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# Hot alkaline treatment on hydrogen storage alloys in sealed Ni/MH batteries

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## Abstract

In the production of Ni/MH batteries the activation after sealing process was adopted and the free internal space is closed to the limit margin, which usually results in quality problems, including high internal pressure, electrolyte leakage and short cycle life during the activation and overcharging at high rates. In the present research we have directed our attention to the hot alkaline treatment conditions and the electrochemical properties of the treated Ni/MH batteries using  $AB_5$  or  $AB_2$  alloys as the negative electrodes. It is found that for Ni/MH batteries the hot alkaline treatment can decrease the internal pressure significantly, even when the battery is overcharged at high rates, for example 1 C, and the comprehensive characteristics are improved, especially the durability of Ni/MH batteries. The hot alkaline treatment can also shorten the activation to one single charge and discharge cycle at 0.2 C. The hot alkaline treatment also offers the possibility to provide more internal space for positive and negative electrodes to increase the battery capacity. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Ni/MH battery; Hot alkaline treatment; Internal pressure

## 1. Introduction

It is very important to decrease the internal pressure of a Ni/MH battery in order to improve its characteristics. The first activation process and the overcharge of the battery at high rates generally quickly results in high internal pressure, as the negative electrode relieves hydrogen and the positive electrode relieves oxygen during these processes. The increase of internal pressure results in opening of the safety valve and escape of hydrogen and oxygen, and consequently the drying up of the electrolytes, capacity decay and a short cycle life. In previous technology, Ni/MH batteries usually needed to be charged and discharged at a lower rate several times to attaining maximum capacity. This activation process takes about 60 h for charge and discharge; therefore, it should be shortened.

In order to decrease the internal pressure in Ni/MH batteries effectively, the ability to eliminate oxygen of hydrogen storage alloy during charging should be improved [1]. When the hydrogen storage alloy reacts with the strong alkaline electrolyte, the alloy surface disproportionates into metallic nickel clusters and oxides or hydroxides of the other metallic elements. Oxygen produced

on the positive electrode when overcharged will disperse onto the surface of the negative electrode. Under the catalytic action of the metallic nickel cluster, oxygen will react with hydrogen atom in the hydrogen storage alloy to produce water. At higher temperatures, the alkaline reacts with the alloy more quickly, and thus accelerates the formation of the catalyst layer on the alloy surface and increases its oxygen-elimination ability more quickly [2].

We have also tried two methods of hot alkaline treatment of the hydrogen storage alloy as follows: (1) hot alkaline treatment of the alloy powder; and (2) hot alkaline treatment of the formed electrode in cell after winding.

Process (1) involves washing-up, percolation and drying up, etc. Precautions should be made to avoid the treated alloy powder coming into contact with air at high temperatures, while the electrode is being prepared, but this is difficult in mass production.

In process (2), the mechanical strength of the electrode is decreased, and this increases the possibility of short-circuit, and the control of the precise electrolyte amount is very difficult. At present, an improved production process has been developed and used, in which, after one charge and discharge cycle, the sealed batteries are kept for 1 week at room temperature and 45°C consecutively. The room and low temperature activation process still takes

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16–17 days, so the activation period should be shortened as well.

In this research, the AA-type Ni/MH battery were treated for about 1–24 h at 45–100°C. When the treated battery was charged at 1 A, its maximum internal pressure was obviously much lower. The treated battery thus exhibited higher durability than the untreated. The process improves the comprehensive behavior of Ni/MH battery and enhances economic effects [3,4].

## 2. Experimental details

### 2.1. Preparation of battery

The positive electrode was prepared by applying active material  $\text{Ni}(\text{OH})_2$ , conductive material  $\text{CoO}$  and  $\text{Co}$ , and the binder HPMC, onto a foamed nickel substrate. The negative electrode was prepared by applying type  $\text{AB}_5$  or  $\text{AB}_2$  hydrogen storage alloy and HPMC binder onto a foamed nickel substrate. The type AA battery was assembled by rolling the positive electrode ( $40 \times 80 \times 0.63$  mm, 6.9 g), negative electrode ( $40 \times 110 \times 0.35$  mm, 9.5 g) and a separator with a thickness of 1.6 mm together, and then 2.6 g of 6 N  $\text{KOH} + 0.5$  N  $\text{LiOH}$  electrolyte were injected into the casing, and finally the cell was sealed.

### 2.2. The pretreatment of the battery

The sealed Ni/MH batteries were then treated for 1–24 h at 45–100°C.

