High-rate dischargeability enhancement of Ni/MH rechargeable batteries by addition of nanoscale CoO to positive electrodes

J.B. Wu [a], J.P. Tu [a,*], T.A. Han [a], Y.Z. Yang [a], W.K. Zhang [b], X.B. Zhao [a]

[a] *Department of Materials Science and Engineering, Zhejiang University, Zheda road, Hangzhou 310027, China*
[b] *College of Chemical and Material Engineering, Zhejiang University of Technology, Hangzhou 310014, China*

Abstract

Nanoscale cobalt oxide (CoO) particles were synthesized by analysis of $CoCO_3$ in vacuum. Four groups of sealed Ni/MH batteries with different ratio of nanoscale CoO in the positive electrodes were assembled. The overall characteristics of Ni/MH batteries were investigated at different discharge rates at room temperature. The high-rate discharge performance of the Ni/MH batteries was improved by the addition of nanoscale CoO in positive electrode as compared with the addition of normal CoO. Under high-rate discharge conditions, the batteries with sufficient nanoscale CoO in positive electrodes presented much better cycling stability, higher discharge mean voltage, lower internal resistance and higher high-rate capacity. The addition of 8 wt.% nanoscale CoO was proved a desired amount to modify the battery performance at high discharge rates. Too much nanoscale CoO contributed no effect on the improvement of overall performance of Ni/MH batteries.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Ni/MH batteries; Nanoscale CoO; Positive electrode; High-rate discharge

1. Introduction

Nickel-metal hydride (Ni/MH) batteries are widely used nowadays due to their high performance and low environmental load. Although Ni/MH batteries are commercially available, further research is still required to improve the high power performance considering their use in electric vehicles and hydrid vehicles. Thus, the high-rate dischargeability is regarded as an important target to evaluate the Ni/MH batteries [1].

Nickel hydroxide ($Ni(OH)_2$), the active material in the positive electrode of Ni/MH battery, is semiconductor which greatly reduces the current density in the positive electrode [2,3]. To minimize the internal resistance of the electrode among active material particles, nickel substrate and electrolyte, it is suggested to incorporate some additives in the electrode. Cobalt and its compounds are convinced effective to shrink the resistance of the positive electrode of Ni/MH batteries [4,5]. By addition of CoO into nickel hydroxide powder directly, Oshitani et al. [6] indicated that CoO contained in the electrode dissolved in alkaline electrolyte to form blue Co(II) complex ion and then precipitated on nickel hydroxide particles as β-$Co(OH)_2$ while standing. After charging, such β-$Co(OH)_2$ converted to β-CoOOH. β-CoOOH has outstanding conductivity, which ensures a very efficient and steady conductive network leading to a higher utilization of the nickel hydroxide.

In addition, the nanostructured additives were studied widely in battery industry. Lv et al. substitute carbon nanotubes (CNTs) for acetylene black [7]. The results showed that the high-rate dischargeability was enhanced by the addition of CNTs. Hermann et al. incorporated copper and nickel nanomaterials into the negative electrode of Ni/MH battery and got a dramatically improved discharge capacity [8]. Encouraged by these results, we extend our investigation to addition of nanoscale CoO. It is anticipated that the fine CoO particles can be mixed more homogeneously with $Ni(OH)_2$ by supersonic and exist among the $Ni(OH)_2$ particles, without

the effect on volume–capacity ratio of the positive electrode. After first charge, a more uniform conductive network is hoped to form.

In this present work, nanoscale CoO particles were synthesized by the decomposition of $CoCO_3$ nanorods in vacuum. Four groups of sealed A-type Ni/MH batteries with different content of nanoscale CoO in the positive electrodes were assembled. The influence of nanoscale CoO on the overall performance of Ni/MH batteries at high discharge current density was discussed in order to investigate the application of nanoscale CoO to sealed Ni/MH rechargeable batteries.

