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Effects of iron phthalocyanine on performance of MH/Ni battery①

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Abstract: Oxygen evolution causes a high inner pressure during charge and overcharge for MH/Ni battery, and an inappropriate eliminating way of the oxygen in the battery results in accumulation of heat. This is the main obstacle to develop and apply high capability and high power battery. How to reduce the ratio of the chemical catalysis rate to the electric catalysis rate in MH/Ni battery is considered as an urgent question. Iron phthalocyanine(FePc) was chosen as an electrochemical catalyst. The batteries were prepared by adding iron phthalocyanine with different dosages. The inner pressure, the capacity attenuation, the discharge voltage and capacity at high current of these three batteries were compared. The battery with 1 mg FePc in the negative electrode exhibits a good performance.

Key words: MH/Ni batteries; iron phthalocyanine; hydrogen storage alloys; electrochemical catalyst; inner pressure
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1 INTRODUCTION

An increase in the inner gas pressure of battery beyond 10^6 Pa causes a release of gas from the safety valve for a normal sealed cell, which leads to a drying out of electrolyte solution[1], and gradually decreases the performance of the battery until finally destroying it.

During charging and overcharging, oxygen is evolved rapidly on the nickel electrode. It is necessary to eliminate oxygen and restrain the rising speed of inner pressure so as to improve the performance of MH/Ni battery[2].

As a kind of functional material, ring-metalated phthalocyanine compounds have a strong ability of activating oxygen[3], and good electrochemical catalysis of oxygen[4-8]. We have reported the effect of iron phthalocyanine(FePc) with different adding mode on the performance of battery previously[9]. In this paper, the effect of the addition of FePc in negative electrode with different dosages on the inner pressure and the whole performance of MH/Ni battery was measured and reported.

2 EXPERIMENTAL

2.1 Preparation of electrode and test batteries

FePc was dissolved in ethanol and the solution exhibited the color of oxford blue. The solution with various dosages of FePc deposited on the powder of the alloy forming a mixture. As chosen from the result of simplified orthogonal experiments, the contents of FePc were 0 mg (A), 1 mg (B), 2.5 mg(C) respectively.

A foamed nickel plate was used as the nickel electrode substrate, β-Ni(OH)$_2$ powder was used as positive material, and the powders of Co and CoO were added as a conductor agent. The negative electrode was a mixture of hydrogen storage alloy powder in the composition of $\mathrm{MlNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}}$ (Ml: La-rich mishmetal) and the FePc of different dosages (A, B, C). The electrolyte was a 6 mol/L KOH solution containing 1 mol/L $\mathrm{LiOH \cdot H_2O}$.

Three kinds of batteries were prepared by using different negative electrodes with various dosages of FePc, and the positive electrodes were carefully selected so as to ensure that the normal capacity of every battery was (1.70 ± 0.05) A·h.

2.2 Test of performance of battery

The high-rate dischargeability was evaluated from the discharge capacity and the plateau voltage during discharging at different rates, i.e. the rates of 1C (1.7 A), 2C (3.4 A), 3C (5.1 A), 4C (6.8 A) and 5C (8.5 A) respectively.

In the capacity attenuation test, the battery was charged at 1C rate for 72 min, after a rest of 15 min, discharged to 1.0 V till 150 cycles.

Floating-charge for 2000 cycles took the following scheme: charging at 0.1C (0.17 A) for 30 min and then discharging at 1.5C for 1 min without rest.

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The 2C(3.4 A) pulse charge/discharge cycles of the batteries were carried out using the following scheme: charging at 3.4 A for 15 min, resting for 15 min, then discharging at 3.4 A until the battery voltage decreased to 1.0 V. The cycle number can reach 500.

2.3 Test of inner pressure

The inner pressure of the battery during charging and discharging was measured by an inner pressure test system[10] at 23 − 25 ℃. The battery was sealed in a chamber and the gas generated during charging was led to a pressure sensor through a hole on the top of the battery.

3 RESULTS AND DISCUSSION

3.1 High-rate discharge characteristics

The discharge capacities of the three AA-size batteries under different currents are shown in Fig. 1.

