

Short communication

Effects of barium and cobalt on electrochemical performance of nickel hydroxide with chemically co-precipitated zinc

Cheng Shaoan ^{*}, Yuan Anbao, Liu Hong, Zhang Jianqing, Cao Chunan

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Received 8 July 1998; accepted 20 August 1998

Abstract

The effects of $\text{Ba}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ on electrochemical performance of nickel hydroxide prepared with chemically co-precipitated zinc in a nickel-metal hydride battery (Ni-MH) are studied. The results show that the oxygen-generation potential and the discharge depth of the nickel electrode are improved by the combined addition of $\text{Ba}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ compared with only $\text{Co}(\text{OH})_2$. The capacity of the Ni-MH battery is also enhanced due to increase in the utilization of the active material of the positive electrode. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Barium hydroxide; Cobalt hydroxide; Nickel electrode; Nickel/metal hydride battery; Charging efficiency

1. Introduction

For nickel/metal-hydride batteries (Ni-MH), the capacity and charge–discharge curve are mainly determined by the electrochemical properties of the positive electrode. This is because the capacity of the negative metal hydride electrode is usually greater than that of the positive nickel electrode. Improvement of positive active-material utilization is critical for the development of Ni-MH batteries with high capacity. Studies in this area have focused on additives in addition to the development of high activity $\text{Ni}(\text{OH})_2$ materials. The typical charge curve of a nickel electrode is shown in Fig. 1 [1]. V_{ox_1} is the median oxidation potential, V_{ox_2} is the maximum oxidation potential, and V_{O_2} is the oxygen evolution potential. The voltage difference between V_{O_2} and V_{ox_2} is the charge efficiency of the nickel electrode. Additions of Ni, Co, CoO, $\text{Co}(\text{OH})_2$, ZnO and $\text{Cd}(\text{OH})_2$ to the active materials have been shown to increase the electron conductivity, oxygen evolution potential and active-material utilization [1–5].

$\text{Ba}(\text{OH})_2$ advanced in the 1950s and 1960s [2] and in the 1990s [6–9] as an effective additive for increasing the oxygen evolution potential. These studies, however, focused mainly on the sole addition of $\text{Ba}(\text{OH})_2$. Simultane-

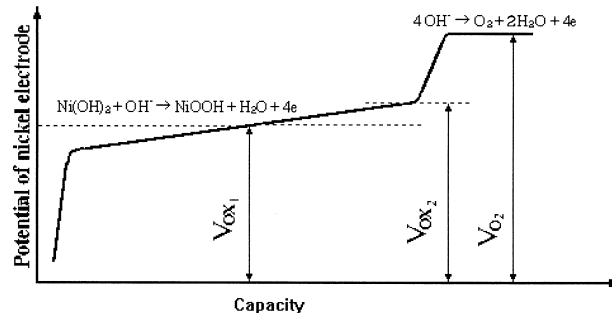


Fig. 1. Typical charge curve of a nickel electrode.

ous use of $\text{Ba}(\text{OH})_2$ with $\text{Co}(\text{OH})_2$ and/or $\text{Zn}(\text{OH})_2$ has not been reported. This paper examines the influence of the simultaneous addition of $\text{Co}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ on the electrochemical performance of nickel hydroxide prepared with chemically coprecipitated zinc.

2. Experimental

2.1. Preparation of nickel hydroxide electrode and Ni-MH battery

The test nickel electrodes were prepared by mixing spherical nickel hydroxide powder (from Canada, co-precipitated with wt. 4% Zn) with a certain proportion of

^{*} Corresponding author. Tel.: +86-571-7951513; Fax: +86-571-7951358; E-mail: cncao@sun.zju.edu.cn

Table 1
Type and amount of additives

Electrode	Acetylene black (wt.%)	Co(OH) ₂ + Co (wt.%)	Ba(OH) ₂ (wt.%)
#0	1	10	0
#1	1	9	1
#2	1	7	3
#3	1	5	5

additives and binder to form a slurry which was applied to a foam-nickel substrate (1.5 mm thick) with an electrical nickel lead. The pasted electrodes were dried at 60°C and press-shaped. The electrode dimensions were 20 × 20 × 0.65 mm. The additives are listed in Table 1.

The nickel electrode used in the test Ni-MH batteries (4/5 A type) was prepared from the 2# mixture. The negative electrode was made from a AB₅ type hydrogen-storage alloy. Both positive and negative electrodes were produced by a slurry-filling technology and a foam-nickel substrate. A PP separator and 7 M KOH + 1 M LiOH solution was used. The test battery with a design capacity of 1700 mA h was assembled and sealed before testing. Battery A contained 10 wt.% Co(OH)₂ + Co and battery B contained 7 wt.% Ba(OH)₂ and 3 wt.% Co(OH)₂.

2.2. Determination of electrochemical performance

To test nickel electrodes, one nickel electrode (wrapped in separator) with a MH electrode in either side was

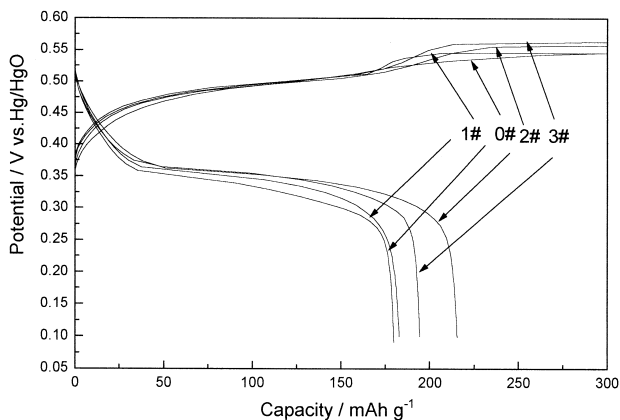


Fig. 2. Third charge-discharge curves of various Ni electrodes. Charging at 50 mA g⁻¹ for 6 h, discharge at 50 mA g⁻¹ to 0.1 V vs. Hg/HgO.