2. Experimental details

2.1. Synthesis of nanoscale CoO particles

Nanoscale CoO particles were synthesized by the decomposition of $CoCO_3$ nanorods. As precursor, $CoCO_3$ nanorods were prepared by a precipitation method. $0.1\,M\,Na_2CO_3$ and $0.1\,M\,Co(NO_3)_2$ solution, which were individually dissolved in distilled water, mixed and reacted fully for about 30 min to form $CoCO_3$ deposition. To get fine deposition, the agitation with a rotary speed of 4000 r/min was needed when mixing them together. The deposition was cleaned by water and dried at 80 °C for 8 h. The as-prepared $CoCO_3$ was then put into a sealed chamber in furnace. After maintained at 380 °C for 4 h in vacuum, the $CoCO_3$ nanorods decomposed into fine CoO particles.

In order to improve the dispersion of as-prepared CoO in the positive electrode material, the finer powder was surged in analytically pure ethanol with a supersonic cleaner for 2 h and dried in vacuum. The $CoCO_3$ and CoO powders were characterized by X-ray diffraction (XRD, Thermo X' TRA X-ray diffractometer with Cu $K\alpha_1$ irradiation) and transmission electron microscope (TEM, Philip 200 UT). Only the pure $CoCO_3$ and CoO Bragg peaks appeared in XRD patterns, and the obtained $CoCO_3$ and CoO particles were well crystallized. As shown in Fig. 1, rod-like $CoCO_3$ has a length of several micrometers and a diameter of 100 nm, while CoO particles are shortened, with a diameter of 100 nm and a length no more than 150 nm.

2.2. Preparation of sealed Ni/MH rechargeable batteries

β-$Ni(OH)_2$ as active material, together with a certain amount of acetylene black, was mixed with different proportion of nanoscale CoO (4, 6, 8 and 12 wt.%). A milling procedure was needed to ensure the uniformity of the mixture. Followed by an addition of proper amount of binders (PTFE and CMC) and distilled water, a homogenous paste with adequate rheological properties was made. The paste was filled to a nickel foam substrate (166 mm × 20 mm × 2 mm) and dried at 80 °C in air. By controlling the amount of the paste immerged into the substrate, the capacity of the positive electrode of Ni/MH battery was designed as 2200 mAh.
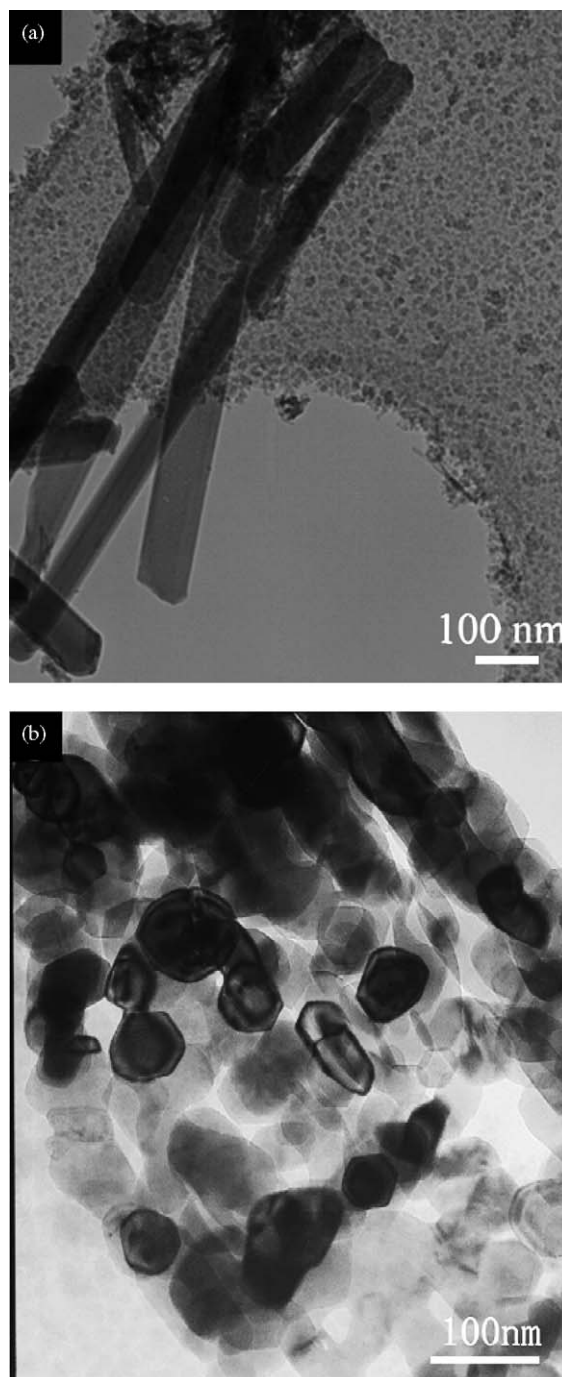

Fig. 1. (a) TEM image of $CoCO_3$ nanorods; (b) TEM image of nanoscale CoO particles.

