

Effects of different methods of cobalt addition on the performance of nickel electrodes

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Abstract

Cobalt is an effective additive which is widely used in nickel electrodes. Three kinds of nickel electrodes with various cobalt levels are made with different methods of cobalt addition. The electrochemical properties, including charge–discharge characteristics of the nickel electrodes are investigated. It is found that the method used to add cobalt exerts a marked effect on electrode performance. Nickel electrodes with cobalt incorporated directly display excellent charge-discharge behaviour. By contrast, nickel electrodes co-precipitated with cobalt exhibit an adverse effect except at high-rate discharge. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

There has been increasing interest in the use of cobalt additives in the positive electrodes of rechargeable alkaline batteries since Edison patented its application for nickel electrodes [1].

The addition of cobalt to nickel electrodes has been studied extensively. Such work has emphasized categorizing the performance gains made by cycling nickel electrodes which have various levels of cobalt [2–6], and the mechanism of cobalt activity in nickel electrodes [7,8]. It is generally thought that Ni(OH)₂, which accumulates at the Ni(OH)₂/electrolyte interface, has poor conductivity and this prevents the discharge process. The presence of cobalt, however, provides a good electrical path between the nickel hydroxide particles and the substrate, and thus greatly improves the utilization of active material. Furthermore, Olivia et al. [9] and Armstrong et al. [6] have claimed that the addition of cobalt not only decreases the redox potential, but also increases the overpotential of oxygen evolution at the nickel electrode and thus gives an improvement in charge efficiency.

The above reports [2–13] [14] present some conflicting results which some investigators have suggested are proba-

bly due to difference in the crystallite size of the Ni(OH)₂, the electrode type, and the kind of electrolytes used in the various experiments. In our research, a difference in the methods of cobalt addition is the critically important feature. As is well known, cobalt additive can be added in different ways e.g., (i) adding cobalt additive to Ni(OH)₂ particles prepared previously, i.e., by mixing cobalt additive with Ni(OH)₂ uniformly or by micro-encapsulating Ni(OH)₂ with a layer of cobalt [15–17]; (ii) co-precipitating cobalt additive with Ni(OH)₂ by chemical reaction or by electrochemical reaction in a mixed solution of nickel and cobalt salts [18,19]. In the present work, the method of adding cobalt is found to exert a marked effect on the performance of nickel electrodes.

2. Experimental

2.1. Preparation of nickel hydroxide

Given amounts of nickel salt solution and alkaline solution were fed to a reaction tank at a fixed temperature with vigorous stirring. The product was filtered, dried, and washed with distilled water in order to remove any residual sulfate ions in the Ni(OH)₂. The product was dried again, pulverized, and sieved.

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Table 1

Effect of incorporation of cobalt and different cobalt content on performance of Type A electrodes

Cobalt content (wt.%)	0	1.0	2.0	3.0	5.0	7.0	9.0
Average discharge voltage (V)	1.226	1.227	1.228	1.227	1.229	1.227	1.228
Specific capacity (mAh g ⁻¹)	265.3	271.4	287.0	288.4	292.5	295.4	295.5
Utilization ratio (%)	91.7	93.8	99.2	99.7	101.1	102.1	102.1

Nickel hydroxide was co-precipitated with cobalt hydroxide by chemical reaction on mixing an alkaline solution and mixed Ni²⁺ and Co²⁺ solutions with different Co²⁺ content.

2.2. Preparation of nickel electrode

The metal fibre substrate was cut to dimensions of 1 cm wide × 1 cm long. Nickel hydroxide powder mixed with certain amount of fine nickel metal powder (Inco 255) was fed directly to the mould with the metal fibre substrate, then pressed under 25 MPa pressure. The electrode dimensions were 1 cm × 1 cm × 0.2 cm. The electrodes were surface treated with PTFE to prevent the active material from falling off the electrode during charge–discharge cycling.

The studies were carried out using the following types of electrodes: (A) a series of electrodes with cobalt metal powder at various levels from 0 to 10 wt.% incorporated directly into the nickel hydroxide; (B) nickel hydroxide samples co-precipitated with different cobalt hydroxide contents; (C) nickel hydroxide samples co-precipitated with different cobalt content, and doped with cobalt metal powder.

2.3. Test procedure

A single nickel electrode was sandwiched between two commercial cadmium electrodes and the assembly was immersed in 30% KOH solution in an open cell for testing.

Constant-current charge–discharge experiments were performed at 25 ± 2°C, 1 atm. The test cell was charged

for 7.5 h at 0.2 C mA, kept for 0.5 h at open-circuit, and then discharged at the 0.2 C rate to 1.000 V vs. a cadmium anode. The same regime was adopted in the following cycles until the discharge capacity became constant. High-rate charge–discharge experiments were performed after the test cell reached a stable condition at the 0.2 C mA rate (usually in three cycles).

