

Degradation analysis of nickel/ metal hydride battery and its electrodes materials^①

LI Li(李 丽), WU Feng(吴 锋), YANG Kai(杨 凯)

(School of Chemical Engineering and Environment, National Development Center of Hi-Tech Green Materials, Beijing Institute of Technology, Beijing 100081, China)

Abstract: The results indicate that during charge and discharge, the expansion of $\text{Ni}(\text{OH})_2$ crystal, pulverization of MH alloy particles and falling off from current collector are identified as the main causes for deterioration of Ni/MH batteries. Meanwhile, the contact resistance of inner battery increases due to the deterioration of the negative and positive electrode, and these changes lead to increasing battery body temperature and damaging its electrode and separator. The fibre's expansion and hole's diminishment of battery's separator after degradation will affect the electrochemical performance and cycle life of Ni/MH batteries.

Key words: Ni/MH battery; electrodes materials; degradation analysis; separator

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1 INTRODUCTION

The nickel/metal hydride (Ni/MH) secondary batteries have been extensively used in various consumer and portable electronics devices recently, especially in battery-powered electric vehicles because of their longer life of charge-discharge cycling and more friendliness to environment than the conventional nickel/cadmium batteries. And an experienced considerable growth of performance and market share are going on^[1-3].

However, the electrochemical performance of nickel/metal hydride batteries deteriorates obviously during the processes of charge and discharge, which leads to short cycle life of the batteries. Zhou et al^[4] showed that the extrusion mechanism has been demonstrated to be the major cause for the capacity decay of the positive electrodes during cycling. XIA et al^[5] showed that the main causes for the degradation of Mm alloy hydride electrodes are the increase of internal stress, the expansion of crystal lattice and the preferential dissolution of Mm, rather than the oxidation of the alloy by oxygen. In this work, emphasis is put on systematically revealing the mechanism of degradation of sealed-type Ni/MH batteries. Both deterioration behavior and microcosmic structure change of electrodes are investigated, as well as its correlative mechanism. This is very effective in improving the electrochemical performance of sealed-type nickel/metal hydride batteries, as well as its recycle process.

2 EXPERIMENTAL

2.1 Preparation of electrodes and Ni/MH batteries

The negative electrode of Ni/MH battery was formed by the alloy powder $\text{MNi}_{1.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{Al}_{0.3}$ (where M1 denotes La-rich mischmetal, La 64.6%, Ce 5.9%, Pr 26.6%, Nd 2.2%) mixed with a small amount of nickel and 3% polytetrafluoroethylene (PTFE, mass fraction) and pressed into nickel foam substrate. Positive electrode was prepared by filling a nickel foam substrate with $\text{Ni}(\text{OH})_2$ mixed with CoO and PTFE. A non-woven polypropylene separator was inserted between the positive and negative electrodes, and then spirally rolled into AA-type cylindrical battery cans. A KOH (7 mol/L)/LiOH (1 mol/L) electrolyte was injected and then the batteries were sealed.

2.2 Measurements of electrochemical performance of Ni/MH batteries

The experiment of testing the charge-discharge cycling-life of battery was carried out with the scheme for each cycle that consisted of charging with 1C for 1.2 h, a pause for 30 min, and then discharging with 1C to 1.0 V after charge/discharge activation at low rate (0.1C). All the tests in this article were performed at room temperature (25 °C). The charge/discharge experiments and cycling-life tests were carried out on ZEEMOO DK2010 and BS9300 apparatus, controlled by an external computer. At the same time, the change of battery body temperature in

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Correspondence: LI Li, PhD; Tel: + 86-10-68912508; Fax: + 86-10-68451429; E-mail: wufeng863@vip.sina.com

charge and discharge process was tested by a temperature sensor.

Scanning electron microscopy was employed to examine the original changes on surface and cross-section morphology of positive and negative electrodes for Ni/MH batteries.