Afterwards, the positive electrodes were rolled to a thickness of 0.6 mm.

A commercial AB_5-type hydrogen storage alloy with the standard composition $Mn(Ni_{3.4}Mn_{0.4}Al_{0.3}Co_{0.7})$ was used for the negative electrode material. The negative electrodes were prepared by roll-pressing the alloy powder onto a copper mesh to form its sheet with a thickness of 0.29–0.30 mm. The ratio of the capacity of positive and negative electrodes was about 1: 1.6, which would assure the capacities of the batteries

determined by the positive electrodes. A solution containing 6 M KOH, 1 M NaOH and 0.5 M LiOH was used as electrolyte, impregnating the electrodes and separator. After being sealed, the A-type Ni/MH rechargeable batteries with a capacity of 2200 mAh were assembled.

Another group of sealed A-type Ni/MH batteries were supplied for comparison by Panfar Batteries Co. Ltd., China. These batteries were made with same process but with 8 wt.% of normal CoO particles, which had sub-micron diameters.

2.3. Test of sealed Ni/MH rechargeable batteries

Before test, the batteries were charged and discharged for several times at low current for activation. In the subsequent charge–discharge cycles, the batteries were charged at 1 C-rate for 1.2 h, together with 10 mV of potential fall as a termination condition. After 10 min of interval the batteries were discharged at respective 1, 5, 10 C-rate discharge current. The cut-off voltages were set as 1.0, 0.8, 0.7 V, respectively. This procedure was performed using computer controlled cycling equipment (Guangzhou Qingtian BS-9365) at room temperature. The capacity and the mean discharge voltage can be read from the computer and the internal resistance of the batteries was measured every 30 cycles using resistance measurement equipment (Guangzhou Qingtian BS-VR2).

3. Results and discussion

3.1. Stability of the specific capacity

Fig. 2 shows the variation of the specific capacity with different content of nanoscale CoO under various discharge conditions. The cycles stopped as the capacity diminished to 80% of the original data. The specific capacity was calculated from the capacity of the battery dividing the total weight of positive electrode except substrate because the negative was excessive. At 1 C discharge rate, as shown in Fig. 2(a), all the positive electrodes exhibit good stability and the batteries can get a long lifespan (467–538 cycles). Among them the battery with 8% nanoscale CoO presented the longest lifespan, more than 18% of the battery with 4% nanoscale CoO. And at 5 C discharge rate, as shown in Fig. 2(b), the batteries with 6, 8 and 12% nanoscale CoO can also get a long lifespan, but the battery with 4% nanoscale CoO seems short-lived, only 62% as compared to the battery with 8% nanoscale CoO. At 10 C discharge rate (Fig. 2(c)), only the electrode with 8% nanoscale CoO is longevous (164 cycles), presenting more than 152, 82 and 37% of cycle numbers for the electrodes with 4, 6 and 12% nanoscale CoO, respectively. Furthermore, at 10 C discharge rate, only the electrode with 8% nanoscale CoO was stable, while the specific capacities of other electrodes diminished very quickly. Fig. 2(a)–(c) also show that the electrode with 8 wt.% of nanoscale CoO exhibited higher specific capacity and better stability than the electrode with the same percent of normal
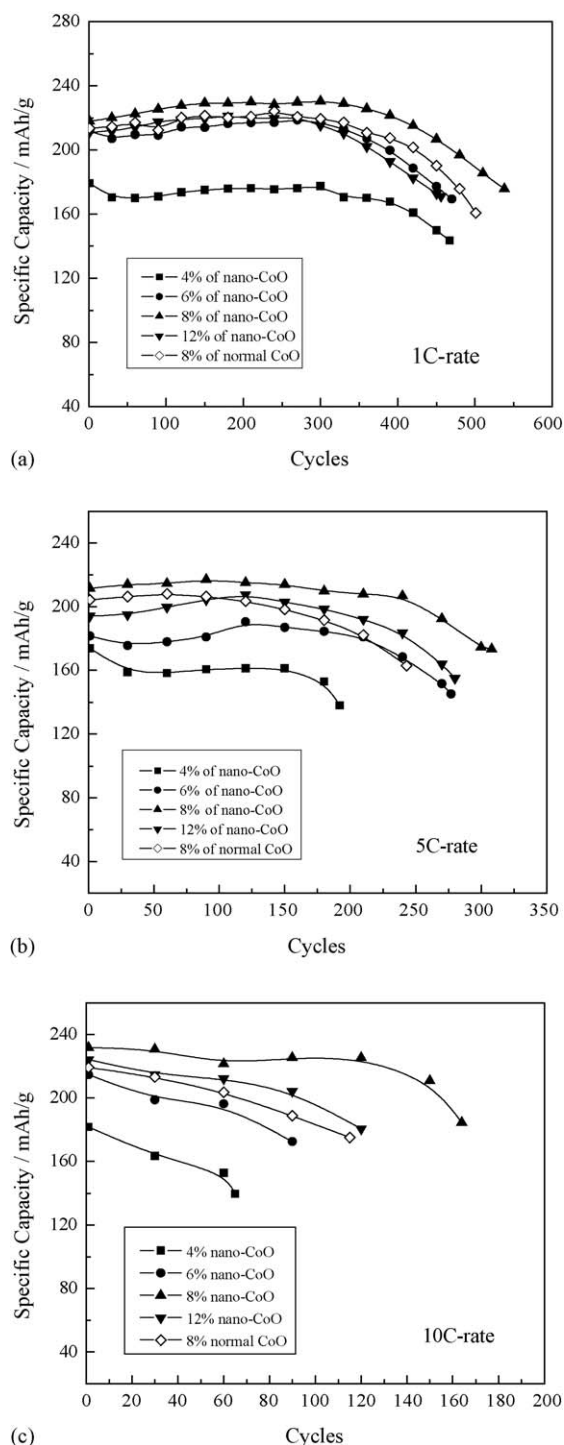

