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Preparation and properties of no-binder electrode Ni/MH battery[☆]

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Abstract

Generally, while the electrodes of an Ni/MH battery are manufactured, binders are universally used. Although the binder can improve the strength of the electrodes and the durability of the battery, the disadvantages are obvious: higher internal resistance and polarization when the battery is being charged and discharged, lower discharge capacity, higher internal pressure and longer activation time. So the amount of binders should be controlled to a low level. Our investigations show that it is more advantageous to abandon binders while manufacturing electrodes. The bare active particles are more available to the electrochemical reaction in the positive and negative electrodes. In this study no-binder electrodes were prepared by smearing active materials into the nickel foam and then high-pressure rolling. The properties of the battery assembled by these electrodes were improved significantly. For example, for the first activation cycle the discharge capacity of a type-AA battery reached 1400 mAh. The discharge capacity at 1C was above 1300 mAh and the portion of plateau above 1.2 V during discharging was more than 70%. Its durability was more than 500 cycles.

Keywords: No-binder electrode; High rate; Ni/MH battery

1. Introduction

With the increasing demand for portable electronic devices and the improvement of our living environment, the development of 'green batteries' becomes more and more important. The nickel/metal hydride battery (Ni/MH) is a new type of green battery which, developed in the 1980's, has a high specific capacity, high discharge capacity, high discharge rate, long cycle life, no pollution and no memory effect. In the first half of 1998 the production output increased to about 150% of that in the same period of 1997 in Japan. For a continuing growth of the Ni/MH market share it is important to improve the properties of the batteries. In the research on Ni/MH batteries, attention has been focused on the metal hydride electrodes, especially on the preparation, performance and surface properties of the active materials. However, if the performance of the battery needs further improvement, more studies should be directed on both the negative and the positive electrodes.

Generally, while the electrodes of Ni/MH batteries are being manufactured by either on job lot basis or on production lines, some binder is universally used, such as HPMC, PVA, CMC, etc.. They can improve the strength of the electrodes and the durability of the battery, but lead to some disadvantages because all these binders are insulators. It is reported that a method of abandoning binders to manufacture electrodes had been developed by Z. Ye [1]. In this paper, the preparation and the performance of Ni/MH battery with no-binder electrode are discussed in detail [2,3].

2. Experimental details

2.1. Preparation of positive electrodes

The foam nickel substrates are cut into a required size, and pre-rolled, then immersed into distilled water. In order to manufacture no-binder batteries, the key point of the method is to prevent active materials from dropping from the electrodes. Therefore, 60-ton high-pressure rolling is needed to ensure the electrode strength. Firstly, $Ni(OH)_2$, Co and CoO are mixed together. Afterwards, the foam nickel substrates are taken out from the water bath and the aforesaid mixture is smeared into it. The mass of active material of the positive electrode is controlled at the total

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wet weight of $0.295 \pm 0.001 g/cm^2$. In the end, the electrodes are dried at room temperature and then rolled to a thickness of 0.62–0.63 mm [2].

2.2. Preparation of negative electrodes

The foam nickel substrates are cut into a required size, and pre-rolled, then immersed in distilled water. At the same time, type-AB_5 hydrogen storage alloy $Mm(NiCoMnAl)_x$ and some conductors are mixed together. Afterwards, the foam nickel substrates are taken out from the water bath and the aforesaid mixture is smeared into it. The mass of active material of the negative electrode is controlled at the total wet weight of $0.245 \pm 0.001 g/cm^2$. In the end, the electrodes are dried at room temperature and then rolled to a thickness of 0.32–0.33 mm [3].

2.3. Assemblage and test of batteries

Group A batteries (type-AA) are assembled with no-binder positive and negative electrodes. Group B batteries (type-AA) are assembled with positive and negative electrodes fabricated with binder. Batteries A and B are both tested at room temperature and $-18°C$. The instruments and facilities used include an internal resistance measurement instrument, an internal pressure measurement instrument [4], DC-5 testing instrument, etc.. Battery A is heat treated at 80°C for 12 h before the cycle life experiment.

3. Results and discussion

3.1. In a Ni/MH battery the electrode reactions Eqs. 1–3 are solid-state intercalative reactions of hydrogen

When the cell is charged, hydrogen leaves $Ni(OH)_2$ to form a water molecule with an OH^- ion from the electrolyte. On the surface of the MH electrode another water molecule is decomposed and a hydrogen atom is intercalated and stored in the MH electrode. When the cell is discharged, the process is reversed.

$$\text{Positive} \quad Ni(OH)_2 + OH^- = NiOOH + H_2O + e^- \quad (E_0 = 0.490V \text{ vs. Hg/HgO}) \tag{1}$$

$$\text{Negative} \quad M + H_2O + e^- = MH + OH^- \quad (E_0 = -0.828V \text{ vs. Hg/HgO}) \tag{2}$$

$$\text{Total} \quad Ni(OH)_2 + M = NiOOH + MH \quad (E_0 = 1.318V) \tag{3}$$

For the high-rate electrochemical reaction of $Ni(OH)_2$ electrodes, proton transport is the controlling step, and in the abovementioned reaction of negative electrodes the hydrogen diffusion is the controlling step, which is well known and proven by our experiments. The conductivity of the electrodes is also very important. Being insulators, the binders markedly decrease the electrode conductivity, not only that of the semiconductor NiOOH electrode but also that of the conductor MH electrode. This effects the properties of the battery. On the contrary, in no-binder batteries, not being tied by the binders, the bare active material particles are easier for hydrogen and electron movement and hence more beneficial to the electrochemical reactions. So, no-binder batteries have higher conductivity and comprehensive properties.

