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Journal of Alloys and Compounds 293–295 (1999) 825–828

Journal of
ALLOYS
AND COMPOUNDS

Effect of cobalt powder on the inner pressure of Ni/MH batteries

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Abstract

The effect of three kinds of cobalt powder of different mean diameter added to the negative electrode on the inner pressure of Ni/MH batteries during charging was examined. Experiments showed that batteries with finer Co powder displayed a much lower inner gas pressure on charging than batteries with coarser Co powder. The inner gas pressure of the cells increased with increasing charge/discharge cycle, and the cell with the finest Co powder showed the slowest inner pressure increase and had the longest cycle life. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Inner pressure; Cobalt powder; Ni/MH battery

1. Introduction

The effect of cobalt and its compounds on Ni/MH batteries is well known and the addition of Co, CoO and Co(OH)₂ to a Ni(OH)₂ electrode has been reported repeatedly [1–3]. Cobalt has also commonly been added to hydrogen-storage alloys during the smelting process to extend the cycle life of the negative electrode [4,5]. The negative electrodes of Ni/MH cells mixed with fine Co powder, Cu powder or Ni powder, as an additive, especially with Co powder, were found to improve the chemical stability of the alloys and the cycle life of the batteries [5]. The inner pressure is an important parameter for Ni/MH batteries. Using an analogue battery, Sakai [6] reported the effect of alloy powder coated with Cu or Ni and alloy powder mixed with Cu or Ni on the inner pressure of batteries. In this paper, the effect of the addition of fine Co powder to the negative electrode on the inner pressure of batteries and the inner pressure changes at various charge/discharge cycles is reported. Three kinds of Co powder were used as additive: one was a fine Co powder (A) and the other two were coarser (B and C).

Measurement of the batteries' inner pressure was usually carried out by leading the gas out from an analogue battery or a real battery to a pressure sensor through a hole in the top of the battery [7,8]. However, this method does not reflect the real condition of the battery precisely and completely. In this work, we adopted a DNY-1 model battery inner pressure test system including a high preci-

sion deformation sensor (precision 0.01 μm), which measured deformation of the battery bottom during charging, an A/D converter and a personal computer, to realize non-destructive, non-contact and in-situ measurements [9].

2. Experimental

2.1. Analysis of Co particle size distribution

The particle size distribution of the Co powder in the samples was determined using a laser diffraction analyzer.

2.2. Preparation of hydride electrode

Hydrogen storage alloy powder (MNi_{3.8}Co_{0.5}Mn_{0.4}Al_{0.3}) (97 wt.%) and 3 wt.% of one of the Co additives (A, B, C) were mixed in an agitator, and HPMC aqueous binder was then added to the mixed powder and mixed again. The mixture was then pasted onto a punched nickel strip, dried, pressed and cut to form the negative electrode (4.0 cm×10.5 cm×0.036 cm, 8.7 g) for an AA size battery. Altogether there were three different kinds of negative electrodes for the test cell.

2.3. Preparation of nickel electrode

A foamed nickel plate (Sumitomo Electric Industries Ltd.) was used as the nickel electrode substrate. β-Ni(OH)₂ powder (Sumitomo Electric Industries Ltd.) (90 wt.%) was mixed with 10 wt.% of conductive material for

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use as positive material. HPMC aqueous binder was added to the powder to form a paste, which was then scrubbed into the foamed nickel substrate with a spatula. The plate was then dried, pressed and cut to form the nickel electrode (7.3 cm×4.0 cm×0.07 cm, 6.8 g) for an AA size battery.

2.4. Preparation of test cell

Each AA size test cell was constructed by rolling one foamed Ni(OH)₂ electrode, one hydride electrode and one piece of non-woven polyamide separator together, placing the roll in a battery can, adding an alkali solution electrolyte of 6 N KOH–1 N LiOH and finally sealing the battery. Three different kinds of cell were prepared by using three different negative electrodes with different Co additives, and the nominal capacity was 1200 mAh.

