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Preparation of an improved positive electrode and its application in Ni/MH batteries☆

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Abstract

The capacity of Ni/MH batteries depends on the specific capacity of the positive electrode and the utilization of active material because of the positive electrode capacity limitation. The present study is engaged in enhancing the specific capacity of the $Ni(OH)_2$ electrode and the utilization of the active material. $Ni(OH)_2$ or NiOOH in the positive electrode is a semiconductor, which is different from the conductive active material (hydrogen storage alloys) of the negative electrode. In this research a new process has been developed to prepare positive electrodes with excellent electrochemical characteristics. The process consists of the positive electrode being despumated, and then coated with conductive metallic materials on the surface. The new positive electrode exhibits a better collective current effect, higher specific capacity and higher utilization of the active material. The new process comprehensively improves the characteristics of the Ni/MH battery, especially concerning the battery capacity and discharge capacity at high rates. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Positive electrode; Positive electrode improvement

1. Introduction

Since some researchers in the Phillips Research Laboratory solved the problems of the capacity attenuation of type-AB_5 hydrogen storage alloy in the process of charge and discharge, in 1984, the type-AB_5 alloys have been widely used to make Ni/MH batteries [1]. For nearly ten years, the hydrogen storage alloy material, as a kind of negative electrode material, has made great progress in the area of research and development [2–4].

A historical review indicated that the enhancement of the overall performance of nickel–metal hydride batteries often began with improvement in the performance of the negative electrodes, including improvement on the alloy composition [5–7], additives [8], wrapped micro-structure [5,9], and the modification of surfaces [10] of the negative electrodes. All these have made contributions to the improvement of the performance of Ni/MH batteries. However, it is well known that the capacity of Ni/MH batteries depends on the capacity of the positive electrode according to the principle of the rechargeable battery. The capacity of the positive electrode depends on not only the mass of active material in the positive electrode but also on the specific capacity of the positive electrode and the utilization of the active material. The active material $Ni(OH)_2$, a semiconductor material, is different from the conductive hydrogen storage alloy of the negative electrode in Ni/MH batteries. So, enhancement of the utilization of the active material in the battery is very important for improvement of the conductivity and collectivity of the positive electrode.

This article is aimed at clarifying a method for the improvement of the positive electrode on the basis of an optimized negative electrode. The process enhanced utilization of the active material and increased conductivity of the positive electrode improved the overall characteristics of the Ni/MH battery effectively [11].

2. Experimental details

The experiment was carried out according to the following procedure: the improved positive electrode was prepared with a paste and a porous foamed nickel substrate. The paste consisted of the active material $Ni(OH)_2$, the conductor agent powder of Co and CoO, the binder HPMC and water. The paste was filled into its substrate, followed

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Table 1
Four-cycle activation process

Cycle	Charge rate(C)	Charge time(h)	Discharge rate(C)	Cut-off voltage(V)
1	0.1	12	0.2	1.0
2	0.2	6.5	0.2	1.0
3	0.2	6.0	0.2	1.0
4	0.3	4.3	0.2	1.0

by drying at 60°C for 2 h. Then the positive electrode is despumated at its surface, followed by coating with a conductive powder (Ni, Cu, Co etc.) and pressing to fixed thickness. The improved positive electrode was assembled into a battery with MH foamed nickel substrate as the negative electrode. The type-AA test battery was injected with 2.6 g of 6 M KOH+0.5 M LiOH electrolyte solution before sealing. The ratio of the capacity of positive and negative electrodes was about 1:1.3. The sealed test battery was heat treated at 80°C for 12 h. After the test battery was cold, the follow-up was a four-cycle activation process, see Table 1.

In the cycle life experiment the test battery was charged and discharged at 1 C. The cut-off voltage of discharge was 1.0 V. The charge time was controlled by $-\Delta V=10$ mV. There was no rest time between charge and discharge.

3. Results and discussions

In the positive electrode the lower value oxidizing state $Ni(OH)_2$ and the higher value oxidizing state NiOOH are both semiconductors, so the conductive agent Co and CoO should be added into the paste to improve its conductivity. All forms of Co is an electrical conductor, not only metallic Co, but also it's lower value oxidizing state CoO, $Co(OH)_2$ and the higher value oxidizing state CoOOH, but adding Co cannot solve all the problems. It is well known that during the charge and discharge process of the positive electrode, the electrode is expanding and shrinking, which induce its lower mechanical strength, higher electric resistance and capacity degeneration. In order to avoid the above shortcomings, the surface of the positive electrode was despumated, and then coated with a conductive metallic material (thickness of about 0.01 mm), then pressed to form the improved positive electrode. This process makes the active material and the conductive coating material contact with each other very tight. Finally, the improved positive electrode was assembled with the negative electrode to make a type-AA improved Ni/MH test battery.