### 2.3. The activation and test of battery

#### 2.3.1. One-cycle activation process

The treated battery was charged at 0.1 C for 15 h and discharged at 0.2 C for 4 h, and then charged at 0.3 C for 5 h and discharged at 0.2 C to 1.0 V on a DC-5 C-D Test Instrument (Zhengfang, China).

#### 2.3.2. Four-cycle activation process:

The hot alkaline-treated battery was: firstly charged at 0.1 C for 12 h, and discharged at 0.2 C to 1.0 V; secondly charged at 0.2 C for 6.5 h, and discharged at 0.2 C to 1.0 V; thirdly charged at 0.2 C for 6 h, and discharged at 0.2 C to 1.0 V; fourthly charged at 0.3 C for 4.33 h, and discharged at 0.2 C to 1.0 V; finally charged at 0.3 C for 5 h, and then discharged at 0.2 C to 1.0 V.

For both activation processes (Sections 2.3.1 and 2.3.2), the battery capacities were measured in the last cycle. The internal pressure of the treated battery was measured with an internal pressure-testing instrument [6].

For the cycle life experiment, the treated battery was charged and discharged at 1 A. The cut-off discharge voltage was 1.0 V. The discharge was controlled by  $-\Delta V =$

10 mV. There was no rest time between charge and discharge.

## 3. Results and discussion

It is well known that, on the hydrogen storage alloy surface, there exist metallic nickel clusters and other metal oxides or hydroxides. The metallic nickel clusters are distributed evenly in the metal oxides and hydroxides. The metallic nickel cluster is the catalyst for hydrogen and oxygen combination reaction on the surface of the negative electrode. The oxides and hydroxides are the carriers of the catalyst. Hot alkaline treatment of the alloy can accelerate the formation of the catalyst layer. Our main investigation revealed that, after the heat alkaline treatment of the alloy powder or alloy electrode separately, the catalytic activity of the alloy surface was not as satisfactory as that treated in a sealed battery. The subsequent drying process in air of the separately treated alloy resulted in the oxidation of the metallic nickel clusters. It is very valuable finding that the hot alkaline treatment of the alloy surface in the sealed Ni/MH battery accelerates the formation of the catalyst layer, while avoiding the oxidation of the catalytic nickel clusters at the same time.

### 3.1. Influence of treatment temperature on internal pressure

Fig. 1 shows the internal pressure curves of the batteries at different treatment temperatures. All test batteries are treated for 12 h. In Fig. 1 the internal pressure of the untreated battery rises quickly, but the internal pressure of the treated battery rises slowly and its curve has a plateau. When the treatment temperature exceeds 60°C, the internal pressure has a plateau which is smaller than 1.1 MPa. There was no leakage for all treated batteries.

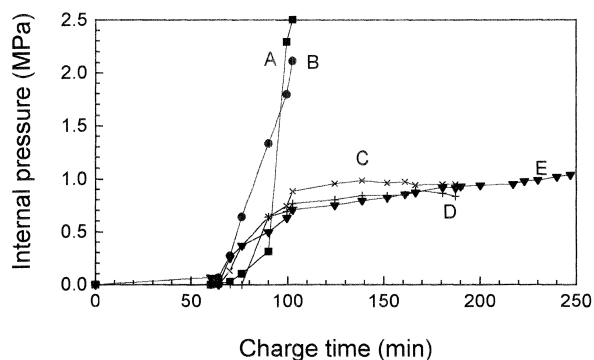


Fig. 1. Effect of treatment temperature on internal pressure ( $I_c = 1$  A). (A) Untreated, (B) 60°C, (C) 80°C, (D) 90°C and (E) 100°C.

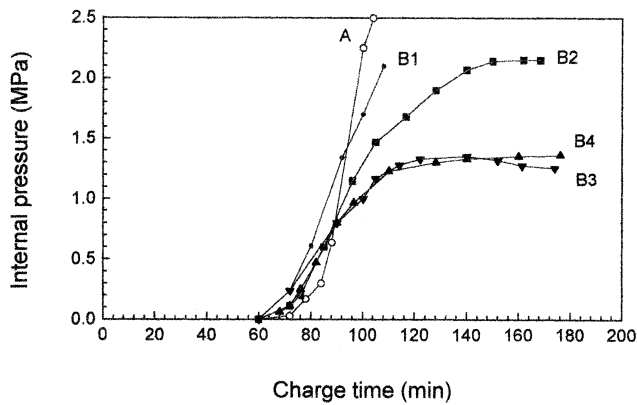


Fig. 2. Internal pressure curves of batteries treated at 60°C for different treatment time ( $I_c=1$  A). (A) Untreated, (B1) 12 h, (B2) 18 h, (B3) 24 h and (B4) 48 h.