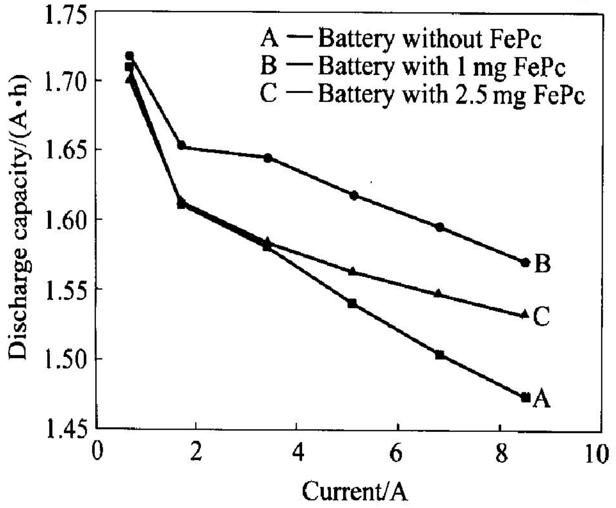


Fig. 1 Discharge capacity under different currents

It can be seen that the battery B kept a high discharge capacity even when being discharged at 5C rate (8.5 A). And as shown in Fig. 2, the battery B with 1mg FePc in the negative electrode had a higher discharging plateau than the battery A without FePc. The battery C with 2.5 mg FePc also had a high voltage plateau but its discharge capacity was a bit lower than that of the battery B (0.04 A·h or so). The increasing of discharge capacity and the rising of voltage plateau when being discharged at high rate should attribute to the FePc's function of eliminating oxygen.

3.2 Capacity attenuation

Fig. 3 shows that the battery B displayed an increase in discharge capacity during cycles that was different from the other two batteries. After 150 cycles, the battery B still had a high capacity of 1.64 A·h, while the battery A and C had the capacity of 1.42 A·h and 1.49 A·h respectively. To all appearances, the battery with FePc had obviously slower capacity attenuation than that without FePc, and at the same time, the former also had a higher discharge capacity than the latter. But it can also be seen that the capacity of the battery C attenuated more quickly than that of the battery B.

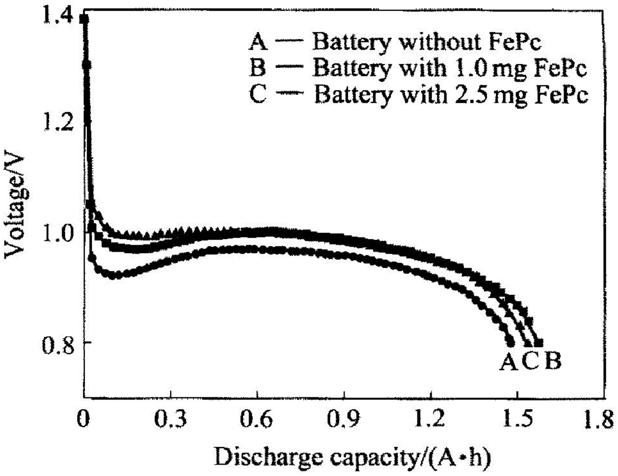


Fig. 2 Relationship between discharge voltage and capacity at 5C(8.5 A)

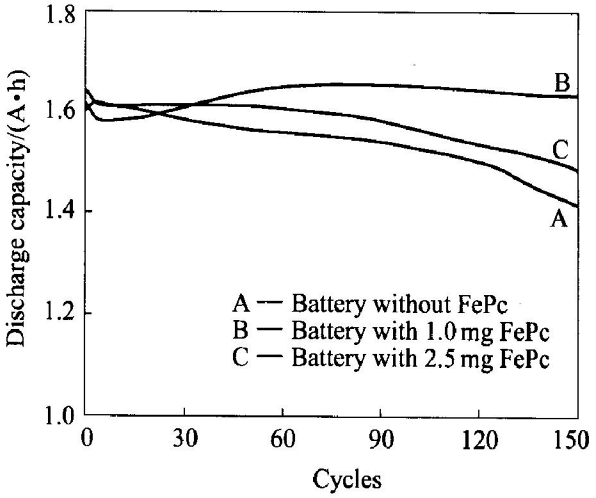


Fig. 3 Capacity attenuation comparison of three AA-type MH/Ni batteries during 1C cycles

After 150 cycles, the EIS of these three batteries were also tested (Fig. 4). It is obvious that the battery B had the lowest equivalent series-wound resistance, and at the same time, it also had the best cycleability and high-rate dischargeability. On all accounts, the battery B had the best performance.

