this paper, the cycle life of MH electrodes is examined for different surface pretreatment set the hydrogen-storage alloy particles and by changing the charge capacity of MH electrode.

2. Experimental

A hydrogen-storage alloy ($La_{0.54}Ce_{0.32}Pr_{0.03}Nd_{0.11}$-$Ni_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$) ingot, which was supplied by Beijing General Research Institute for Non-Ferrous Metals, was crushed mechanically to produce a powder of less than 200 mesh. Two kinds of hydrogen-storage alloy particles, which were pretreated either by a copper-coating method [8] or by a electroless nickel-plating method [14], were prepared. The electrodes were constructed by the following procedure. After mixing 75 wt.% alloy particles with 25 wt.% binder (60 wt.% PTFE + 3 wt.% CMC, weight ratio = 3/7), the paste was poured into a foam nickel substrate with a thickness of 2 mm. The resulting electrode was dried in vacuum and pressed to a thickness

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of 0.7 mm. Two sintered nickel hydroxide electrodes, which were placed either side of the MH electrode, and a Hg/HgO electrode were used as the counter and the reference electrodes, respectively. All potentials are reported with respect to this reference electrode. The electrolyte was a 30 wt.% KOH + 1 wt.% LiOH solution. A three-electrode flooded cell with a Luggin capillary for the Hg/HgO reference electrode was used in all the studies.

Cycle tests were carried out with an automatic battery instrument made by Arbin. The charge–discharge cycle conditions usually included a discharging step at a constant current of 100 mA per g to −0.6 V, and a charging step at a constant current of 100 mA per g to a charge return of 125% of the highest capacity of electrode. Scanning electron microscopic studies were performed on a S-520 instrument. The experiments were performed at ~ 25°C.

3. Results and discussion

3.1. Cycle performance of MH electrodes subjected to different surface pretreatment

Copper-coated and electroless nickel-plated hydrogen storage alloy particles were used to investigate the effects of different surface pretreatment methods on the cycle performance of the MH electrode. The discharge capacity of a bare MH electrode and two copper-coated MH electrodes as a function of cycle number are shown in Fig. 1. Compared with the bare MH electrode, the initial discharge capacity of both copper-coated MH electrodes increases faster with cycling. The 5 wt.% copper-coated and the 10 wt.% copper-coated MH electrode recorded ~ 200 mAh per g, (which approaches the actual discharge capacity of a MH electrode in a MH/Ni battery) after 5 and 3 cycles, respectively, while a bare MH electrode gave this capacity after 11 cycles. Copper-coated and bare MH electrodes reached a maximum discharge capacity (~ 274 mAh per g) after about 20 cycles and 30 cycles, respectively. Moreover, after reaching the maximum value, the discharge capacity of these MH electrodes decreased progressively with increasing cycle number; it dropped by about 20% for both the bare and the copper-coated MH electrodes after 500 cycles. The initial charge–discharge curves also indicated that copper-coated electrodes have better charge–discharge potential characteristics than the bare MH electrode. These results show that although the initial electrochemical performance of the two copper-coated electrodes is enhanced, the cycle life is unaffected.

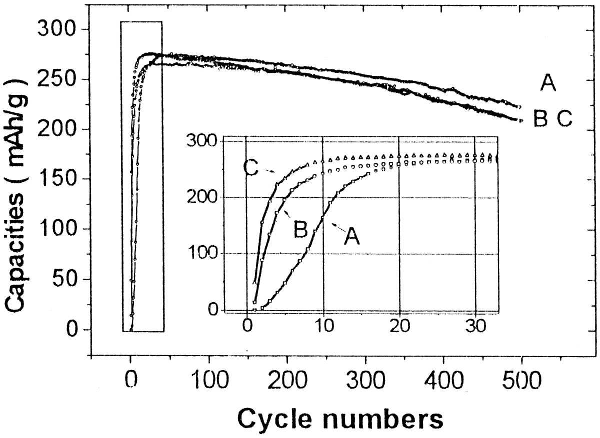

Fig. 1. Discharge capacity vs. cycle number for bare MH electrode and two copper-coated MH electrodes at 100 mA per g, (A) bare, (B) 5 wt.% Cu, (C) 10 wt.% Cu.

Other studies demonstrate that the copper-coated layer on the alloy particles in the MH electrode is easily oxidized and dissolves in the electrolyte via a cupric oxide route when the electrode is exposed to air or anodic oxidation. The cupric oxide in the electrolyte causes a decrease in the electrochemical performance of the $Ni(OH)_2$/NiOOH electrode [15]. Thus, it is concluded that a copper coating is not a suitable pretreatment method compared with surface reduction [11–13] or other pretreatment methods [16].