(a)

(b)

(c)

Fig. 2. Variation of specific capacity of Ni(OH)$_2$ electrodes with charge–discharge cycle at different discharge rates.

CoO. The stability was improved especially at high discharge rate.

The results discussed above indicated that the addition of nanoscale CoO in positive electrode enhanced the stability of the cycles and extended the lifespan of Ni/MH batteries, especially at high discharge rates. It is known that the lifespan and the stability of Ni/MH batteries depend on the successfully

Table 1
Specific capacity of Ni(OH)$_2$ electrodes with different content of nanoscale CoO

Discharge rate	4% nano-CoO (mAh/g)	6% nano-CoO (mAh/g)	8% nano-CoO (mAh/g)	12% nano-CoO (mAh/g)	8% normal CoO (mAh/g)
1 C	195.3	244.9	262.7	261.2	254.8
5 C	177.4	213.3	247.4	245.1	236.5
10 C	200.0	240.4	264.0	264.7	249.2

reversible conversion between β-Ni(OH)$_2$ and β-NiOOH. But the conversion from β-Ni(OH)$_2$ to γ-NiOOH lead to the lose of the specific capacity and the swelling of the Ni electrodes [9]. β-CoOOH conductive network transformed from CoO particles can increase the charge-acceptance of Ni electrodes and prevent the formation of γ-NiOOH [6]. At high discharge rate, a high current density exists in the Ni electrode, which requires a more efficient conductive network. It is suggested that sufficient nanoscale CoO can form a perfect conductive network in active material. The network meets the requirement of charge-acceptance at high discharge rate very well and prevents the formation of γ-NiOOH. Thus, the loss of capacity was reduced and swelling of the positive electrode was diminished. As a result, the stability of the specific capacity was improved and the lifespan of the Ni/MH batteries was prolonged with addition of 8% nanoscale CoO at high discharge rate.