3.3 Performance of floating charge

Fig. 5 shows the comparison of charging plateau of the three batteries. A_f, B_f, C_f represent voltage plateau for the first cycle. And A_l, B_l, C_l denote the charging plateau for the last cycle (the 2000th cy-

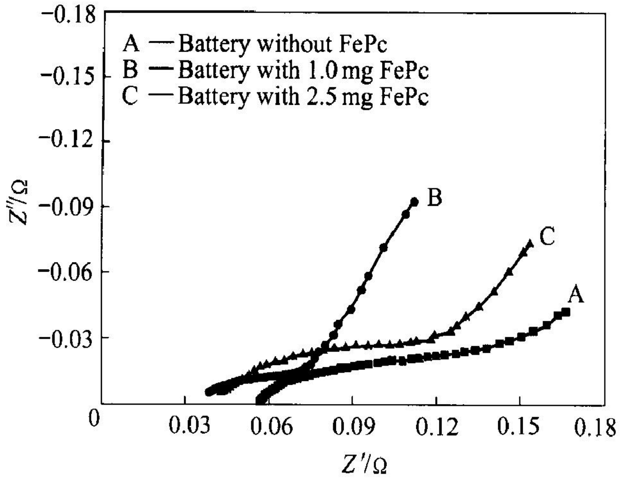


Fig. 4 EIS of three AA-size MH/Ni batteries after 150 cycles

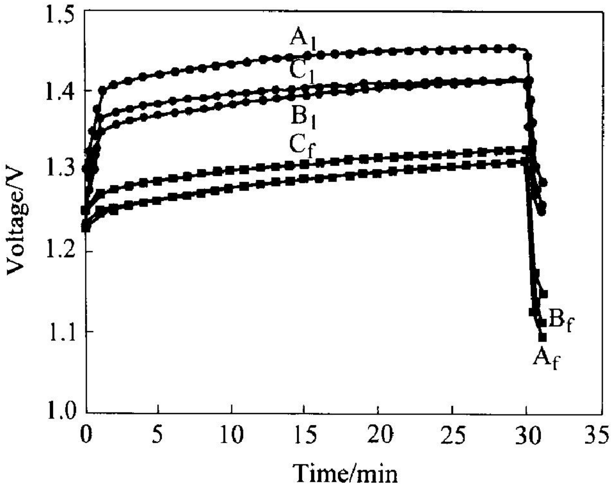


Fig. 5 Charging plateau comparison during floating-charge
(f —the first cycle; l —the last cycle)