### 3.2. Influence of treatment time on internal pressure

Fig. 2 is the internal pressure curves of batteries when treated at 60°C for different treatment times and overcharging at 1 A. For this test, the four-cycle activation process is adopted. It shows that the internal pressure of the untreated battery rises quickly, but the internal pressures of the treated batteries rise slowly and have a plateau of internal pressure. The 24-h treated battery shows the lowest plateau.

Fig. 3 is the internal pressure curves of batteries treated at 80°C for different treatment times and with the cell overcharged at 1 A. In this test, the one-cycle activation process is adopted. It shows that the internal pressure of the untreated battery rises quickly, but the internal pressures of the treated batteries rise slowly and have a plateau like those in Fig. 2. A plateau will appear when the treatment time is increased to 4 h. The plateau of the 12-h

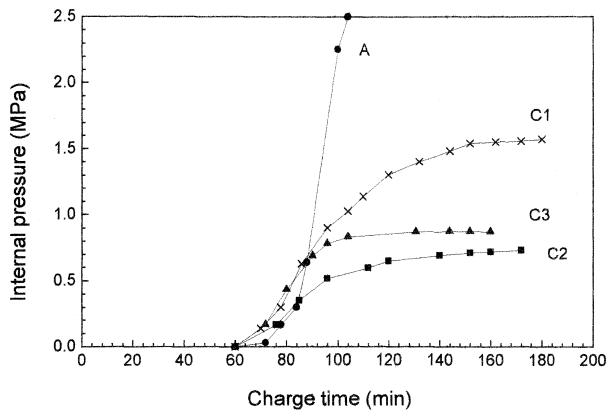


Fig. 3. Internal pressure curves of batteries treated at 80°C for different treatment times ( $I_c=1$  A). (A) Untreated, (C1) 4 h, (C2) 12 h and (C3) 24 h.

treated batteries is the lowest and their internal pressure is only 0.75 MPa. In the experiment with the one-cycle activation process, the activated capacity of the type AA battery reaches 1200–1250 mAh. Compared with the four-cycle activation process, the activation time has been shortened to less than 60%.

### 3.3. Influence of heat treatment on capacity and durability

The four-cycle activation process is adopted for the 12-h treated batteries at different temperatures. The capacity curves of the first one to five charge and discharge cycles are shown in Fig. 4. The capacity of the treated batteries is about 4% less than that of the untreated ones. The loss of capacity is believed to be due to the corrosion of the alloy by the strong alkaline electrolyte solution. The cycle life curves of the treated and the untreated batteries are plotted in Fig. 5. In the experiment, a higher rate and no rest time are used in order to investigate the behavior of the batteries under very disadvantageous conditions. In this experiment, the treated batteries exhibit better durability, in spite of the initial capacity of the treated batteries being 4% lower than the untreated ones. The crossover point of the two cycle life curves is at the 15th cycle. The 50th cycle discharge curve of the treated battery has a midpoint voltage of about 60 mV higher than that of the untreated one. For the treated battery, the part of the discharge curves over 1.2 V is 72.5% of discharge capacity, while for the untreated one that portion is 33.3% only.

It is found that heat pretreatment decreases the internal pressure significantly when the Ni/MH battery is overcharged at high rates, because the heat pretreatment can produce quickly enough nickel clusters to catalyze the oxygen-eliminating reaction. The internal pressure is lowered by the highest ability of eliminating oxygen of the

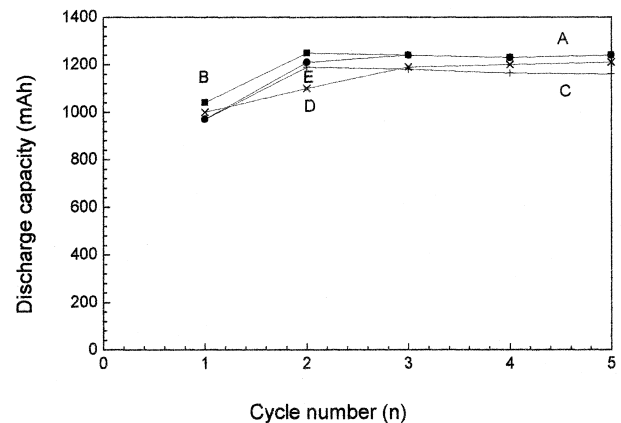


Fig. 4. Curves of capacity to cycle number of batteries treated at different temperatures. (A) Untreated, (B) 60°C, (C) 80°C, (D) 90°C and (E) 100°C.