It also can be inferred from Fig. 2 that the specific capacity of the positive electrode increases with increasing of the content of nonoscale CoO, but too much nanoscale CoO lead to a decrease in capacity, as shown by the curves with 12% nanoscale CoO. CoO cannot provide capacity itself, though it is helpful to the conductivity of the electrode [10]. Without regard to the weight of CoO, acetylene black and binders, the maximal specific capacity of Ni(OH)$_2$ is listed in Table 1. It can be seen the continuous enhancement of the specific capacity of Ni(OH)$_2$ with the content of nonascale CoO. But adding of 8 and 12% CoO to the electrodes the specific capacity of Ni(OH)$_2$ is even the same. It indicates that the addition of 8 wt.% nanoscale CoO is sufficient for the positive electrode considering the specific capacity. Table 1 also shows that the specific capacity of Ni(OH)$_2$ of the electrode with normal CoO was obviously lower than the electrode with same content of nanoscale CoO. The utility of Ni(OH)$_2$ was greatly improved by substituting nanoscale CoO for normal CoO.

A survey of the internal resistance of the Ni/MH batteries indicates that the resistance is optimized through the addition of nanoscale CoO, as shown in Fig. 3. The internal resistance gradually decreased with increasing the content of nanoscale CoO from 4 to 12%. And the internal resistance decreased when replacing 8% of normal CoO by 8% of nanoscale CoO. The differences of original internal resistance for all the batteries were less than 1 mΩ, but during the charge–discharge cycles, the differences were enlarged. During the charge–discharge process the electrodes expanded and shrinked, resulting in the loss of the active material from substrate and the increase in internal resistance [9].
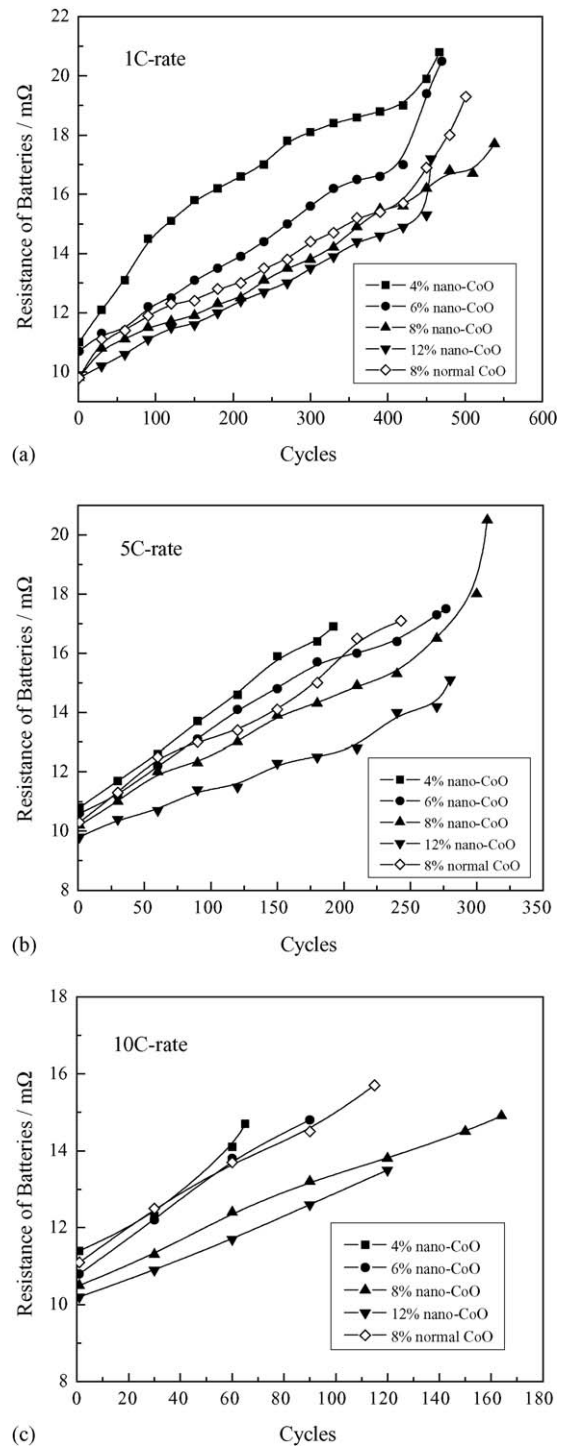

(a)

(b)

(c)

Fig. 3. Variation of the internal resistance with the charge–discharge cycle at different discharge rates.

A fine conductive network of β-CoOOH transformed from nanoscale CoO could prevent the emergence of γ-NiOOH and hold back the swelling of the positive electrodes. Thus, the augmentation of internal resistance was weakened subsequently.