The X-ray diffraction (XRD) patterns of electrodes were obtained on a Rigaku D/max-III A diffractometer using Cu K α radiation and graphite monochromatic filter at 50 kV and 150 mA. The scanning rate is 4.0(°)/min.

3 RESULTS AND DISCUSSION

3.1 Change of discharge capacity and inner pressure of Ni/MH battery

The discharge capacity and internal resistance of AA size sealed Ni/MH batteries as a function of the number of charge-discharge cycling (n) are shown in Fig. 1. It can be observed that, with increasing n , the discharge capacity of the battery ascended at first before $n = 300$, and descended bit by bit till $n = 750$, then decayed dramatically until it reached 80% of the original capacity at the 900th cycle.

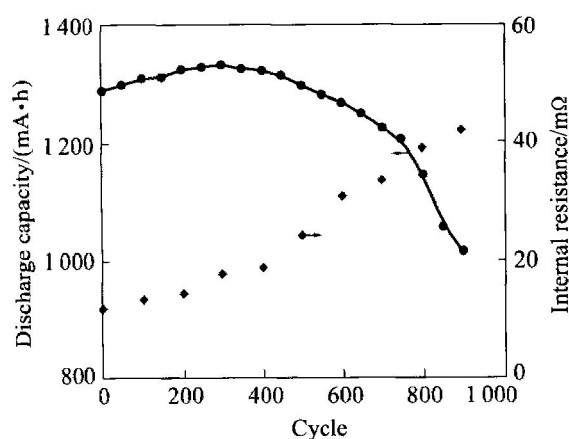


Fig. 1 Dependence of discharge capacity and internal resistance on cycle (n) for Ni/MH batteries at 1C rate (25 °C)

The battery is considered as failure at the point where the battery discharge capacity was reduced down to 80% of the original capacity. In the meantime, the internal resistance is increased continuously as a function of n . The cause leading to this phenomenon is the alloy particles pulverization during the process of charge and discharge. Leblanc et al.^[6] have explained this phenomenon as the impedance increase caused by a lack of electrolyte or water which leads to a separator dry-out. This viewpoint was confirmed by introducing a small quantity of electrolyte into the failure battery and seeing the internal resistance recover to some extent.

During the charge/discharge cycling, the electrolyte was redistributed among the electrodes and the separator due to the increase in surface area, porosity and swelling (Table 1). The over-high internal pressure made the gas (H $_2$ and O $_2$) release out of the battery and led to the losing of electrolyte. Most researchers considered that the main origin of degradation behavior of Ni/MH battery is the shortage of electrolyte^[7]. The failure batteries (after 900 cycles) were cut open and immersed in plenty of electrolyte (KOH (7 mol/L) / LiOH (1 mol/L)) for 24 h, then charge and discharge at 1C rate was conducted. It was shown that in this case the discharge capacity could be partially resumed, obtain 10% of the original capacity (Fig. 2). The results indicated that the degradation behavior of Ni/MH battery is not only due to the lack of electrolyte, but also due to the deterioration of the active materials on the positive and negative electrodes of Ni/MH batteries.

Table 1 Electrolyte distribution of Ni/MH batteries (%)

Battery	Positive	Separator	Negative
New battery	26	45	29
Failure battery	54	7	39

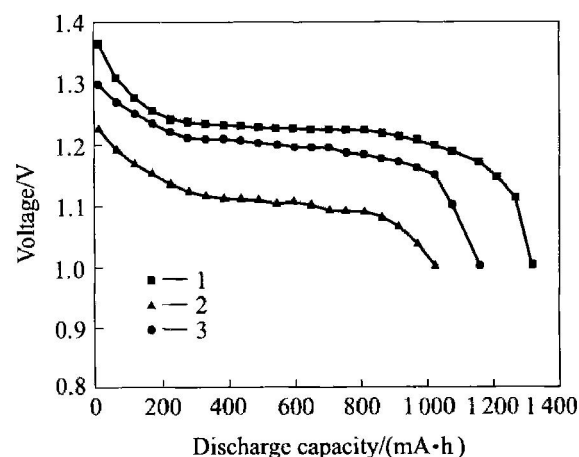


Fig. 2 Discharge curves before cycle, after 900 cycles and the latter immersed in fresh electrolyte for Ni/MH batteries at 1C rate (25 °C)
(1—Before cycle; 2—After 900 cycles; 3—After 900 cycles immersed in fresh electrolyte)