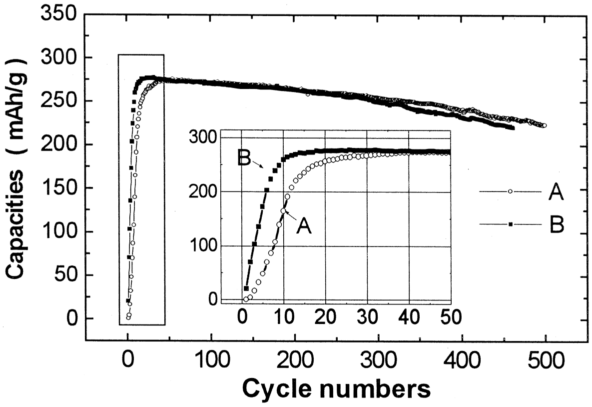

Fig. 2. Discharge capacity vs. cycle number for bare MH electrode and electroless nickel-plated MH electrode at 100 mA per g. (A) bare, (B) electroless nickel-plated.

The discharge capacity of a bare MH electrode and an electroless nickel-plated MH electrode with cycling is given in Fig. 2. The results indicate that the initial discharge capacity of the electroless nickel-plated MH electrode is increased compared with that of the bare MH electrode, but its cycle life is the same. Together with the performance of copper-coated MH electrodes, it is considered that the effects of these surface pretreatment methods on the long-term cycle life of the MH electrode are negligible.

In order to obtain greater insight into the characteristics of the cycle performance of the MH electrode, the change in the hydrogen-storage alloy particles in a bare MH electrode at different charge–discharge cycle stages was examined by scanning electron microscopy. Electron mi-

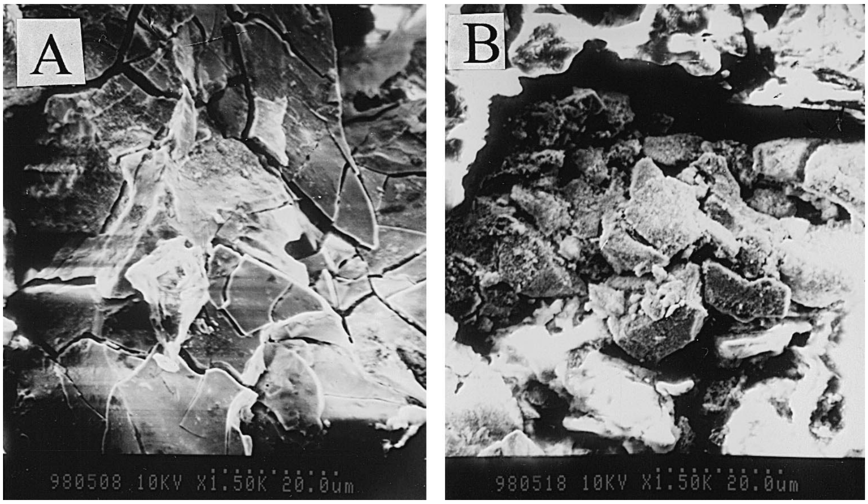

Fig. 3. Electron micrographs of hydrogen-storage alloy particles in a bare MH electrode after (A) full activation (30 cycles) and (B) 500 cycles.

crographs after full activation (30 cycles) and 500 cycles are presented in Fig. 3.

Many cracks are produced on the surface of the hydrogen-storage alloy particles after the electrode is fully activated (Fig. 3(A)). The alloy particles disintegrate into many small particles with cycling (Fig. 3(B)). The production of cracks in the alloy particles exposes a fresh alloy surface which would react easily with electrolyte and produce oxides [3]; this process finally leads to pulverization of the alloy particles.

For electroless nickel-plated alloy particles in a MH electrode, the initial surface morphologies of the hydrogen-storage alloy particles are different to those in a bare MH electrode, but the production of cracks is similar at the same charge–discharge cycle. An electron micrograph of electroless nickel-plated alloy particles after 500 cycles is given in Fig. 4. Similar results are obtained for copper-coated alloy particles in a MH electrode, and this suggests that pulverization of the alloy particles in these MH electrodes is also similar. Thus, it is concluded that though these pretreatment methods affect the initial electrochemical performance of the MH electrode, they do not retard the generation of cracks and subsequent formation of oxides in the alloy particles. The cycle lives of these MH electrodes will mainly depend on the bulk properties of the alloy particles.

Fig. 4. Electron micrograph of electroless nickel-plated alloy particles in a MH electrode after 500 cycles.

It is well known that the initial electrochemical performance of the MH electrode is very important for the production of the MH/Ni battery. Although the initial electrochemical performance of the MH electrode can be increased by using the repeated hydrogen absorption–desorption method [17], the cost of the production equipment and the destruction of the microstructure of the alloy particles in the pretreatment process renders this method impractical. Therefore, it is essential to choose stable hydrogen-storage alloy particles and develop a more simple and efficient surface pretreatment method for the production of MH/Ni batteries with higher performance [16].

3.2. Effect of charge capacity on cycle performance of MH electrodes

The charge–discharge mode exerts a major influence on the cycle life of the MH electrode. Therefore, in attempts to increase the electrochemical performance of MH/Ni batteries, it will be helpful to study the characteristics of the MH electrode under different charge–charge modes. Accordingly, the cycle performance of a bare MH electrode with different charge capacities has been examined. The discharge capacity of the bare MH electrode discussed above was used as the normal discharge capacity of the MH electrode. The discharge capacity of the bare MH electrode with cycling is shown in Fig. 5 for electrodes with 80, 125 and 170% charge capacity.

