Studies on Sintered-Type Alkaline Storage Batteries. VII

Effect of Cobalt on the Positive Plates of Sintered-Type Alkaline Storage Batteries*

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Received June 25, 1963

The author studied the effects of cobalt on the positive plates of sintered-type alkaline storage batteries by the experiments as follows.

- (1) Charge-discharge curve of the active material of Ni-Co system.
- (2) Durability test (capacity change by repeating charge-discharge for long period).
- (3) Low rate charge test.
- (4) X-ray diffraction diagram and electronmicrophotograph of active material.

According to these experimental results, charge-discharge potential dropped with increasing content of cobalt and active material seems to be solid solution (Ni, Co) (OH)₂ up to 20% Co, but mixture of (Ni, Co) (OH)₂ and Co(OH)₃ over 30%. The availability of active material increased by only 5% addition of cobalt.

Capacity drop by charge-discharge for long period and by low rate charge may be fairly prevented by the addition of cobalt.

This behavior of cobalt is probably due to the formation of solid solution (Ni, Co) (OH)₂ in active material.

1. Introduction

The addition of cobalt to the active material of positive plates was applied in the practical use of Ni-Cd alkaline storage batteries¹⁾.

S. Januszkiewicz reported²⁾ that the addition of cobalt results to raise the availability of active material and the author studied on the reaction mechanism and on the effects on capacity change by repeating charge-discharge and on low rate charge, which were not yet reported in details.

2. Experimental

2.1 Grid

As previously reported^{3), 4)}, the iron nets of 14 meshes were spotwelded on an iron plate frame 30×30 mm wide and annealed after nickel plating.

2.2 Sintering

Nickel carbonyl of apparent density 1.0 g/cc

was used and sintered at 930°C for 15 min. under hydrogen atmosphere. The porosity of the product was about 80%.

2.3 Charge-discharge Curve of Ni-Co Active Material

Positive plates (Table 1) were prepared as follows. After preheating at 220°C for 10 min., plaques were thrown into the fused mixture of nickel and cobalt nitrates and repeated for four times to heat at 220°C for 30 min. and to throw, then plaques were electrolytically reduced in 25% KOH solution at 80°C and dried. The plates which have no cobalt were used as standard and were charge-discharged under 0.20 A and all other plates were charge-discharged under the same hour rate. Potential curve was obtained by use of potentiometric autobalance recorder, referring its potential to Hg/HgO/N-KOH standard electrode. These curves are shown in Fig. 1.

Charge curve: Potential falls with increasing

* Presented partly at 29th Annual Meeting of Electrochem. Soc. Japan held on April 30, 1962 at Sendai.
The original written in Japanese can be seen in *Denki-Kagaku* 31, 228, (1963).

Table 1 Positive Plates Containing Cobalt

No. of plates	1	2	3	4	5	6	7	8	9	10	11
Co content (%)	0	5	10	20	30	50	70	80	90	95	100
Wt. of plaque (g)	3.63	3.53	3.31	3.21	3.78	4.06	3.83	3.88	3.86	4.10	3.72
Wt. of nickel powder (g)	1.74	1.72	1.47	1.38	1.95	2.10	1.96	1.91	1.98	2.22	1.82
Thickness of plate (mm)	1.5	1.5	1.4	1.4	1.6	1.7	1.6	1.6	1.6	1.7	1.6
Wt. of active material*	1.11	1.03	0.84	0.83	1.27	1.35	1.33	1.36	1.62	1.42	1.49
Capacity calculated (AH)*	0.323	0.299	0.245	0.241	0.370	0.387	0.383	0.392	0.465	0.407	0.430
Initial capacity (AH)**	0.170	0.240	0.220	0.200	0.350	0.416	0.310	0.286	0.280	0.240	0.233
Availability (%)	52.6	80.3	90.0	83.0	94.5	107.5	81.0	73.1	60.1	59.0	54.2

* Capacity is calculated considering weight increase of plaque after drying as Ni(OH)₂.
** Capacity is obtained by discharging to 0.5 volt.

Fig. 1 (A) Charge curve (25°C).

Fig. 1 (B) Discharge curve (25°C).

content of cobalt, but at the end of charge the potential almost equal to that of the sample which has no cobalt. Especially high potential appears at the sample of 30% cobalt and it keeps almost constant to that of 100% Co, while initial potential falls with increasing content of cobalt.

