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Effect of Co additives on the cycle life of Ni–MH batteries

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Abstract

The effects of Co powder of different particle size and Co suboxide ($Co_{1+x}O$, $0 \leq x \leq 2$), used as additives to the negative electrode, on battery cycle life were investigated. The study shows that the addition of finer Co powder or $Co_{1+x}O$ has a significant effect on improving the cycle life of the Ni–MH battery. In addition, the oxidation resistance of the MH negative electrode increases and the charging efficiency of the cell is enhanced. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Co additive; Ni–MH battery; Cycle life

1. Introduction

Several factors, such as negative/positive electrode material, separator, binder, and the rolling, forming process during manufacture, especially the first factor, affect the cycle life of the Ni–MH battery. Increasing the Co content of the alloy and the partial substitution of La with Zr can improve the alloy charge/discharge cycle life [1–3]; surface treatment of the alloy powder, such as Cu or Ni coating [4], or alkaline treatment and acid treatment of the alloy powder [5], can also enhance the Ni–MH battery cycle life.

In this paper, work on the improvement of electrode performance and cycle life during charging/discharging of the cell with a heavy current by adding fine Co powder or Co suboxide powder to the negative electrode is reported. Three kinds of Co powder of different particle size and one kind of Co suboxide were used as additives to the electrode. The mean diameter of these powders was: 5.9 μm (A), 9.5 μm (B) and 22.5 μm (C), respectively. Cobalt suboxide was a product of the incomplete reduction of CoO, represented as $Co_{1+x}O$ ($0 \leq x \leq 2$), the mean diameter of which was 0.8 μm.

2. Experimental

2.1. Preparation of the positive electrode

Spherical $Ni(OH)_2$ (Sumitomo Electric Industries, Ltd.) (90 wt.%) was mixed with conductive powder and HPMC binder to form a paste, which was then scrubbed into a foamed nickel substrate. The substrate with paste was then dried, pressed to 0.70 mm thickness and cut to 4.0 cm×7.3 cm size for use as the positive electrode for an AA size battery. The weight of the electrode was 6.8 g.

2.2. Preparation of the negative electrodes

One of the following Co additives (Co powder A, B and C and $Co_{1+x}O$ powder) (3 wt.%) and 97 wt.% $MlNi_{3.8}Co_{0.5}Mn_{0.4}Al_{0.3}$ alloy powder were mixed in an agitator. HPMC aqueous binder was added to the mixed powder and mixed again. The mixture was then pasted onto a punched nickel strip, dried, pressed and then cut to a size of 4.0 cm×10.5 cm to form a negative electrode for an AA size battery. In addition, a comparative AA size negative electrode without additive was prepared in the same way. Altogether there were five different kinds of negative electrode as experimental batteries.

2.3. Assembly of the test cells

Cylindrical batteries of AA size were made by the following process. The foamed nickel electrode prepared in Section 2.1 was used as the positive electrode. One kind of electrode prepared in Section 2.2 was used as the negative electrode. Both electrodes, which were separated from each other by a non-woven polyamide separator, were rolled together, placed in a Ni-plated cylindrical battery case, a solution of 6 N KOH–1 N LiOH was injected into the case, and the case was sealed with a cap.

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A cell of 1200 mAh nominal capacity was thus finally assembled.

2.4. Tests of the cells

The above cells were first charged/discharged at a rate of 0.4C for five cycles. Then one of each kind of cell was opened by removing the cap, immersed in a solution of 6 N KOH–1 N LiOH, and then the initial capacity of the negative electrode was measured (charging at a rate of 0.4C for 5 h, discharging at 0.4C until the voltage of the negative electrode decreased to −0.74 V vs. the HgO/Hg reference electrode). After 400 cycles at a rate of 1C, measurement of the capacity of the negative electrode was carried out in the same way.

The cycle tests at 1C charge/discharge were performed by charging at 1.2 A for 75 min and then discharging at 1.2 A until the voltage of the cell decreased to 1.0 V. The inner pressure of the cell was measured using a DNY-1 model battery inner pressure test system (Tianjin University) and measurement of the electrochemical parameter were carried out under potentiodynamic conditions with a Model 283 potentiostat/galvanostat (EG&G PAR).

3. Results and discussion

The high charge/discharge rate of Ni–MH batteries is gaining increasing attention. The rapid charging performance of the cell is very important for some applications such as mobile phones and electric vehicles. Together with the high charge/discharge rate, the cycle life is also expected to be long.

Fig. 1 shows the cycle life of the five kinds of AA size cells with different cobalt additives when fully charged/discharged at a rate of 1C. As can be seen, the cell with finer Co powder A and that with $Co_{1+x}O$ powder in the negative electrode had the best cycle life. When the capacity decrease reached 20%, the cycle numbers of the test cells were 510 (with Co powder A), 520 (with $Co_{1+x}O$), 450 (with Co powder B), 250 (with Co powder C) and 200 (without any additive). It can be seen from Fig. 1 that the cycle life of Ni–MH batteries can be improved notably by the addition of Co powder or $Co_{1+x}O$ powder. The finest Co powder and $Co_{1+x}O$ proved to be most efficient for increasing the cycle life.