Table 2
Charge/discharge data for various Ni electrodes

Electrode	Oxygen evolution potential (V vs. Hg/HgO)	Median oxidation potential (V vs. Hg/HgO)	V _{O₂} - V _{ox₂} (mV)	Active material utilization (%)	Recovery potential (V vs. Hg/HgO)
#0	0.543	0.486–0.488	14	72	0.325
#1	0.545	0.486–0.488	19	73	0.321
#2	0.554	0.486–0.488	37	86	0.312
#3	0.557	0.486–0.488	44	82	0.310

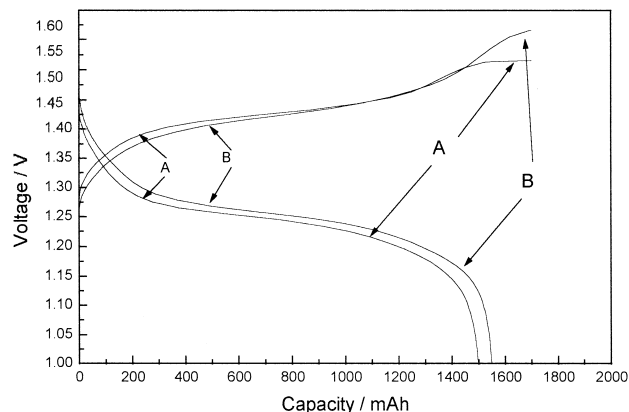


Fig. 3. Influence of addition of Ba(OH)₂ on the charge-discharge curve of a Ni-MH battery: (A) without Ba(OH)₂; (B) with Ba(OH)₂.

immersed in KOH solution and a Hg/HgO electrode was used as a reference electrode. The test nickel electrodes were charged at 0.1 C for 15 h and discharged at 0.2 C to 0.1 V (vs. Hg/HgO), followed by two cycles of charge for 6 h and discharge to 0.1 V, both at the 0.2 C rate. The activation process for the test Ni-MH batteries was charge at 0.1 C for 15 h and discharge at 0.2 C to 1.0 V, followed by four cycles of charge for 6.5 h and discharge to 1.0 V, both at the 0.2 C rate. The batteries are tested at charge/discharge currents of 300, 500 and 1000 mA, respectively in order to compare the capacity at high rates.

3. Results and discussion

The third charge-discharge curves of various Ni electrodes are shown in Fig. 2. The related characteristic data are listed in Table 2. It can be seen that the addition of Ba(OH)₂ has no influence on the median oxidation potential of the Ni electrode, but it increases the potential of oxygen evolution and median discharge, and so increases the active-material utilization. From the recovery potential after discharge, it is found that the addition of Ba(OH)₂ increases the discharge depth. It is generally agreed that the mechanism of the effect of Ba is similar to that of Co, i.e., the added Ba(OH)₂ dissolves and then precipitates on the surface of nickel hydroxide particles and, hence, raises the oxygen evolution potential. The reason for low active-material utilization of electrode #3 may be due to a decrease of conductivity because of the lower Co content.

Table 3
Discharge capacity of batteries

Battery	Amount of Ba(OH) ₂ (wt.%)	Discharge capacity at 300 mA	Discharge capacity at 500 mA	Discharge capacity at 1000 mA
A	0	1587	1512	1420
B	3	1616	1561	1489

The charge–discharge (charge at 850 mA and discharge at 500 mA) curves for batteries which have positive electrodes with 3 wt.% or zero Ba(OH)₂ are shown in Fig. 3. The data show that battery B with Ba(OH)₂ exhibits a slightly lower initial voltage. The maximum charge voltage is elevated and the battery discharge voltage decreases slowly during the last phase of discharging such that the discharge capacity is prolonged. This suggests that the elevation of the potential of oxygen evolution increases the active-material utilization of the nickel electrode.

A comparison of the discharge performance of the two batteries is given in Table 3. The data reveal that the addition of Ba(OH)₂ also improves the high-current charging–discharging capability of the Ni-MH battery.

4. Conclusions

(1) Simultaneous addition of Ba(OH)₂ and Co(OH)₂ can increase the oxygen evolution potential, the charge efficiency, the discharge depth, and the active-material utilization of the nickel electrode.

(2) The addition of Ba(OH)₂ improves the high-rate charge–discharge capability of Ni-MH batteries.

Acknowledgements

The authors thank the Zhejiang Provincial Natural Science Foundation of China and the Chinese ‘863’ Project for supporting this work.

References

- [1] M. Oshitani, Y. Sasaki, K. Takashiwa, *J. Power Sources* 12 (1984) 219.
- [2] H. Bode, K. Dehmelt, J. Witte, *Electrochim. Acta* 11 (1969) 1079.
- [3] B. Ezhov, O. Malandin, *J. Electrochem. Soc.* 138 (1991) 885.
- [4] M. Oshitani et al., *J. Appl. Electrochem.* 16 (1986) 403–412.
- [5] B.C. Cornilsen, X. Shan, P.L. Loyselle, *J. Power Sources* 29 (1990) 453–466.
- [6] I. Munchisa, EPO, 523284, 1991.
- [7] I. Matsumoto, H. Ogawa, T. Iwaki, M. Ikeyama, *The Electrochem Soc. Proc.* 90 (1990) 203.
- [8] W.H. Zhu, J.J. Ke, H.M. Yu, D.J. Zhang, *J. Power Sources* 56 (1995) 75–79.
- [9] M. Unates, M. Folqier, *J. Electrochem. Soc.* 139 (1992) 2697.