3.1. Capacity

Figs. 1 and 2 show the discharge curves and the charge curves of the type-AA improved battery at 0.29 A and 0.58 A, respectively. The capacity of the improved battery was about 1400 mAh. According to a calculation based on the discharge curves in Fig. 2, the specific energy of the Ni/MH battery is up to 69 Wh/kg. The utilization of the active material of the foamed nickel positive electrode is increased from 83% to 93%.

Figs. 3 and 4 show the discharge and the charge curves of the type-AA improved batteries at 1.45 A. The discharge capacity of the improved battery at the high rate is above 1200 mAh. It can be seen that the improved battery shows excellent discharging characteristics which are different from the original one.

3.2. Durability

Fig. 5 shows the comparison of the cycle life curves of the improved batteries and the original batteries at 1.2 A using $-\Delta V=10$ mV protection. The improved batteries exhibit satisfactory durability. It can be seen that the two discharge capacities at 1.2 A are very different. The improved batteries had a higher and more stable discharge capacity. Their ohmic resistance was measured and for the improved battery it was 19 mΩ, but for the original one it was about 27 mΩ.

3.3. Discharge properties at high rate and low temperature

Fig. 6 shows the comparison of the discharge curves of improved batteries and original batteries at 3 C. At a higher discharge rate the improved batteries exhibited a higher discharge capacity than that of the original one.

Fig. 7 shows the discharge curves of the improved

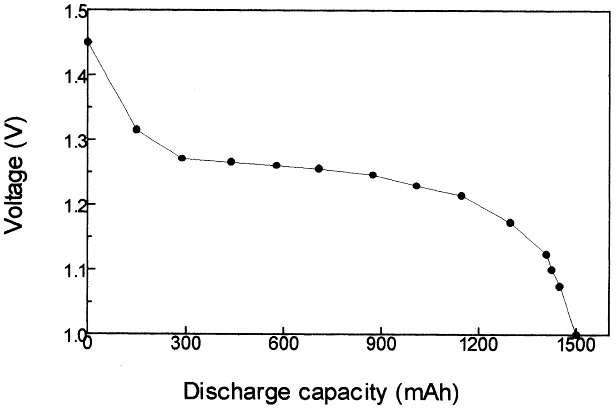

Fig. 1. The discharge curve of the type-AA improved battery at 0.29 A.

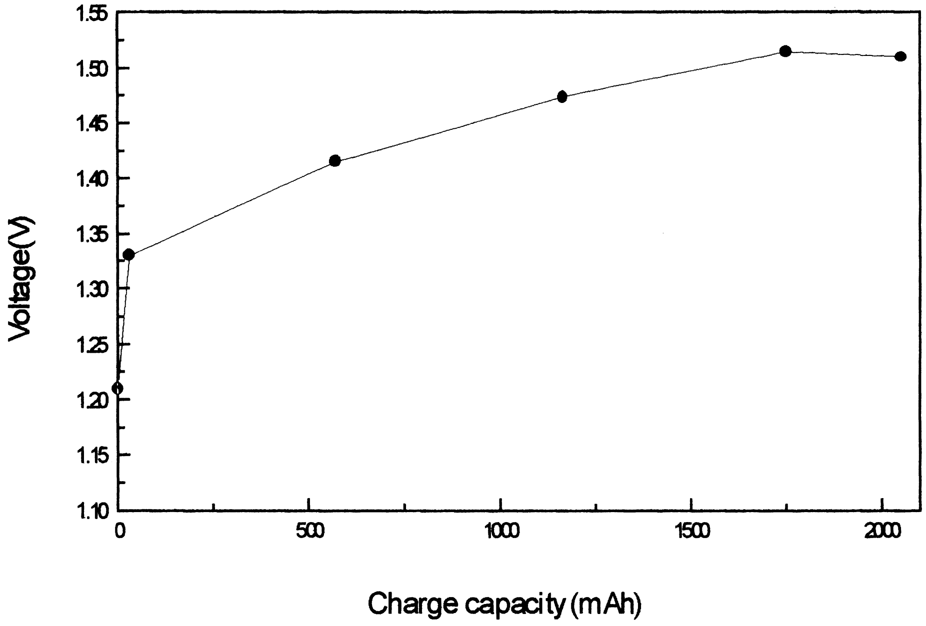

Fig. 2. The charge curve of the type-AA improved battery at 0.58 A.