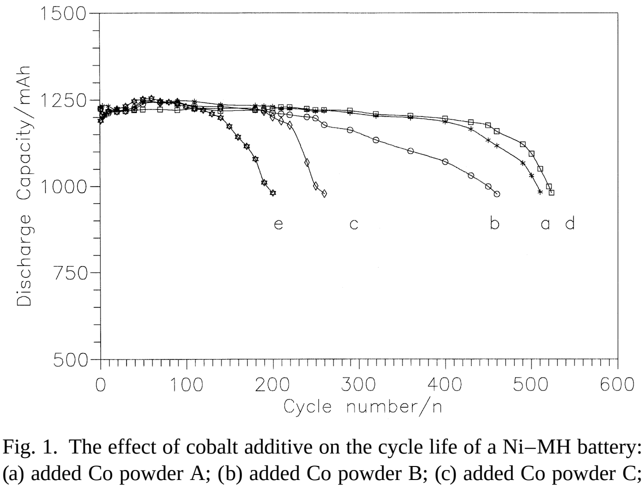

Fig. 1. The effect of cobalt additive on the cycle life of a Ni–MH battery: (a) added Co powder A; (b) added Co powder B; (c) added Co powder C; (d) added cobalt suboxide; (e) without cobalt additive.

The above results are believed to be caused by the following two factors.

On one hand, the Co or $Co_{1+x}O$ in the negative electrode dissolves during the battery discharging process and then reprecipitates to form Co on the alloy surface during the charging process [6]. The following reaction occurs during the charge/discharge process of the cell:

$$Co(OH)_2 + 2e^- = Co + 2OH^-,\ E_0 = -0.73\ V \qquad (1)$$

Therefore, Co and its compound are well distributed on the alloy surface after several charge/discharge cycles. They have the same effect as a chemical coating of Co.

When overcharged, O_2 evolves on the positive electrode and is consumed quickly on the negative electrode according to

$$O_2 + MH \rightarrow M + H_2O \qquad (2)$$

In addition, the catalytic reduction of O_2 on the Ni, Co surface is mainly the result of the superoxide consuming two electrons [7,8]:

$$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-,\ \phi^0 = -0.065\ V \qquad (3)$$

The electrochemical reduction reaction of HO_2^- then begins:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-,\ \phi^0 = 0.867\ V \qquad (4)$$

or chemical decomposition:

$$2HO_2^- \rightarrow 2OH^- + O_2 \qquad (5)$$

HO_2^- is a strong oxidizing agent and can oxidize metals easily. It is hard to reduce the oxidized metal again except with Co with a electrochemical reaction. Cobalt is first oxidized by HO_2^- to form $Co(OH)_2$ on the surface of Co-coated alloy. $Co(OH)_2$ is readily reduced to Co under the charge potential (reaction (1)), so the $Co \rightarrow Co(OH)_2 \rightarrow Co$ cycle is effective in protecting the alloy against oxidation. This is believed to be the reason for the slow decay of the capacity of the negative electrode with Co additive after 400 cycles (see Table 1). Therefore, the alloy electrode mixed with Co additive displayes a longer cycle life.

The negative electrode charging efficiency was also improved by the Co additive. Fig. 2 shows the i/E cyclovoltametric curves for the alloy electrodes. The reaction current i of the alloy electrode with Co additive was higher than that of the alloy electrode without Co

Table 1
Comparison of the capacity of AA size test negative electrodes with different additives

	Capacity of negative electrode (mAh)				
	With Co powder A	With Co powder B	With Co powder C	With Co suboxide powder	Without any additive
Initial	1765	1723	1760	1749	1770
After 400 cycles	1414	1230	1200	1430	1178