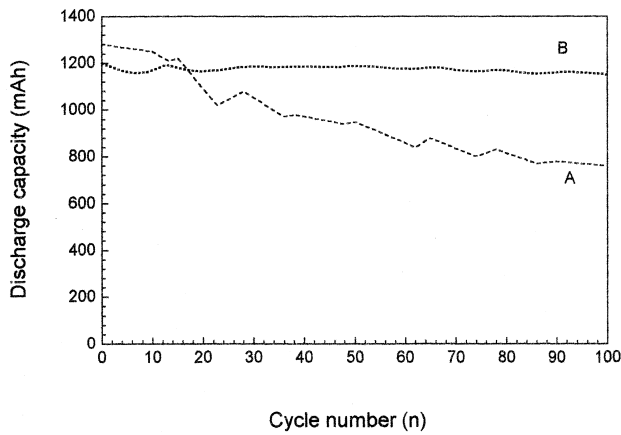


Fig. 5. Cycle life curves of treated and untreated batteries at 1 A. (A) Untreated, (B) treated (80°C, 12 h).

hydrogen storage alloy. The alloy surface of the negative electrode reacts with strong alkaline electrolyte solution and disproportionates into metallic nickel clusters and oxides and hydroxides of other metallic elements. Higher temperatures generally accelerate the reaction rate and form a thicker catalyst layer. Oxygen produced by the positive electrode when the battery is overcharged is dispersed to the negative electrode, where it reacts with hydrogen atoms in hydrogen storage alloys and produces water under the catalyst action of the metallic nickel clusters. So the heat pretreatment obviously decreases internal pressure when the battery is overcharged. Although the strong alkaline electrolyte solution would react with the alloy at the room temperature, the reaction is much slower than the reaction in heat treatment. Fig. 6 shows the internal pressure curves of type AA batteries after the four-cycle activation process and 2 months storage. This curve is similar to the one treated for 12 h at 60°C. We believe conjecture that the higher treatment temperature accelerates the reaction rate of strong alkaline

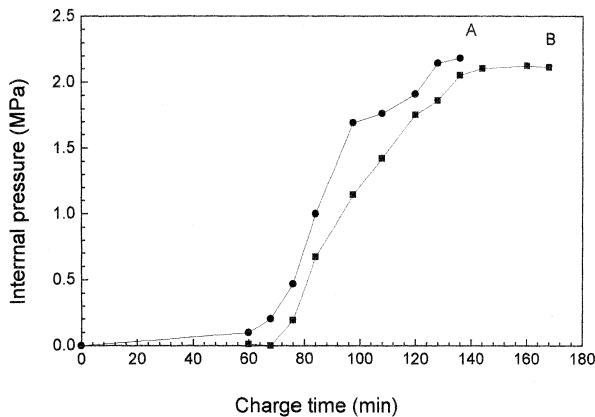


Fig. 6. Internal pressure curves of treated and untreated batteries. (A) Untreated (stored for 2 months at room temperature) and (B) treated (60°C, 12 h).

electrolyte solution with the alloy. The reaction rate is increased over 100 times that at room temperature.

### 3.4. Pretreatment of Ni/MH batteries using $AB_2$ alloy

The above-mentioned research shows that heat treatment of Ni/MH batteries using type  $AB_5$  alloy as the negative electrode improves its comprehensive characteristics significantly. Ni/MH batteries using type  $AB_2$  alloys suffers more from higher internal pressure, electrolyte and gas leakage, capacity degeneration, shorter cycle life during initial activation and charging at high rates, because the type  $AB_2$  alloy is more difficult when active and has worse kinetic characteristics than type  $AB_5$  alloy. It is found that, for Ni/MH batteries with type  $AB_2$  alloy as the negative electrode, hot alkaline treatment can also improves its durability significantly.