The theoretical capacity of nickel hydroxide is 289.4 mA h (g-active material)⁻¹ by assuming the electrode reaction is Ni(OH)₂ + OH⁻ ⇌ NiOOH + H₂O + e⁻.

3. Results and discussion

3.1. Electrochemical characteristics of type A nickel electrodes

The effect of different contents of cobalt upon the utilization of active material and the average discharge voltage type A of the electrodes are shown in Table 1.

It can be seen that the method of incorporating cobalt directly to electrode greatly improves the utilization of the active material and increases the average discharge voltage of the battery. Furthermore, the effect becomes more marked with increase in cobalt content. The 5 wt.% cobalt electrode exhibits the highest average discharge voltage among these electrodes. Increasing the cobalt content only leads to a slight improvement in characteristics.

The utilization of active material in electrodes containing cobalt is close to or even over 100%. This result agrees

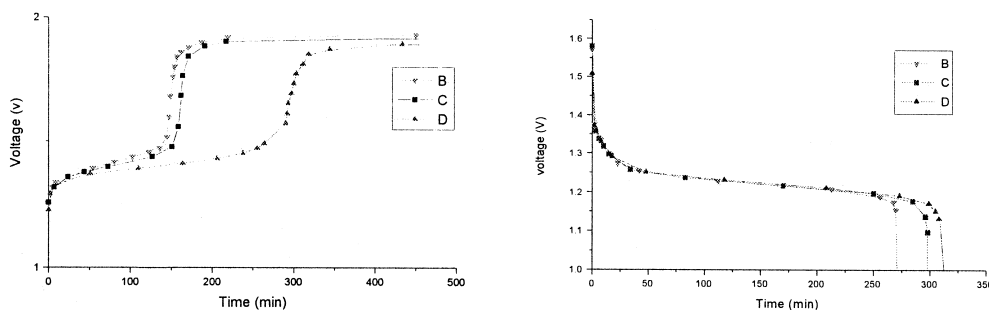


Fig. 1. Constant-current charge and discharge curves of electrode A at 0.2 C containing different content cobalt: (B) nickel electrode without cobalt; (C) incorporation of 3 wt.% cobalt; (D) incorporation of 7 wt.% cobalt.

Table 2

Effect of co-precipitation of cobalt and different cobalt contents on performance of type B electrodes

Cobalt content (wt.%)	0	0.5	1.0	1.5	3.0	5.0	7.0
Average discharge voltage (V)	1.226	1.214	1.213	1.211	1.208	1.201	1.200
Specific capacity (mAh g ⁻¹)	265.3	254.4	241.0	247.2	250.0	257.6	262.5
Utilization ratio (%)	91.7	87.9	83.3	85.4	86.5	89.0	90.7

with the work of M. Oshitani [14] who added cobalt additives in the same manner. It is generally thought that the nickel electrode's difficulty in discharging is due to poor current conduction between the nickel hydroxide and the substrate. Oshitani claimed that the addition of nickel powder does not improve the active-material utilization, because mere mixing of nickel powder with Ni(OH)₂ cannot provide the continuity of a good electrical path. It is therefore believed that the use of cobalt provides a good electrical path between nickel hydroxide and the substrate, and, thereby, will improve the active-material utilization of the nickel electrode during discharging.

Typical constant-current charge and discharge curves of type A electrodes containing different content cobalts are shown in Fig. 1. For comparison the curve for a Ni(OH)₂ electrode without cobalt is also presented. It is found that the charge potential and the top-of-charge potential of a cobalt-containing electrode are lower than that of electrodes, and decrease with increase in cobalt content. A cobalt-containing nickel electrode exhibits a higher oxygen overpotential. It can be seen that the discharge curves of a cobalt-containing electrode have a longer plateau, a greater

capacity, and a higher average discharge voltage than those obtained from an electrode without cobalt.

3.2. Electrochemical characteristics of type B nickel electrodes

The effect of co-precipitation of cobalt on the electrochemical performance of type B electrodes is shown in Table 2.

The data show that co-precipitation of cobalt does not improve the performance of nickel electrode. Indeed, the active-material utilization and the average discharge voltage both decrease in the presence of cobalt. Furthermore, the average discharge voltage decreases with increase in the cobalt content. The relationship between cobalt content and the utilization is complex. The utilization begins to increase when the cobalt content is greater than 1.0 wt.%.