Discharge curve : Potential falls suddenly even at the sample of 5% cobalt, but keeps constant to that of 30% cobalt, while the availability of active material increases with increasing content of cobalt.

Potential falls as the cobalt content increases and it shows extremely low value at that of about 100% cobalt.

2.4 Durability Test
2.4.1 Preparation of Positive Plates for Durability Test

Positive plates were prepared along the method as shown in Table 2 and the properties of the plates are listed in Table 3.

2.4.2 Durability Test

Positive plates obtained by the above mentioned method were fixed between two negative pocket type cathodes and added 25% KOH solution as electrolyte. Capacity change caused by repeating charge-discharge were measured with use of automatic charge-discharge apparatus.

Charge-discharge condition : (A) 0.20 A 40

Table 2 Impregnation Methods (A and B)

A	B
1) Heating plaques at 220°C for 10 min.	
2) Throwing in to fusing mixture of Ni(NO ₃) ₂ ·6H ₂ O and Co(NO ₃) ₂ ·6H ₂ O at 60°C.	
3) Electrolytically reduced in 25% KOH at 80°C	3) Heating again at 220°C for 30 min.
4) Washing	4) Soaking in 25% KOH at 80°C for 16 h.
5) Drying	5) Washing
	6) Drying

Table 3 Positive Plates for Durability Test

Impregnation method	(A)					(B)		
	Plaques preheated at 220°C for 10 min. are thrown into fused nitrate and electrolytically reduced in 25% KOH.					Plaques preheated at 220°C for 10 min. are thrown into fused nitrate and soaked in 25% KOH at 80°C for 16 h.		
No. of plates	12	13	14	15	16	17	18	19
Cobalt content (%)	0	5	10	20	30	0	5	10
Wt. of plaque (g)	3.63	3.43	3.45	3.60	3.60	3.79	3.80	4.05
Wt. of active material (g)	0.351	0.275	0.362	0.385	0.309	0.571	0.445	0.543
Capacity calculated (AH)	0.102	0.080	0.105	0.112	0.090	0.151	0.115	0.136
Initial capacity (AH)	0.087	0.067	0.107	0.094	0.064	0.140	0.120	0.133
Availability (%)	85.6	71.3	102.0	84.0	71.3	93.0	104.5	97.9

min. charge, 0.20 A 20 min. discharge, (B) 0.30 A 40 min. charge, 0.30 A 20 min. discharge. At 1000 cycles electrolyte was replaced.

The results obtained in this test are shown in Figs. 2 and 3. The capacity change is shown regarding initial capacity as 100.

According to these test, the effects of cobalt appeared distinctly after 1000 cycles and the degree of capacity drop decreases with increasing content of cobalt.

Fig. 2 Capacity change by durability test (Table 2 A).

Fig. 3 Capacity change by durability test (Table 2 B).

2.5 Low Rate Charge Tests

In order to investigate the influence of low rate charge, plates containing cobalt <30% as shown in Table 2 were overcharged to 150% of initial capacity under 0.20 A and discharged under the same rate and these capacity was regarded as 100.

Then after charging under 20~95 hours rate, capacity was measured under 0.20 A discharge. These results are shown in Fig. 4. The capacity drops remarkably at 0% cobalt, but become fairly small at 5% cobalt and extremely small at 30% cobalt.

2.6 X-ray Diffraction Diagram of Active Material

2.6.1 Change of X-ray Diffraction Diagram by Repeating Chare-discharge

Every sample contains nickel hydroxide in large amount of nickel powder. Fig. 5 shows X-ray diffraction diagram of active material in discharged state (in the plates prepared along

Fig. 4 Capacity change by low rate charge.

(a) 2,000 cycles Co 10% (c) 2,000 cycles Co 0%
(b) 2,000 cycles Co 5% (d) 2 cycles Co 0%

Fig. 5 Change of X-ray diagram by charge-discharge (CuK_α).

the method shown in Table 2 (A)) at 2000 cycles. In this diagram the line of the plates containing no cobalt grows fairly, but that of the plates containing cobalt grows relatively little.