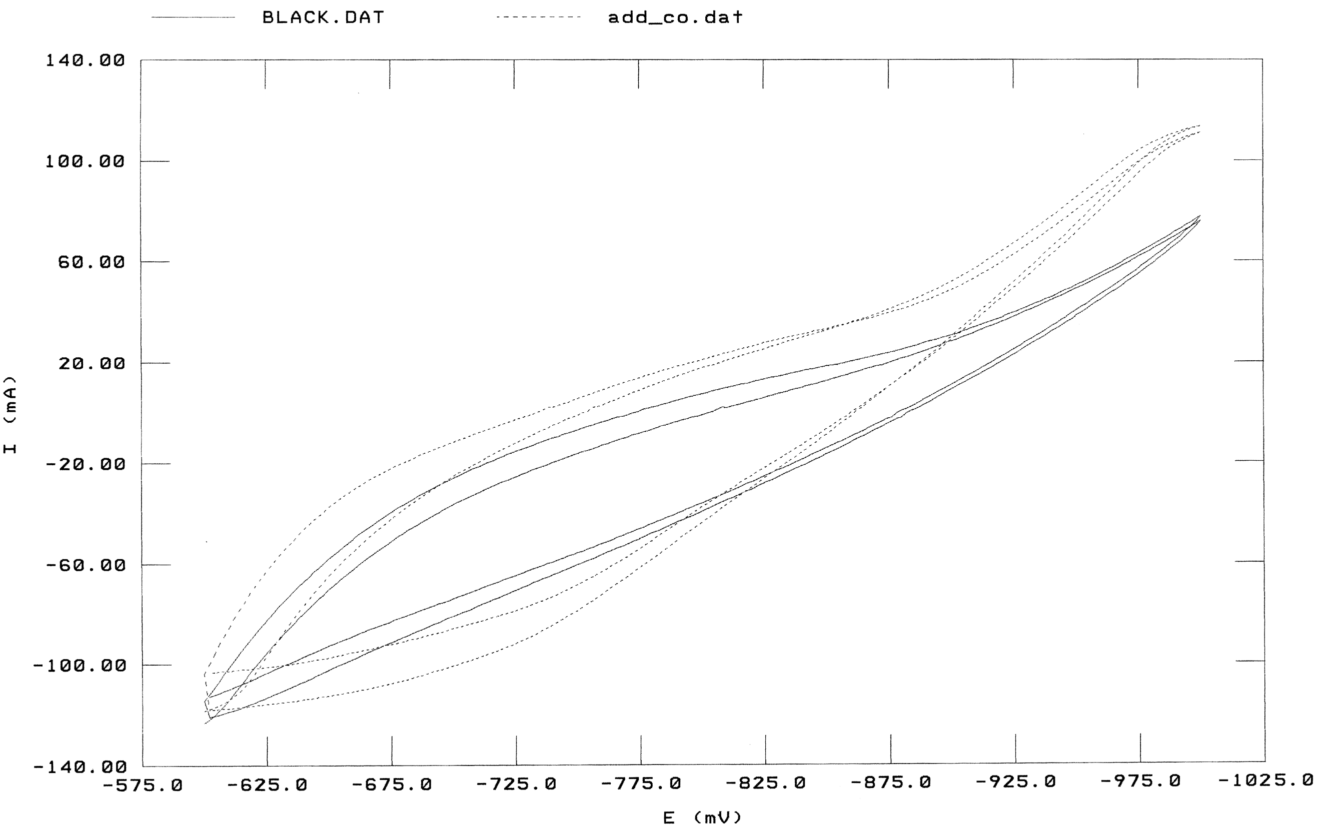

Fig. 2. Cyclovoltametric curve for an alloy electrode in 6 N KOH–1 N LiOH, $V = 20$ mVS^{-1}, E is the potential of the alloy electrode vs. the HgO/Hg reference electrode. (———) Without Co additive; (· · ·) with Co powder C.

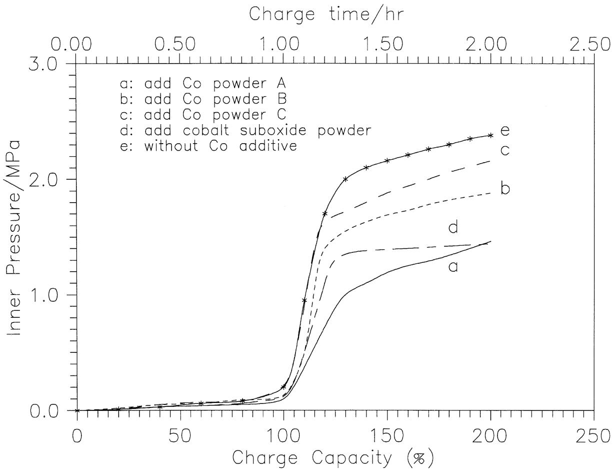

Fig. 3. The effect of cobalt additive on the inner pressure of a Ni/MH battery at 1C charging rate.

additive. Therefore, Co on the surface of the alloy repressed H_2 gas evolution and reduced the H_2 pressure and hence the battery inner pressure (see Fig. 3). In a typical commercial Ni–MH cell, a fitted safety vent is designed for 2.5 MPa, so when the inner pressure exceeds 2.5 MPa, the cell starts to leak. The loss of electrolyte makes the cell unusable. Lowering the inner pressure is important for improving the cycle life of a cell.

4. Conclusion

Cobalt additive, which is oxidized before the alloy powder in the negative electrode by the O_2 that evolves from the positive electrode during overcharging, protects the alloy from oxidation and improves the chemical stability of the electrode alloy. The addition of Co to the negative electrode also enhances the cell's charging efficiency, decreases the inner pressure and hence prolongs cell cycle life remarkably. A finer Co additive produces a better effect on battery cycle life than coarser Co additives.

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