2.5. Test of the cell inner pressure

The above cells were first charged/discharged at a rate of 0.4C for five cycles. Changes in the inner pressure of the cells with change of charging time at different charging currents (0.4C and 1C) were measured using a DNY-1 model battery inner pressure test system at 20–25°C. Charge/discharge cycles of the cells were carried out using the following scheme: charging at 1.2 A for 75 min, then discharging at 1.2 A until the cell voltage decreased to 1.0 V. The cell's inner pressure was measured at 0.4C charging to 200% of nominal capacity after 50, 100, 150 and 300 charge/discharge cycles.

3. Results and discussion

Fig. 1 shows the grain size distribution of the three Co powder samples. As can be seen, the mean diameter of Co powders A, B and C was 5.9, 9.5 and 22.5 μm, respectively. The grain size distribution of Co powder A was narrower than those of powders B and C, with Co powder C, especially, containing a large quantity of big grains.

Fig. 2 shows the inner pressure change of AA size Ni/MH batteries with different Co powders added to the negative electrodes when charged at 0.4C. It can be seen that the battery inner pressure increased after charging up to 100% of nominal capacity. Battery A with the finest Co powder A displayed the slowest increase of inner pressure, which reached equilibrium at 145% of nominal capacity, and up to 200% of nominal capacity, the inner pressure remained constant (0.5 MPa). This indicates that, in this period of time, the rate of gas evolution equalled the rate of gas consumption during charging. Pressure equilibrium was attained when the inner pressure reached 0.8 MPa for the batteries with Co powder B, and 1.0 MPa for the batteries with Co powder C. These two values of inner

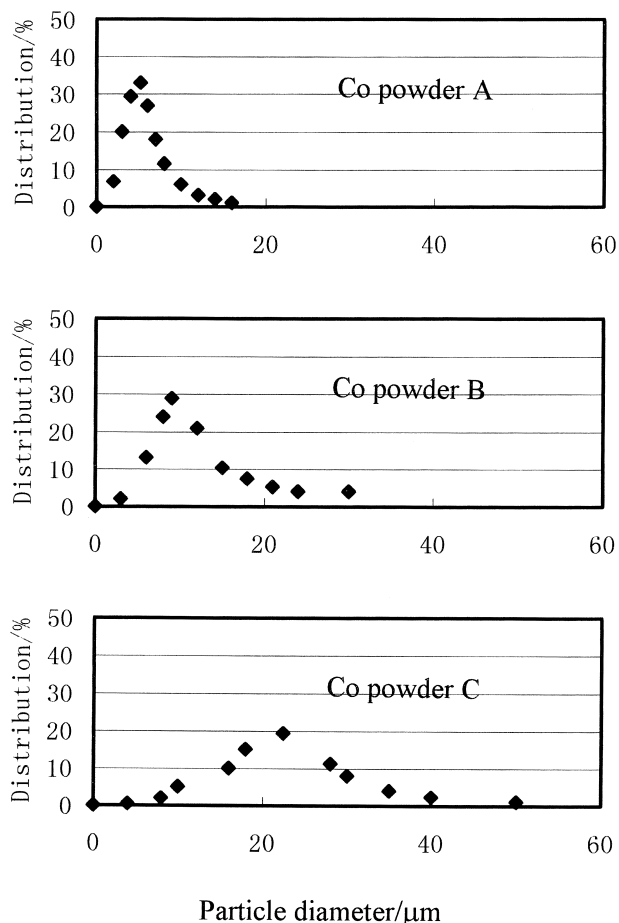


Fig. 1. Particle size distribution of Co powder samples.

pressure are much higher than those of the batteries with the finer Co powder A in the negative electrode.