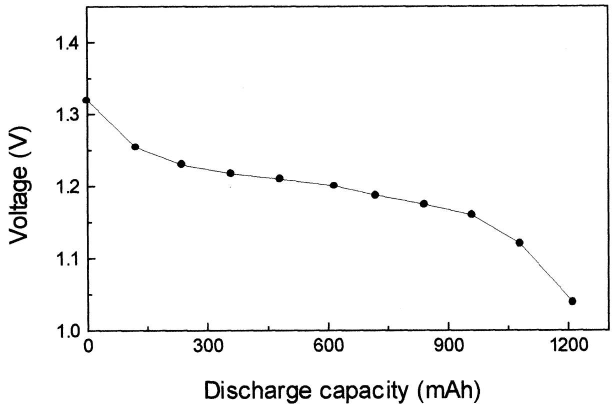

Fig. 3. The discharge curve of the type-AA improved battery at 1.45 A.

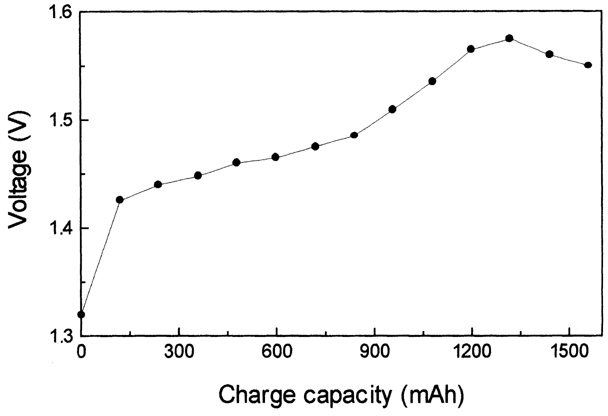

Fig. 4. The charge curve of the type-AA improved batteries at 1.45 A.

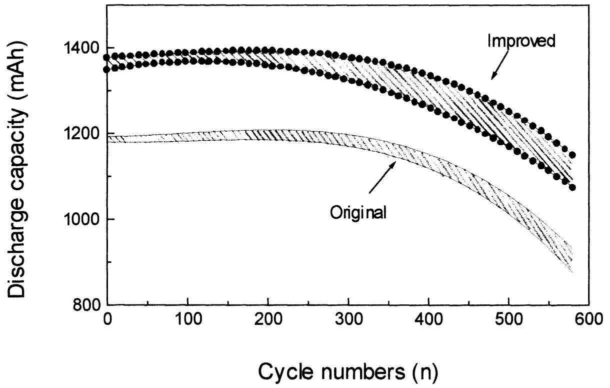

Fig. 5. The comparison of the cycle life curves of the improved and original batteries at 1.2 A.

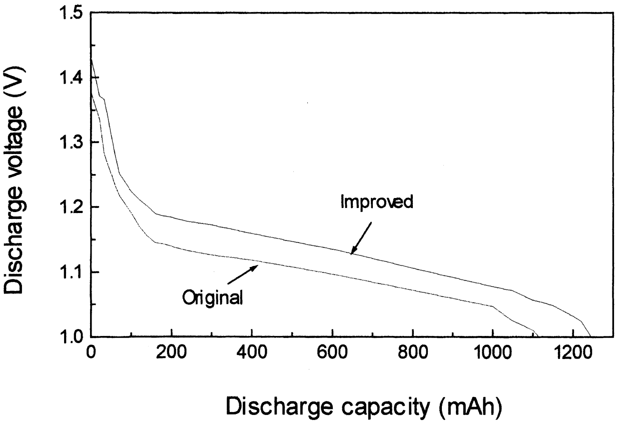

Fig. 6. The comparison of the discharge curves of the improved and original batteries at 3 C.

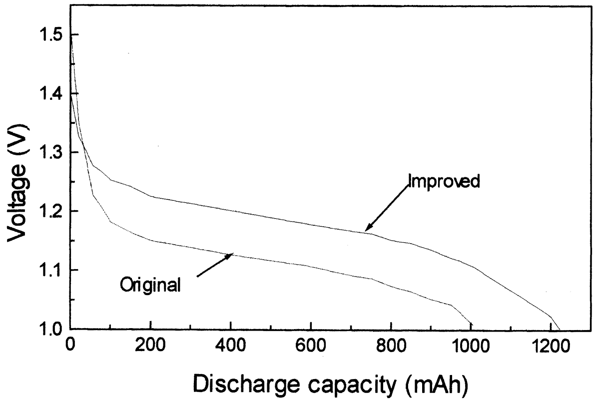

Fig. 7. The comparison of the discharge curves of the improved and original batteries at 1 C and −18°C.

batteries and original batteries at 1 C and −18°C. The result clearly shows that the improved positive electrode exhibited much higher low temperature discharge ability and better characteristics than the original positive electrode.

3.4. Charge retention

Fig. 8 shows the comparison of the discharging curves of the improved and original batteries at 0.2 C after having been kept for 28 days at room temperature. The improved positive electrode showed better charge retention than the original electrode.