3.2 Battery body temperature during charge and discharge process

Battery body temperature during charge and discharge process was tested by a temperature sensor (as shown in Fig. 3). Battery (a) is before cycle, (b) is after 400 cycles and (c) is after 900 cycles. It

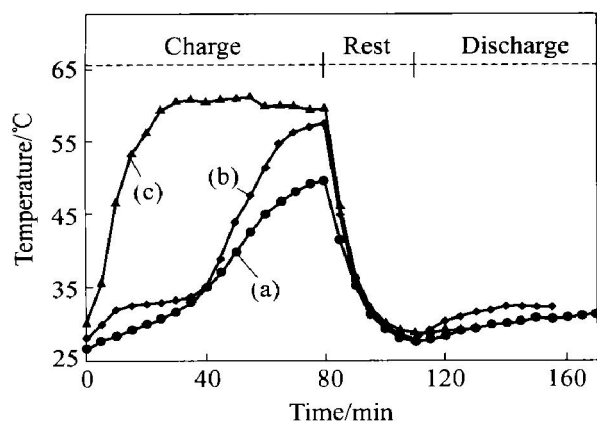


Fig. 3 Curves of battery body temperature vs time in charge and discharge process

can be observed that body temperature of battery (a) ascended slowly and continuously, that of battery (b) ascended slowly at the beginning and quickly after charging for 40 min, while battery (c) ascended quickly at the beginning and gradually calm after reaching 60 °C. Body temperatures of battery (a), (b) and (c) descended quickly during rest, while ascended slightly during discharge. The reason is that the contact resistance and heat consumption of inner battery increased due to the deterioration of the negative and positive electrode, and it will lead to ascending of battery body temperature.

3.3 X-ray diffraction pattern of both electrodes

Fig. 4 shows the X-ray diffraction patterns for the positive electrodes after 400 and 900 cycles of charge-discharge, respectively. The X-ray diffraction patterns for the positive electrode after the cycle-life test show that the reflections corresponding to γ -NiOOH phase have appeared and the intensity increase with increasing n . This phase is formed under conditions of overcharge, high charging and discharging rates, and high electrolyte concentrations. A 44% volume increase is associated with the formation of this phase, so that it causes the swelling or volume expansion of positive electrode. As a consequence, micro-cracks in the positive electrode appeared, leading to the failure and the decline of capacity of the electrode^[8].

From the X-ray diffraction patterns for the negative electrode after cycle-life test (as shown in Fig. 5), it can be seen that the alloy after degradation still retains the CaCu_5 type structure as the main structure. However, it was found that the intensity of re-

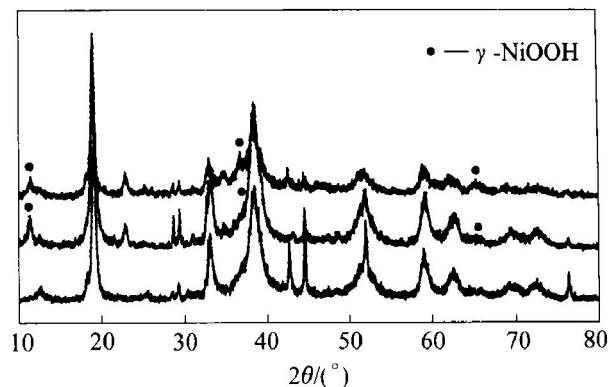


Fig. 4 XRD patterns of positive electrodes after different charging-discharging cycles
1—Before cycle; 2—After 400 cycles; 3—After 900 cycles