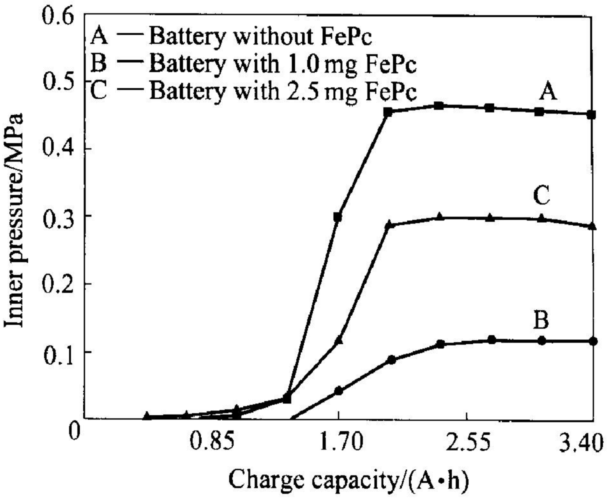


Fig. 6 Inner pressure comparison at 0.4C(0.68 A) charging rate

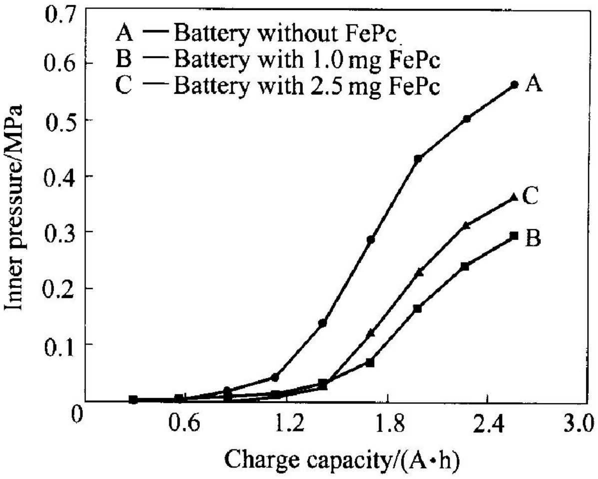


Fig. 7 Inner pressure curves of three batteries at 1C (1.7 A) charging rate

cle).

At the first cycle, the battery A without FePc had a low plateau like the battery B. But during cycles, the plateau of battery A without FePc increased quickly until finally attained a high median voltage of 1.445 V.

After cycles, the inner pressure of charging and overcharging to 200% and 150% of the normal capacity at the rate of 0.4C (0.68 A) and 1C (1.7 A) respectively were also compared (Figs. 6 and 7).

The battery inner pressure increased sharply when being charged at 0.4C up to 100% of the normal capacity (Fig. 6). The battery A without FePc displayed the fastest increase of inner pressure, which reached 0.46 MPa when just being charged to 2.04 A•h (120% of normal capacity). While the battery B with 1 mg FePc reached the equilibrium at 140% of normal capacity, and up to 200% of normal capacity, the inner pressure of battery remained constant (0.12 MPa). This indicates that in this period, the rate of gas evolution equals tothe rate of gas consumption during charging. The pressure equilibrium was attained when the inner pressure reached 0.46 MPa and 0.30 MPa for the battery A and C respectively. These two values of inner pressure are much higher than that of the battery B with 1 mg FePc in the negative electrode.

Fig. 7 indicates that the inner pressure changes with charging capacity at 1C rate charging to 150% of normal capacity(2.55 A•h). Similar to the 0.4C rate charging process, the inner pressure of the battery A increased sharply when just being charged to 88% of normal capacity, while the inner pressure of the battery B and C changed evidently after charging capacity approaching 100% of normal capacity. Then the inner pressure changed more slowly but did not reach equilibrium when the batteries were charged at 0.4C rate.

During overcharging, oxygen is evolved on the nickel electrode, but the pressure rise is greatly reduced by adulterating negative electrode with FePc and the charging efficiency of the battery is significantly improved. But as a kind of organic compound with a big-ring, FePc has poor conductibility, which may be the reason why battery C with much more FePc exhibits a higher pressure than that of battery B.

3. 4 High rate pulse-charge cycles' performance

After high-rate testing, the batteries were used to charge and discharge at 2C rate to test their performance of high rate pulse-charge (Fig. 8). The results showed that the battery B with 1mg FePc had the best pulse performance as we expected. But the battery C with 2. 5 mg FePc in the negative electrode showed a bad pulse-charge cycleability which was even greatly worse than the reference battery A. It might come down to the increase of resistance of the battery C during cycles which was brought about by adding too much FePc.

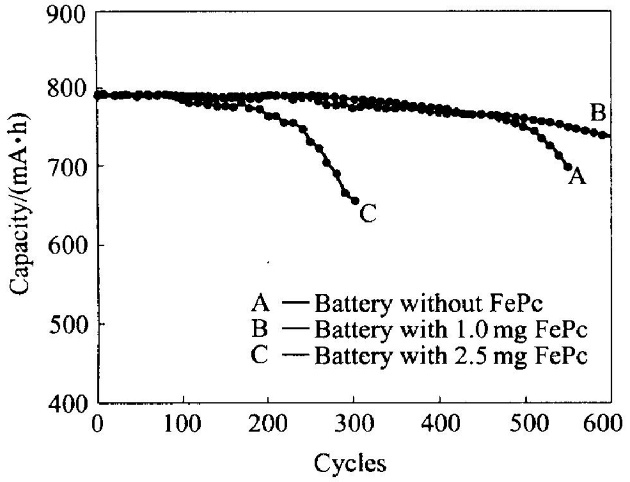


Fig. 8 Discharge capacity comparison of three batteries during 2C pulse-charge

3. 5 Reaction mechanisms

In a MH/Ni battery, the electrochemical reactions taking place at the electrode/electrolyte interface during charge and discharge are given by the possible reactions below:

Positive electrode

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^- \quad (1)$$

$$4OH^- \rightleftharpoons 2H_2O + O_2 + 4e^- \text{ (side reaction)} \quad (2)$$

Negative electrode

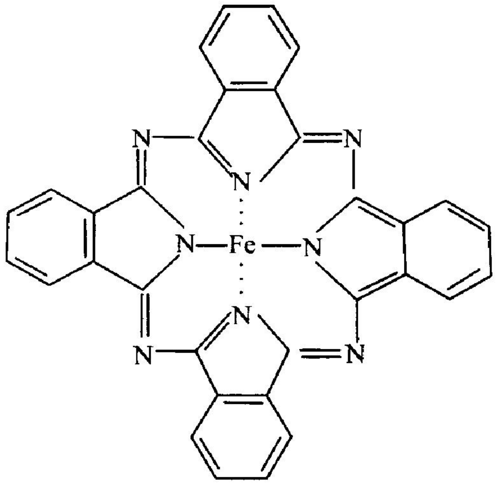
$$M + H_2O + e^- \rightleftharpoons MH + OH^- \quad (3)$$

$$4MH + O_2 \rightleftharpoons 4M + 2H_2O \text{ (side reaction)} \quad (4)$$

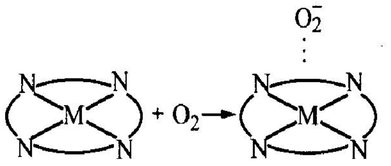
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \text{ (side reaction)} \quad (5)$$

The side reactions (2) and (5) constitute the oxygen circulation inside the battery. In the presence of oxygen, a MH/Ni battery is a three-phase system consisting of the solid matrix, the liquid electrolyte and a gas phase[11]. During charging and overcharging, oxygen is generated at the nickel/electrolyte interface and may evolve into the gas phase after exceeding its solubility in the electrolyte solution. The oxygen can then be transported, via the liquid and gas phases, from the nickel to MH electrode where the oxygen gas may dissolve in the electrolyte and be reduced at the MH/electrolyte interface. Such a process forms an internal oxygen cycle in a recombinant battery like the MH/Ni battery[11]. The accumulation of oxygen in the gas phase will lead to a battery pressure build-up.

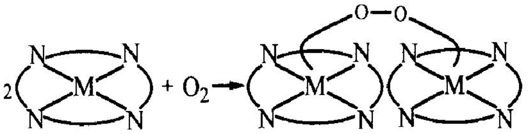
A phthalocyanine compound of transition metal is constituted of a big heterocyclic ring in planar construction and transition metal ions at the center of planum[12]. The conjugated molecule exhibits a high flatness as follows:



And the catalytic reaction can take place at the direction of axial[13]:



or



From the results above, the adding of FePc can catalyze the reducing reaction of the oxygen, and decrease the reducing potential of the oxygen. At the same time, as a carrier[11], FePc also plays a role in transmitting the oxygen from the positive electrode to the negative one. All these are helpful for increasing the speed of oxygen elimination, and therefore decreasing the inner pressure and increasing the high-rate charging/discharging efficiency.

4 CONCLUSION

The pressure rise was greatly reduced by using FePc mixed alloy and the charging efficiency of the battery was significantly improved.

Adding FePc in the negative electrode with appropriate quantity (1 mg per battery) can effectively restrain the pulverization of alloy. Also it can improve the charging efficiency and overchargeability, and depress the capacity attenuation. All these above ameliorate the performance of the battery, especially for high-power use.

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