The effect of co-precipitation of cobalt on the charge and discharge curves at different rates is presented in Fig. 2. For the charge curves, oxygen overpotential and the top-of-charge potential both increase with increase in cobalt content, but the charge potential decreases. The discharge

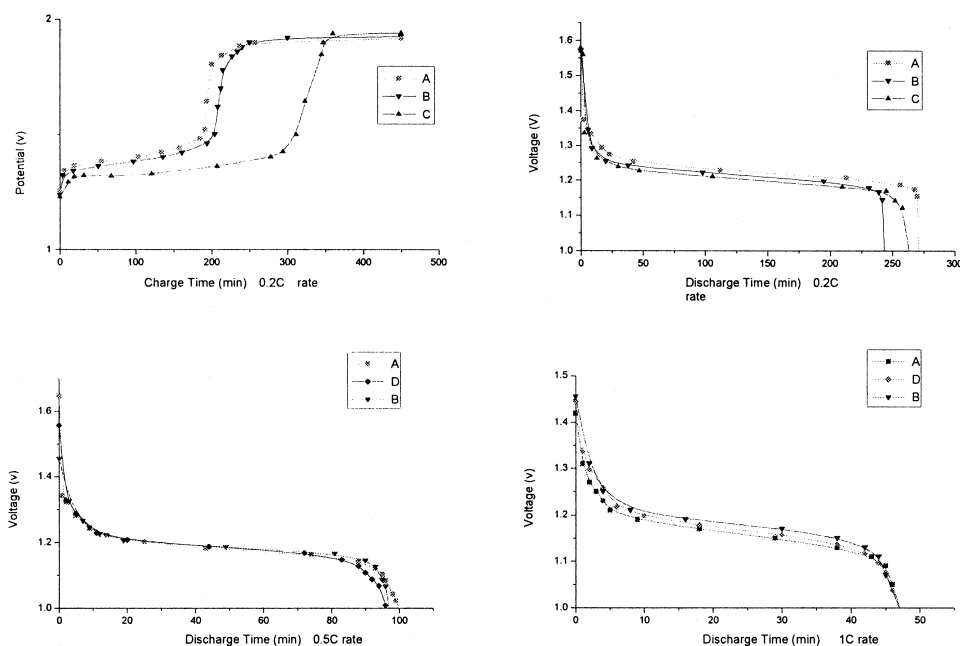


Fig. 2. Effect of co-precipitation of cobalt on charge and discharge curves at different rates: (A) nickel electrode without cobalt; (B) co-precipitation of 3 wt.% cobalt; (C) co-precipitation of 7 wt.% cobalt; (D) co-precipitation of 1 wt.% cobalt.

Table 3
Electrochemical characteristics of type C electrode

Incorporation of cobalt (wt.%)	Co-precipitation of cobalt (wt.%)	Average discharge voltage (V)	Utilization ratio (%)
0.5	2.5	1.219	95.9
0.5	4.5	1.216	97.7
1.0	2.0	1.217	93.8
1.0	4.0	1.220	95.2

curves also decrease with increase in cobalt content. Increase in the top-of-charge potential and depression of the discharge potential is considered in general, to be detrimental as the cell operating voltage is lowered. The result is in reasonable agreement with the studies of Watanabe et al. [12] and Armstrong et al. [6] who examined samples co-precipitated with cobalt. The cobalt-containing electrode displays good performance compared with electrodes without cobalt in discharge curves performed at a high-discharge rate.

3.3. Electrochemical characteristics of type C nickel electrodes

The characteristics of type C electrodes are listed in Table 3. Clearly, the characteristics are superior to those of

type B electrodes, but inferior to those type A electrodes which contain the same cobalt content. Similar effects are found for the discharge performance at 0.5 C rate. Only at the 1 C discharge rate, does type C electrodes exhibit slight superiority over type A electrodes.

4. Conclusions

Analysis of our experimental results, as well as the curves showing the effects of different methods of cobalt addition are presented in Figs. 3 and 4, shows that incorporation of cobalt into the electrode invokes excellent charge-discharge behaviour. By contrast, the chemical co-precipitation method exerts the opposite influence. As can be seen from the high-rate discharge curves, the curves obtained by the two methods of adding cobalt both display superior discharge behaviour composed with that of an electrode without cobalt. Furthermore, discharge curves for electrodes with cobalt exhibit the longest plateau and the highest average discharge voltage. The method of adding cobalt directly to the electrode appears to be more effective than the chemical co-precipitation method. Only at the 1 C discharge rate, does the electrode incorporating a certain amount cobalt metal powder and co-precipitated with a small content cobalt display slight superiority.