3.2. Internal resistance

Table 1 is the internal resistance of batteries A and B. It can be seen that the internal resistance of group A batteries is all in the range of 16–17 mΩ, but that of group B batteries exceeds 20 mΩ. The total resistance of a battery consists of ohmic resistance and polarization resistance, with the ohmic resistance including the resistance of the electrodes, materials, electrolyte, separator and the contact resistance between these. The electrolyte and separator are the same for battery A and B. Only the electrode is different. For battery A, the bare active material particles are easier for hydrogen and electron movement, therefore, its ohmic resistance is smaller. Additionally, the polarization resistance of battery A is also smaller than battery B due to its higher conductivity, see Section 3.4. As the amount of binder used is rather small, the resistance difference of battery A and B is not very large, even so, many properties of battery A are better than those of battery B.

3.3. Activation

Fig. 1 shows the first activation curves of battery A and B (charged for 16 h at 0.1C, discharged at 0.2C to 1.0 V). It shows that during charging, polarization of battery B is much larger than that of battery A, which is caused by the binder. It shows also that the charge curves are quite different. In the beginning, the battery A charge curve is much lower than that of the battery B. The beginning V-shaped curve of battery A can be explained by more and more electrolyte being soaked onto the particle surface of active materials. Bigger electrochemical surface decreases the electrode polarization. For battery B, the binder causes bigger electrode polarization and prevents the soaking of electrolyte on all particle surfaces. As charge continues, the battery A charge curve stays lower than that of battery B. Generally at 1.45 V, oxygen is evolved at the NiOOH

Table 1
The internal resistance (mΩ)

	#1	#2	#3	#4
Battery A	16.6	16.4	16.0	16.8
Battery B	23.2	25.6	24.1	22.3

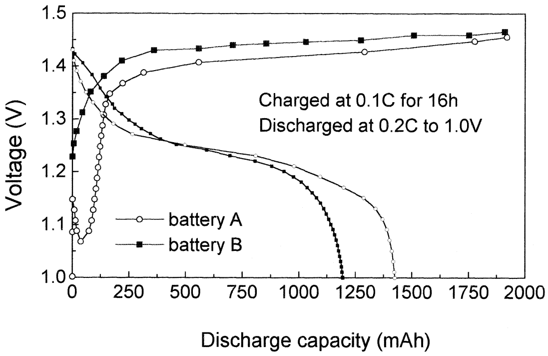

Fig. 1. The first activation charge/discharge curves of battery A and B at room temperature.

electrode and reacts with hydrogen from the hydrogen storage alloy in the MH electrode. Here the reaction is at low rate and the heat effect is so little that $-\Delta V$ does not appear for both batteries. It also can be seen that the first activation capacity of battery A is more than 1400 mAh and the portion of plateau above 1.2 V is about 74%, but for battery B, those are respectively 1200 mAh and 70%. All this means that the no-binder batteries can be activated more easily than the binder-included batteries. The alkaline solution can be more easily soaked into the entire surface of active material particles to form a solid–liquid–gas three-phase interface that is needed for electrochemical reactions. The no-binder battery gives high capacity and shows complete activation at the first charge and discharge cycle.

3.4. Discharge capacity at high rate

Fig. 2 is the high rate charge and discharge curves of battery A and B (charged for 1.25 h at 1C, $-\Delta V=10$ mV, discharged to 1.0 V at 1C). It can be seen that at this higher charge rate the battery polarization of battery B is 25 mV higher than that of battery A. Battery B reaches its charge-end earlier. The 1C discharge capacity of A is above 1300 mAh and the portion of plateau above 1.2 V is 70%, while those of battery B are respectively 1150 mAh and 65%. The high rate discharge property of no-binder battery A is better than that of binder-included battery B. As mentioned above for battery B, besides the ohmic resistance, the polarization resistance was much higher than that of battery A when they were charged and discharged at high rates. The large polarization that mainly resulted from electrochemical polarization decreases the charge and discharge efficiency, leads to a lower discharge capacity. This shows that for no-binder battery A, a large reaction surface of active particles and lower internal resistance are beneficial to the electrochemical reaction and comprehensive properties of Ni/MH battery.