Fig. 3 demonstrates that the inner pressure changes with charging capacity at a 1C rate. Similar to the 0.4C rate

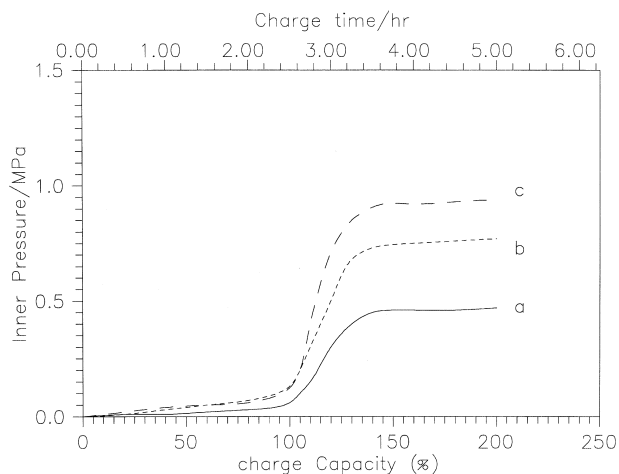


Fig. 2. Inner pressures of the Ni/MH batteries at 0.4C charging: (a) added Co powder A; (b) added Co powder B; (c) added Co powder C.

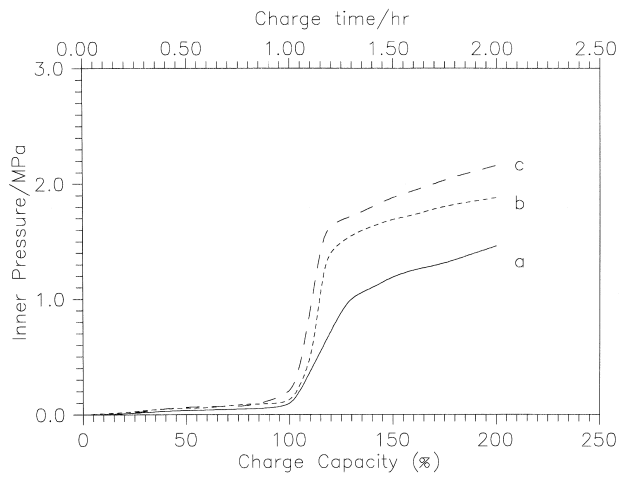


Fig. 3. Inner pressure of Ni/MH batteries at 1C charging rate: (a) added Co powder A; (b) added Co powder B; (c) added Co powder C.

charging process, the batteries' inner pressure increased markedly when approaching 100% of nominal capacity. Then at 125 to 200% of nominal capacity, the inner pressure changed more slowly, but did not reach equilibrium as charged at 0.4C rate.

The batteries' inner pressure reached 1.5 MPa at 200% of nominal charge capacity for the batteries with finer Co powder A, 120% of nominal charge capacity for the batteries with Co powder B, and 110% of nominal charge capacity for that with Co powder C. If the latter two batteries were charged to 200% of nominal capacity, the inner pressure would reach 1.85 MPa for the batteries with Co powder B and 2.1 MPa for the batteries with Co powder C. Therefore, the addition of Co powder A to the negative electrode significantly improved the batteries' charging efficiency.

Figs. 4–6 show the inner pressure changes of AA size batteries when charged at 0.4C rate after various cycles (discharged at 1C rate), i.e. after the 1st, 50th, 100th, 150th and 300th cycle. It can be seen that the charging inner pressure increased with increase of cycle number, as reported by Sakai [5] and Kanda [7]. However, the battery capacities were still increasing before 100 cycles (Table 1), therefore at the beginning of the cycle life, the decay of the battery capacity was not the main factor causing the increase of inner pressure, which was a result of a side-reaction of hydrogen evolution which reduced the charging efficiency of the negative electrode during overcharging [7].

The inner pressure of the battery with Co powder A added to the negative electrode increased more slowly than those of the batteries with Co powders B and C added, i.e. the electrode with the finer Co powder A displayed a more significant improvement in decreasing battery inner pressure and prolonging battery cycle life than Co powders B and C.