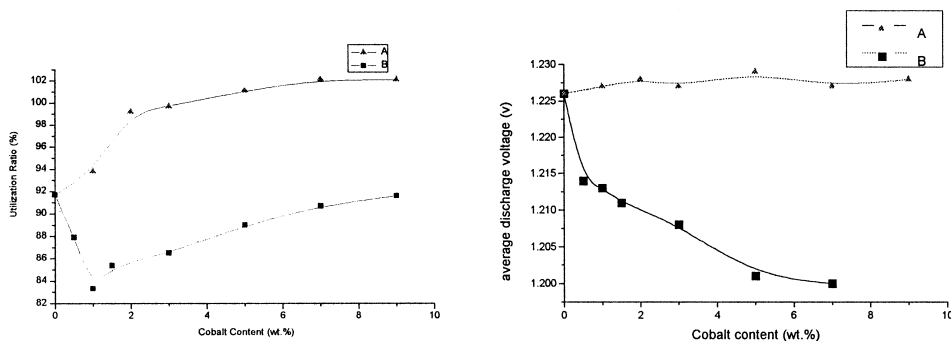


Fig. 3. Effect of different methods of adding cobalt and cobalt content on the utilization and average discharge voltage of nickel electrodes: (A) incorporation of cobalt; (B) co-precipitation of cobalt.

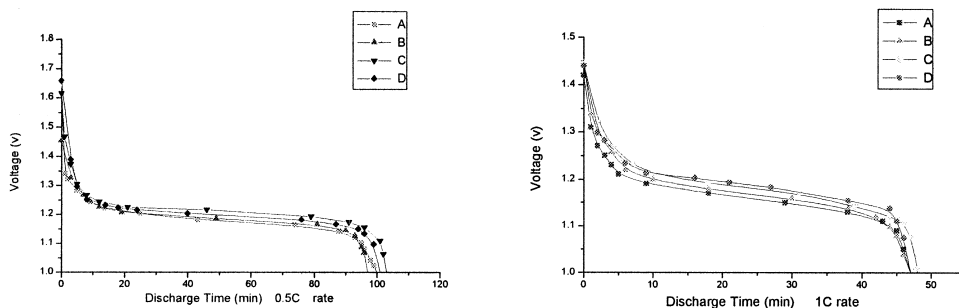


Fig. 4. Effect of different methods of adding cobalt on discharge curves at different discharge rates (A) 0 wt.% cobalt electrode; (B) co-precipitation of 3 wt.% cobalt electrode; (C) incorporation of 3 wt.% cobalt electrode; (D) co-precipitation of 1 wt.% and incorporation 2 wt.% cobalt electrode.

References

- [1] T.A. Edison, US Patent No. 1 083 356, 1914.
- [2] D.F. Pickett, J.T. Maloy, J. Electrochem. Soc. 125 (1978) 1026.
- [3] P.R. Herman, S. Lerner, H.N. Seiger, NASA Technical Report CR-72128, 1966.
- [4] H.H. Kroger, Air Force Technical Report AFAPL-TR-71-21, 1971.
- [5] D.W. Maurer, R.L. Beauchamp Abstract 7, P. 23, The Electrochemical Society, Extended Abstracts, Fall Meeting, Cleveland, OH, Oct. 3–7, 1971.
- [6] R.D. Armstrong, G.W.D. Briggs, E.A. Charles, J. Appl. Electrochem. 18 (1988) 215.
- [7] D.H. Fritts, J. Electrochem Soc. 129 (1982) 118.
- [8] B.E. Ezhov, O.G. Malandin, J. Electrochem. Soc. 138 (1991) 885.
- [9] P. Oliva, J. Leonardi, J.F. Laurent, J. Power Sources 8 (1982) 229.
- [10] D. Yamashita, Denki Kagaku 31 (1963) 228.
- [11] K. Watanabe, T. Kikuoka, J. Power Sources 25 (1995) 219.
- [12] K. Watanabe, M. Kumagai, K. Kumagai, N. Kumagai, J. Power Sources 58 (1996) 23.
- [13] M.E. Uñates, E. Folquer, J. Electrochem. Soc. 139 (1992) 2697.
- [14] M. Oshitani, H. Yufu, K. Takashima, J. Electrochem. Soc. 136 (1989) 1590.
- [15] Jpn Patent No. 60 170 [161 85 170 161].
- [16] Jpn Patent No. 61 124 061 [86 124 61].
- [17] D. Yunchang, Y. Jiongliang, J. Power Sources 66 (1997) 55.
- [18] Eur. Patent No. EP 523 284.
- [19] Jpn. Patent No. 59 165 370 [84 165 370].