The number of initial cycles for these MH electrodes to reach maximum capacity decreases with increasing charge capacity. The maximum discharge capacity of the electrode with 170% charge capacity is slightly higher than that of the electrode with 125% charge capacity. With further cycling, the discharge capacity decreases progressively; the discharge capacity of the electrode with 170% charge capacity declines more quickly, while changes in discharge capacity of the electrode with 80% charge capacity are very small. Thus, overcharging accelerates the degradation in the performance of the MH electrode.

Because the electrochemical charge-discharge capacity of the MH electrode is designed to be larger than that of the $Ni(OH)_2/NiOOH$ electrode in the sealed design of MH/Ni battery, a charge capacity of 80% corresponds to the actual charge capacity of a MH electrode in a MH/Ni battery. Therefore, it is concluded that the MH electrode used in this experiment has a stable cycle performance.

On the other hand, the maximum discharge capacity of the MH electrode with 80% charge capacity is still smaller than the discharge capacity of other two electrodes after 500 cycles. The utilization ratio of the hydrogen-storage alloy particles in the MH electrode with 80% charge capacity does not approach 100% even if the velocity of the generation of metal oxide on the alloy particles is equal to that of the other two electrodes. To understand this behaviour, the coulombic efficiency of the MH electrode with 80% charge capacity as a function of cycle number is presented in Fig. 6.

The maximum charge–discharge coulombic efficiency of 99.5% is obtained after the electrode is fully activated. The efficiency then decreases with cycling and is 95.5% after 500 cycles.

In our opinion, the decrease in the charge–discharge coulombic efficiency contributes to the decrease in the charge efficiency of the MH electrode, and mainly originates from the formation of an oxide film on the alloy particles and the reduction in the alloy content. Although the amount of oxides formed on the alloy particles is small, and its effect on the cycle performance of a single experimental MH electrode might be neglected, the accumulated effect during charge–discharge cycles will provoke a degradation of the performance of the sealed MH/Ni battery, surface treatment to obtain more stable hydrogen-storage alloy particle surfaces, and an improved preparation method should be considered as efficient ways to increase the performance of the MH/Ni battery.

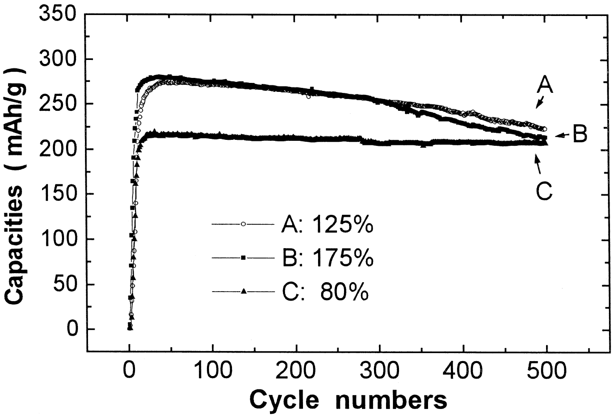

Fig. 5. Discharge capacity vs. cycle number for bare MH electrode with different charge capacities (30, 125, 175%) at 100 mHg^{-1}.

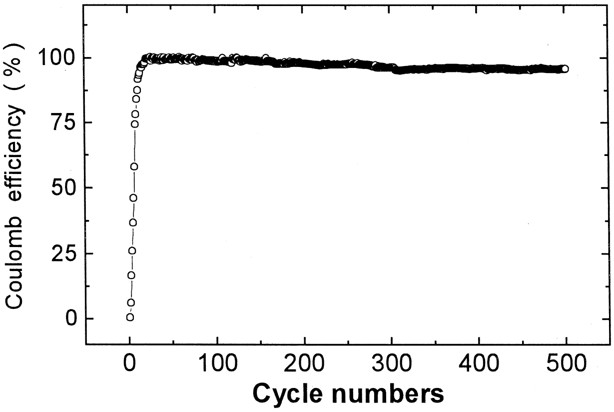

Fig. 6. Coulomb efficiency vs. cycle number for MH electrode with 80% charge capacity.

4. Conclusions

For AB_5-type, hydrogen-storage alloy particles with stable properties, it is demonstrated that proper surface pretreatment of the alloy particles will improve the initial electrochemical performance of the MH electrode. By contrast, the effect of surface pretreatment on cycle life is insignificant. The similarity in the pulverization of the hydrogen-storage alloy pretreated by different methods produces similar changes in the characteristics during long-term cycling. In addition, it is shown that overcharging will accelerate the decrease in discharge capacity of the MH electrode. The decrease in charge efficiency, which originates mainly from the formation of an oxide film on the alloy particles and the reduction in the alloy content, contributes to the decline in the charge–discharge coulombic efficiency of a MH electrode with 80% charge capacity during the course of charge–discharge cycling. The latter is an important factor that provokes degradation of the performance of sealed MH/Ni batteries.

Acknowledgements

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