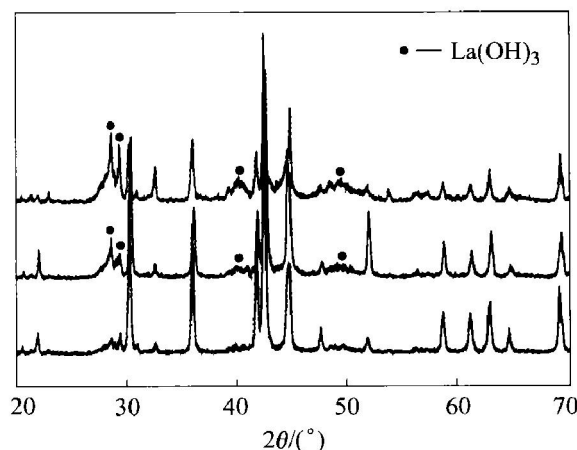


Fig. 5 XRD patterns of negative electrodes after different charging-discharging cycles
1—Before cycle; 2—After 400 cycles; 3—After 900 cycles

flection corresponding to the hydroxides of rare earths (eg $\text{La}(\text{OH})_3$) and the amount of corrosive product increase with increasing n . Since the alloy powder is corroded in the sealed battery, an oxide layer ($\text{M}(\text{OH})_x$) is formed on the surface of the negative electrodes. These compounds may be formed during the discharge step of the main reaction.

The surface of alloy particles plays an important role during the process of hydrogen absorption and desorption. However, hydroxides of rare earths (eg $\text{La}(\text{OH})_3$) formed due to transfer of the low potential of lanthanum. These hydroxides, as insulator phases, are used not only to prevent further corrosion of the negative electrode and increase the cycle-life of the Ni/MH battery, but also to increase the resistance of the electrode and decrease the electrocatalytic activity. This can initiate a deterioration of the charge-discharge performance for Ni/MH batteries^[9, 10].

3.4 Changes of surface morphology and electrolyte of separator

In Ni/MH battery, the separator, often thinner to allow for a larger nickel electrode, must still main-

tain an adequate pore structure for gas transfer and allow for the diffusion of oxygen to the negative electrode at the end of charge. At the same time, the electrolyte contained in separator can influence the formation of the interface of gas, liquid and solid on the surface of the positive and negative electrode. Therefore, it plays an important role in high performance and management of the critical gas reaction in Ni/MH battery beside being a electrolyte reservoirs. The separators of Ni/MH batteries were taken out of the batteries before cycle, after 400 and 900 cycles, respectively and inspected under SEM after washing and drying, respectively. Table 2 lists the variations of the electrolyte contained in separator before and after cycling. And it can be seen that the separator became starved after cycles.

Table 2 Variations of electrolyte contained in batteries before and after cycling (g)

Before cycle	After 400 cycles	After 900 cycles
1.170	0.832	0.182

Size of separator for testing is 18.2 cm × 4.4 cm

Fig. 6 shows the surface morphologies of the separator before cycling, after 400 and 900 cycles of charge-discharge, respectively. The separator fiber is seen to swell and deform, and the holes of the separator become smaller with impurities in it with increasing n . The greater the n and the greater the rate of

discharge are, the more seriously the active material scales off from the electrode is. This can increase the resistance of the separator and block off the diffusion of inner gases in Ni/MH batteries.

4 CONCLUSIONS

1) The expansion of $\text{Ni}(\text{OH})_2$ crystal, pulverization of MH alloy particles and falling off from current collector are identified as the main causes for deterioration of the Ni/MH batteries.

2) The contact resistance of inner battery increases due to the deterioration of the negative and positive electrode, and these changes lead to increasing the temperature of battery electrolyte and damaging the performance of its electrodes and separator.

3) The separator fiber is seen to swell and deform, and the holes of the separator become smaller with impurities in it with increasing charge-discharge cycling. This can increase the resistance of the separator and block off the diffusion of inner gases in Ni/MH batteries.