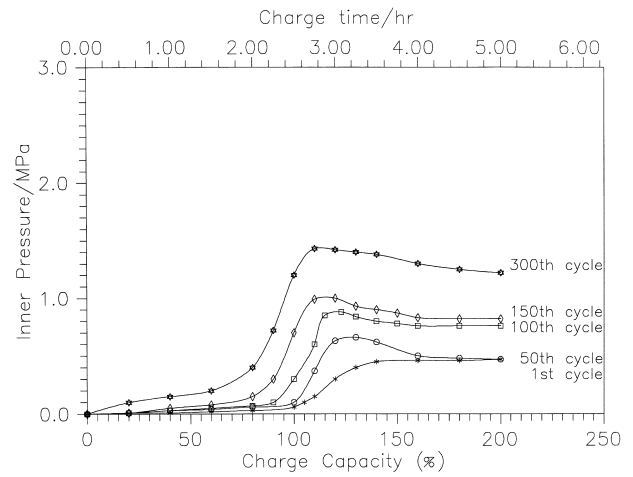


Fig. 4. Changes of the inner pressure at 0.4C charging rate with cycle number. Co powder A used as additive.

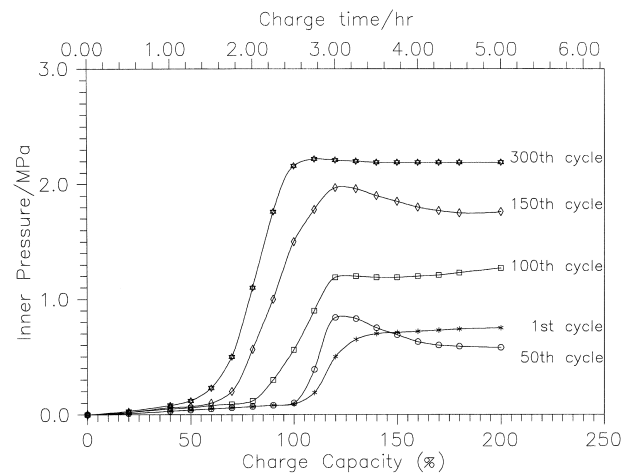


Fig. 5. Changes of the inner pressure at 0.4C charging rate with cycle number. Co powder B used as additive.

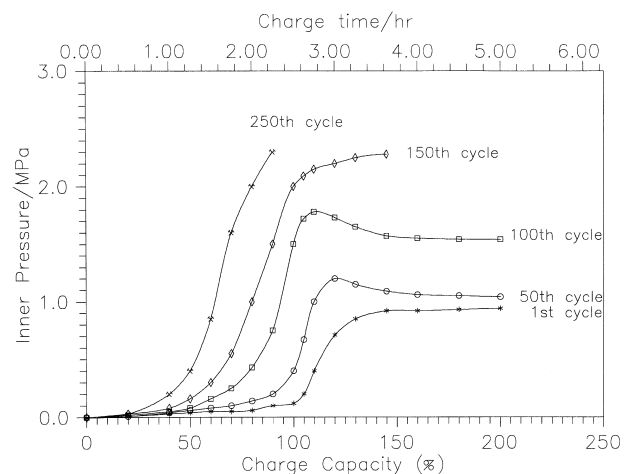


Fig. 6. Changes of the inner pressure at 0.4C charging rate with cycle number. Co powder C used as additive.

Table 1
Discharge capacity after 1, 50, 100, 150 and 300 charge/discharge cycles at 1C rate

Cycle No.	Discharge capacity of the cells with Co additive (mAh)		
	Co powder A	Co powder B	Co powder C
1	1226	1225	1223
50	1243	1239	1248
100	1250	1241	1225
150	1233	1230	1210
300	1215	1160	

4. Conclusion

The inner pressure of Ni/MH batteries increases remarkably during overcharging. It can be reduced by adding Co powder, especially fine Co powder, to the negative electrode. The increase in pressure was accelerated during overcharging and an obviously high pressure appeared

more early with increasing charge/discharge cycling. The increase in pressure decreased during overcharging by adding fine Co powder to the negative electrode. The battery with finer Co powder added to the negative electrode displayed a slower inner pressure increase and a longer cycle life.

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