3.5. Low temperature property

Fig. 3 shows the discharge curves of battery A and B at 0.2 C and −18°C. The battery was charged at the room temperature and 0.2C and rested for 6 h. In the meantime the temperature of the cell was lowered to −18°C. Although the increased internal resistance at the low temperature significantly reduced the capacity of battery A from 1400 mAh at room temperature to 1230 mAh, it (1230 mAh) is still larger than that of battery B (1080 mAh). This can also be attributed to the higher conductivity of battery A. Battery A exhibits higher specific power, because of its 0.2 V higher discharge voltage than battery B.

3.6. Durability

Fig. 4 is the cycle life curve of battery A (charged for 1.25 h at 1C, $-\Delta V=10$ mV, and discharged to 1.0 V at 1C). It shows that the no-binder battery has good durability reaching more than 500 cycles, as demanded by commerce. For battery A, a 12-h heat treatment process is to improve the battery durability. The heat treatment causes an oxide layer on the alloy surface of negative electrode. The oxide layer is the carrier of the catalyst nickel cluster. During charge and discharge, the oxide layer becomes loose and beneficial for the catalytic reaction of the nickel cluster in electrochemical reaction 2, so the discharge capacity increases after a little decrease. The loss of cycle

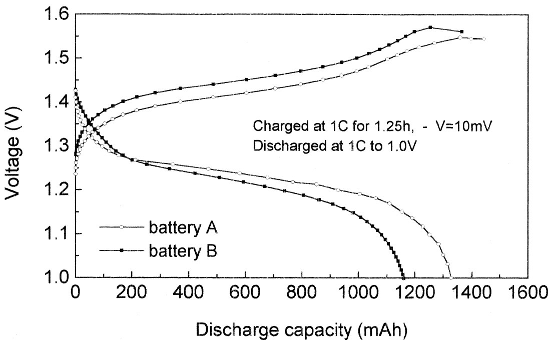

Fig. 2. The charge and discharge curves of battery A and B at high rate and room temperature.

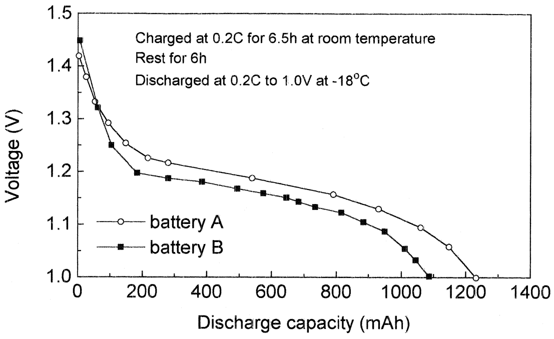

Fig. 3. The discharge curves of battery A and B at −18°C.

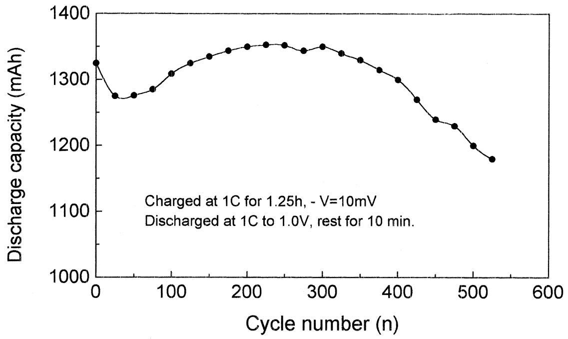

Fig. 4. The cycle life curve of battery A at room temperature.

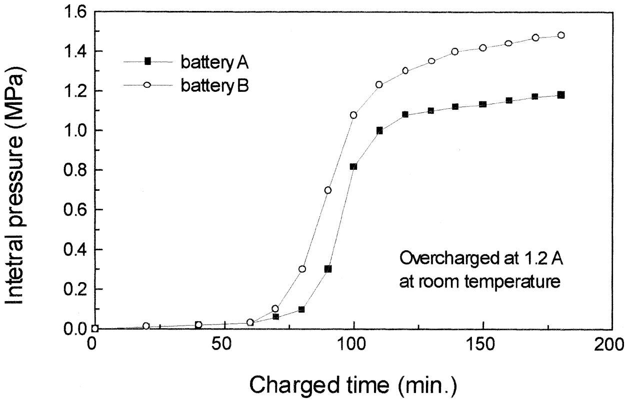

Fig. 5. The internal pressure curves of battery A and B.

life is usually caused by a loss of the electrolyte. In battery A overcharge, the bare hydrogen storage alloy particle gave more alloy surface to take part in oxygen consumption and water formation reactions. The internal pressure of battery A is lower (1.2 MPa vs. 1.5 MPa), see Fig. 5, reducing the micro-leakage of oxygen and hydrogen gas from the sealed battery and keeping it adequate for a longer time. Besides, the reduction of oxygen evolution would also protect the hydrogen storage alloy from oxidation in some degree. All these are beneficial to the battery durability.

4. Conclusion

The no-binder Ni/MH battery shows lower internal resistance and lower internal pressure and exhibits more easy activation, higher discharge capacity at a high rate and low temperature, and satisfactory durability. The properties of the electrodes and the batteries are all improved markedly by abandoning the binder.

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