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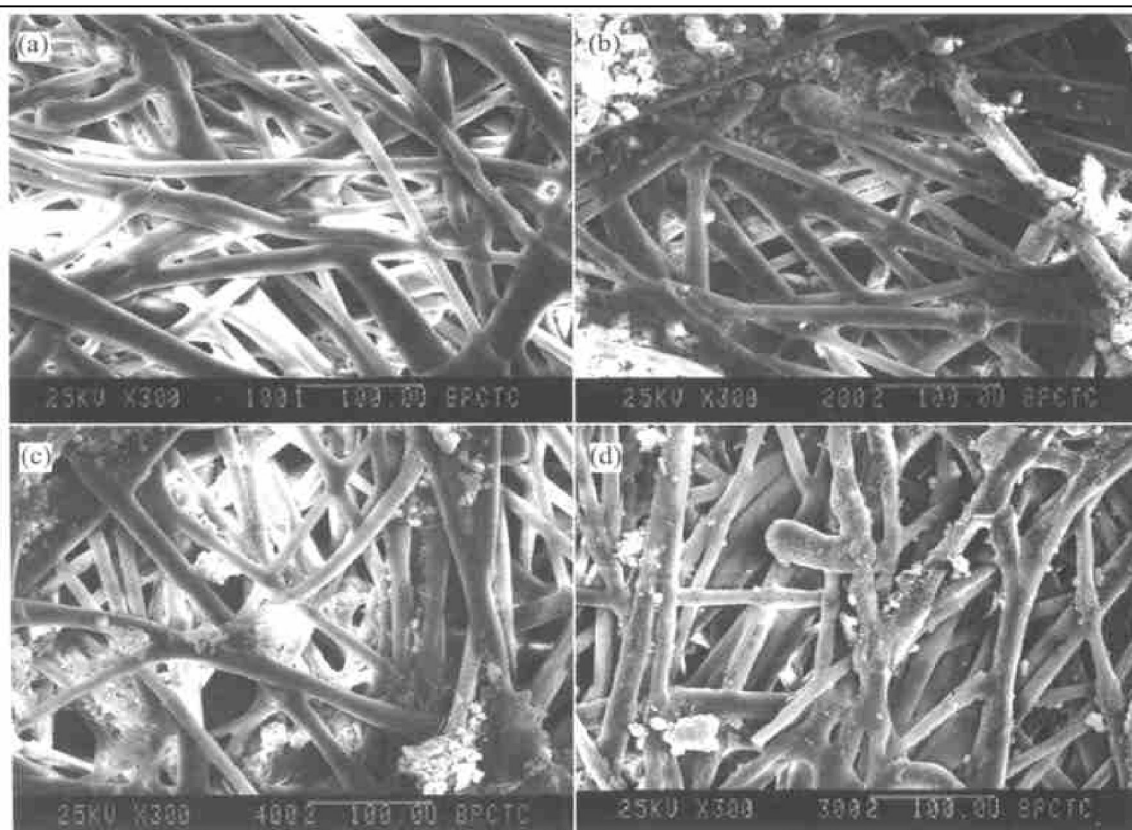


Fig. 6 SEM morphologies of separators before and after cycles
(a) —Original; (b) —Before cycle; (c) —After 400 cycles; (d) —After 900 cycle

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ANNOUNCEMENT

The authors of the article "Mechanism for phase boundary sliding and its relevance to diffusion-solution zone in SPD" published in 《Transactions of Nonferrous Metals Society of China》(2002, 12(5): 952 - 955) and their affiliations are as follows:

SHI Zhī-qiang^{1,2}, YE Yī-fu^{2,3}, LI Shī-chun¹, ZHANG Lei¹

(1. College of Mechanical and Electrical Engineering,

University of Petroleum, Dongying 257061, China;

2. Key Laboratory of Liquid Structure and Heredity of Materials of Ministry of Education,

Shandong University, Jí nan 250061, China;

3. College of Resource and Environment Engineering,

East China University of Science and Technology, Shanghai 200237, China)

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