Previously, a type  $AB_2$  alloy with a dendrite-free structure was prepared and its electrochemical properties investigated [5,6]. The alloy shows not only higher capacity and better durability, but also easier activation and better kinetics than those of the other common type  $AB_2$  alloys [7,8], so the type  $AB_2$   $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.5}$  alloy with dendrite-free structure is used for investigating the applicability of the heat pretreatment process in Ni/MH batteries with type  $AB_2$  alloy as the negative electrodes. For comparison, the type  $AB_2$   $Zr-Ti-V-Ni-Cr-Mn$  alloy with dendrite structure is used to prepare Ni/MH batteries and to test the heat pretreatment effect at the same time. In Fig. 7 the performance of test batteries using  $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.5}$  alloy as electrode is illustrated (T0, untreated; T1, treated for 3 h at 80°C; T2, treated for 12 h at 80°C; T3, treated for 23.5 h at 80°C and then for 0.5 h at 120°C). At first T1 and T0 batteries have the same capacity, but after 115 cycles the capacity of the T0 battery is decreased by 12.6%, and the T1 battery is decreased by only 3.1%. ESCA results show that the oxide layers of the alloy surface of the T2 and T3 batteries are, respectively, 1.8 and 2.7 times thicker than that of the T1 battery.

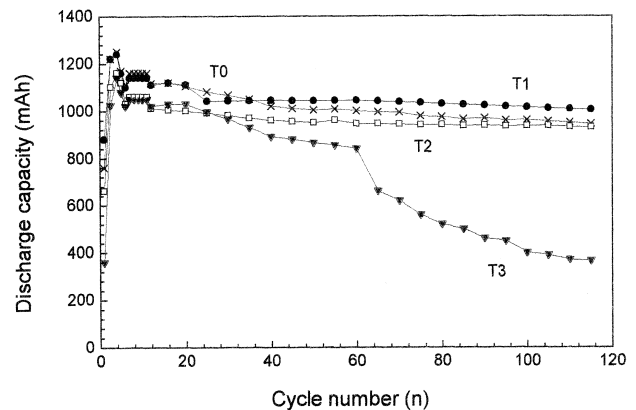


Fig. 7. Comparison of cycle life curves of treated and untreated batteries using  $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.5}$  alloy ( $I_c=1$  A,  $t_c=1.6$  h,  $I_d=1$  A,  $V_c=1.0$  V).

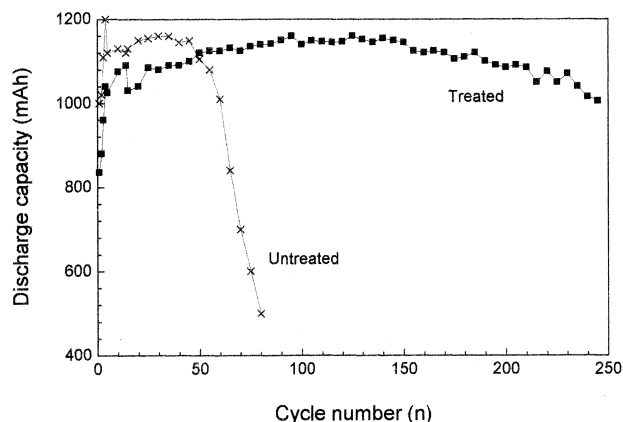


Fig. 8. Comparison of the cycle life curves of the treated and untreated batteries using Zr–Ti–V–Ni–Cr–Mn alloy ( $I_c=1$  A,  $t_c=1.6$  h,  $I_d=1$  A,  $V_e=1.0$  V).

Longer treatment times and higher treatment temperatures result in too thick oxide layer, too high resistance and too high internal pressure, and cause the electrolyte solution to dry up easily and the battery durability is worse. In Fig. 8 the treated battery exhibits better durability than the untreated battery. In the first 60 cycles the discharge capacity of the treated battery increases gradually. In the 40th cycle the charge voltage of the treated battery is 60 mV lower than the untreated one. From the 60th cycle the discharge capacity of the untreated battery decreases quickly, but the discharge capacity of the treated one keeps increasing slowly.

#### 4. Conclusions

In conclusion, hot alkaline treatment can decrease the internal pressure significantly when Ni/MH batteries of

both  $AB_5$  and  $AB_2$  alloys are overcharged at high rates. The comprehensive characteristics, especially the durability of the treated Ni/MH battery are improved strikingly. The hot alkaline treatment can shorten activation time to one single charge and discharge cycle at 0.2 C. The hot alkaline treatment also provides the possibility to provide more internal space to the positive electrode and the negative electrode to increase the battery capacity.

#### Acknowledgements

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