3.2. Mean voltage of discharge

The high power performance of Ni/MH batteries is not only depending on the high-rate discharge current, but also depending on the working voltage. High mean discharge voltage means higher discharge potential and more energy that the batteries can store and release. Fig. 4 shows the comparison of the mean discharge voltage curves of batteries with different content of nanoscale CoO at various discharge rates. As shown in Fig. 4, the addition of nanoscale CoO in the positive electrode has enhanced the mean discharge voltage obviously, especially at high discharge rate.

The load voltage of chemical power source is attributed to total polarization, and the high total polarization lead to low load voltage. The fine β-CoOOH conductive network, transformed from nanoscale CoO, not only reduced the ohmic polarization but also helped to reduce the charge transfer polarization. Therefore, the total polarization was restrained to a low level and the mean voltage was optimized by the addition of nanoscale CoO.

3.3. High-rate capability

Table 2 shows the high-rate capability of batteries with different content of nanoscale CoO. The high-rate capability of Ni/MH battery is calculated from the formula as:

$$\text{High-rate capability (\%)} = \frac{C_{nC}}{C_{nC} + C_{0.2C}} \times 100$$

In the formula, the batteries are charged with 0.2 C constant current for 6.5 h, rest for 10 min, then discharged with nC ($n = 1, 5, 10$) constant current to the cut-off voltages of 1.0 V, the discharge capacity is C_{nC}. After each discharge at nC rate and 20 min rest, the batteries are further discharged at 0.2 C rate down to 1.0 V, the discharge capacity is $C_{0.2C}$.

As shown in Table 2, the battery with normal CoO in the positive electrode exhibits high-rate capabilities of 93.7% at 1 C, 86.3% at 5 C and 77.1% at 10 C discharge rate. The battery with 4% content of nanoscale CoO presents a capability of 92.7% at 1 C, but the capabilities deteriorate seriously at higher discharge rates, with a result of 75.9% at 10 C discharge rate. With increasing the content of nanoscale CoO, the high-rate discharge capabilities were enhanced. For
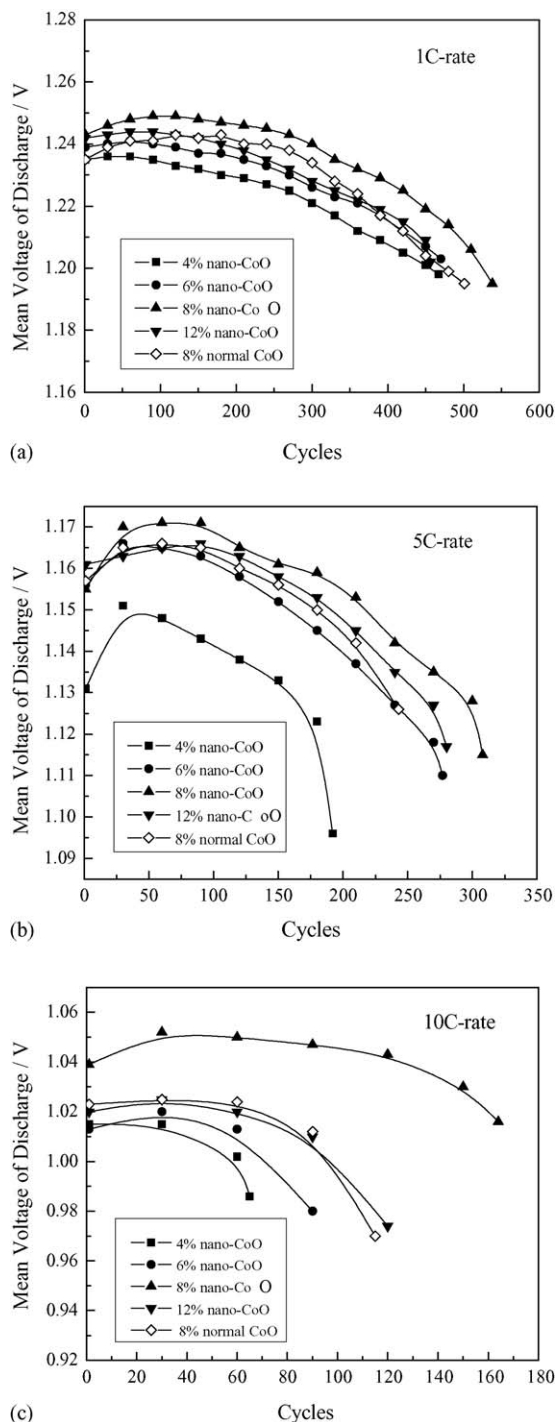

Fig. 4. Variation of the mean discharge voltage with the charge–discharge cycle at different discharge rates.