A further detailed inspection of the 60 pieces of the type-AA improved battery by the Quality Supervision & Inspection Center for Chemical & Physical Power Source of the Ministry of Electronics Industry of China, including inspection of shape and size, weight (actual measurement), discharging at 20°C or −18°C (at 0.2 C, 1 C, 3 C, 5 C respectively), charge retention ability, overcharging, mechanical performance, safety valve performance, cycle life etc. was performed. The inspection showed that the improved positive electrode was the direct cause for the high performance of Ni/MH batteries. The performance of the improved batteries reached: at 20°C and 0.2 C the capacity was 1402 mAh; after shocking as required, the capacity at 0.2 C was 1395.8 mAh; at 20°C the discharge capacities at 1 C, 3 C and 5 C was 1357.5, 1380 and 1400 mAh; at −18°C the discharge capacities at 0.2 C and 1 C was 1329 and 1280 mAh respectively; the charge retention after 28 days being 79%; after being continually charged at 0.1 C for 28 days and discharged at 0.2 C to 1.0 V, the capacity of the improved battery was 1597 mAh and no leakage was detected. The improved battery was charged at 1 C for 1.25 h, with no −ΔV control protection, then discharged to 1.0 V at 1 C immediately. For 100 cycles, the improved battery could still function properly.

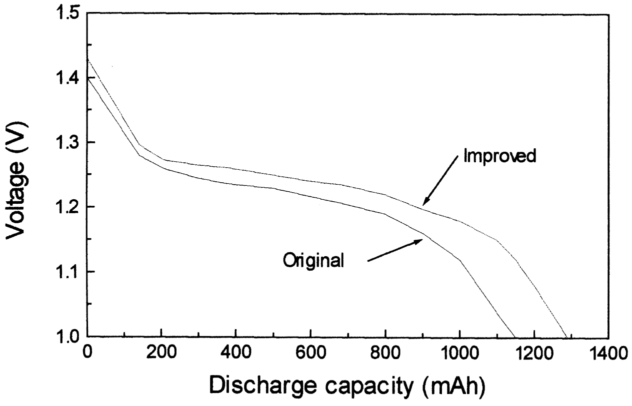

Fig. 8. The comparison of the discharging curves of the improved and original batteries at 0.2 C after having being kept for 28 days at room temperature.

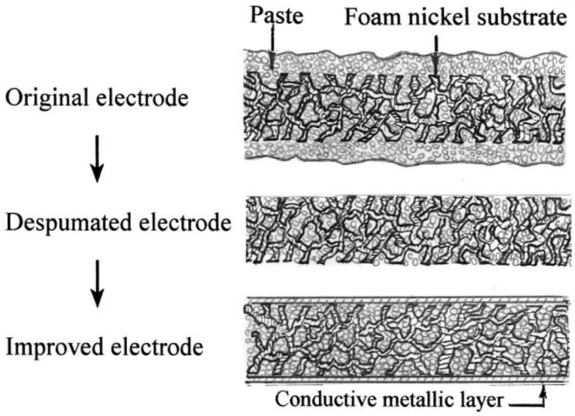

Fig. 9. The schematic diagrams of the improved and original positive electrodes.

3.5. Discussion

Fig. 9 shows the schematic diagrams of the improved and the original positive electrodes. After despumating and coating treatment, the floating paste on the electrode surface was removed, and a conductive metallic layer covered the wholly exposed surface of the foamed nickel. So, the utilization of the positive active material has been increased and the overall characteristics of the Ni/MH battery has been improved significantly.

4. Conclusions

The surface of the foamed nickel positive electrode was despumated and coated with conductive materials to increase the collective current effect, the utilization of the active material and the specific capacity of the positive electrode, which led to the performance improvement of the battery in many aspects. The improved batteries exhibited higher capacity, including higher discharge capacities at high rates, better durability, better low-temperature discharge ability and much better charge retention characteristics.

References

[1] J.J.G. Willems, J. Phillip, Res. Suppl. 39 (1) (1984) 1.
[2] T. Sakai et al., J. Electro. Chem. Soc. 134 (1987) 558.
[3] T. Sakai et al., J. Alloys Comp. 192 (1993) 155.
[4] A.H. Boonstra, T.M.N. Bermards, J. Less-Common Met. 161 (1990) 245.
[5] T. Sakai, J. Electro. Chem. Soc. 3 (1987) 137.
[6] J.J.G. Willems, J. Less-Common Met. 129 (1987) 13.
[7] Y.S. Zhang et al., CN 1 076 313
[8] H. Inowe et al., J. Electro. Chem. Soc. 143 (1996) 2527.
[9] Y.S. Zhang et al., J. Less-Common Met. 190 (1992) 137.
[10] K. Ikawa et al., Electrochem 62 (9) (1994) 822.
[11] D.Y. Yan, J.G. Wang, Chinese Patent, 97120114.5