Table 2
High-rate capabilities of four groups of Ni/MH batteries

Discharge rate	4% nano-CoO (%)	6% nano-CoO (%)	8% nano-CoO (%)	12% nano-CoO (%)	8% normal CoO (%)
1 C	92.7	94.5	95.4	94.8	93.7
5 C	82.0	87.7	91.3	90.1	86.3
10 C	75.9	84.7	88.6	85.2	77.1

instance the battery with 8% content exhibits a capability of 88.6% at 10 C discharge rate. But too much CoO addition results in a decline of capability, such as the battery with 12% nanoscale CoO shown in Table 2.

4. Conclusions

(1) The general performance of Ni/MH batteries was enhanced by the addition of nanoscale CoO instead of normal CoO. The specific capacity increased as well as the mean discharge voltage, and the internal resistance decreased. The charge–discharge processes were more stable and the decline of capacity was weakened.

(2) The enhancement of general performance was especially obvious when discharged at high-rate. The batteries with sufficient nanoscale CoO still exhibited high specific capacity, high mean discharge voltage and low internal resistance. High-rate capability was also enhanced by the addition of nanoscale CoO. The results indicate that the nanoscale CoO is excellent additive for high power Ni/MH batteries.

(3) Addition of 8 wt.% nanoscale CoO is a suitable content for $Ni(OH)_2$ electrodes. Too much nanoscale CoO presents no improvement on the battery performance.

Acknowledgement

References

[1] D. Ohms, M. Kohlhase, G. Benczur-Urmossy, G. Schadlich, New development on high power alkaline batteries for industrial applications, J. Power Sources 105 (2002) 127–133.

[2] H. Bode, K. Dehmelt, J. Witte, Zur kenntnis der nickelhydroxidelektrode-I. über das nickel(II) –hydroxidhydrat, Electrochem. Acta 11 (1966) 1079–1087.

[3] A.H. Zimerman, P.K. Effa, Discharge kinetics of the nickel electrode, J. Electrochem. Soc. 131 (1984) 709–713.

[4] Anbao Yuan, Shaoan Cheng, Jiangqing Zhang, Chunan Cao, Effects of metallic cobalt addition on the performance of pasted nickel electrodes, J. Power Sources 77 (1999) 178–182.

[5] Wu Jiangbo, Tu Jiangping, Han Taian, Zhou Caiming, Zhang Wenkui, Zhao Xinbing, CoO as additives in positive electrode of nickel-metal hydride battery, J. Chem. Ind. Eng. (China) 55 (s) (2004) 197–200.

[6] M. Oshitani, H. Yufu, K. Takashima, S. Tsuji, Y. Matsumaru, Development of a pasted nickel electrode with high active material utilization, J. Electrochem. Soc. 136 (1989) 1590–1593.

[7] J. Lv, J.P. Tu, W.K. Zhang, J.B. Wu, H.M. Wu, B. Zhang, Effects of carbon nanotubes on the high-rate discharge properties of nickel/ metal hydride batteries, J. Power Source 132 (2004) 282–287.

[8] A.M. Hermann, P.A. Ramakrishnan, V. Badri, P. Mardilovich, W. Landuyt, Metal hydride batteries research using nanostructured additives, Int. J. Hydrogen Energy 26 (2001) 1295–1299.

[9] J. Yan, Z. Zhou, Y.X. Li, D.Y. Song, Y.S. Zhang, Structure and property changes of positive and negative electrode in Ni/MH batteries during charge/discharge cycles, Inorg. Chem. 14 (1998) 74.

[10] P. Elumalai, H.N. Vasan, N. Munichandraiah, Electrochemical studies of cobalt hydroxide – an additive for nickel electrodes, J. Power Sources 93 (2001) 201–208.