2.6.2 X-ray Diffraction Diagram of Active Material

Fig. 6 shows X-ray diffraction diagram of active material and the samples (a), (b), (c) and (d) were prepared as follows. In case of (c) as shown in Fig. 7, several nickel nets of about 50 meshes were piled tightly in plastic vessel A and nickel nitrate fused at 80°C was poured into this vessel until about half of the depth of nickel net was immersed. The electrolysis was carried out, using 25% KOH as electrolyte, vessel A as cathode and nickel net B as anode under 10 A/dm^2 at 80°C for 20 min. Then the active material was taken out, washed and dried (this sample is considered as that prepared along the method shown in Table 2 A).

Samples (a), (b) and (d) were prepared as follows. Fused salt heated in air at 220°C for 1 hour was soaked in 25% KOH at 80°C for 16 hours and then washed and dried. Sample (a) contains 10% cobalt, (b) 5% cobalt and (c) 0% cobalt.

Shapes of diffraction diagram were different from each other and the strength of diffraction line increases and diffusion degree decreases in

(a) Fused salt (Co 10%). Heating at 220°C , for 1h. Soaking at 80°C in 25% KOH for 16 h.
(b) Fused salt (Co 5%). Heating at 220°C , for 1h. Soaking at 80°C in 25% KOH for 16 h.
(c) Fused salt (Co 0%). Electrolyzing under 2 A for 20 min in 25% KOH at 80°C .
(d) Fused salt (Co 0%). Heating at 220°C , for 1h. Soaking at 80°C in 25% KOH for 16 h.

Fig. 6 X-ray diffraction diagram of active material.

Fig. 7 Apparatus for reducing nickel nitrate.

order of (a), (b), (c) and (d).

2.7 Electron-microphotograph of Active Material

To confirm the effects of cobalt, samples were prepared by the following three methods:—

(a) Plaques were prepared as follows, nickel nets 30×30 mm wide and of 200 and 50 meshes were alternately piled and their edges were gripped by nickel frame. Plaques impregnated by nickel nitrate were electrolytically reduced in 25% KOH solution at 80°C . A nickel net of 200 meshes was taken out from the center of plaques was washed with water and dried with alcohol at room temperature. Nickel nets of 3×3 mm wide were cut from edge and center of these nets were observed in deposited state.

(b) Plaques were prepared by the same method as (a). After heating impregnated fused salt at 220°C for 1 hour, plaques were soaked in 25% KOH solution for 16 hours and washed and then observed like (a).

(c) Nitrate heated at 220°C for 1 hour

was soaked in 25% KOH solution for 16 hours and then dispersed in alcohol. The samples were observed after air drying. Representative examples prepared by (a), (b) and (c) methods are shown in Photo 1.

It is considered by this photograph that the dispersion of active material is produced by addition of cobalt. Moreover, the separation of needle crystal appears by the addition of cobalt.

3. Discussion

In the charge curve shown in Fig. 1 (A), the initial potential drops with increase of cobalt content to 20%, but at the end of charge every plate has almost the same value. But over 30% high potential appears especially at the end of charge and the potential equals to that of the plate of cobalt 100%. According

- (a) Active material separated on nickel net by electrolysis.
 (b) Active material separated on nickel net by heating.
 (c) Active material decomposed by heating, dispersed in alcohol, dried in room temp.

(Black part is active material)

Photo 1 Electronmicrophotographs of active materials.

to the X-ray diffraction diagram (Fig. 6), the intensity increase of diffraction lines of (a) cobalt 10% and (b) cobalt 5% was smaller than that of (d) cobalt 0% and the diffusion of lines was found in (a) and (b).

On the samples prepared as follows—after preheating at 220°C for 1 hour, the mixed nitrate was soaked in 25% KOH solution for 16 hours and washed with water and dried—pale green nickel hydroxide has red grey color a little in the case of < cobalt 20%, but black grey color appears in the case of cobalt 20~30%. This color tone is fairly similar to that in case of cobalt 100%.

From these facts, cobalt was considered to exist as solid solution $(\text{Ni, Co})(\text{OH})_2$ in case of < 20% and excess cobalt was to separate as $\text{Co}(\text{OH})_3$ in case of > 20% and therefore active material formed two phases.

It is considered that charge curve of cobalt 30% is corresponding to the charge curve of solid solution of $(\text{Ni, Co})(\text{OH})_2$ and $\text{Co}(\text{OH})_3$. About discharge curve shown in Fig. 1 (B), initial potential drops suddenly by adding 5% cobalt and such state continues to that of cobalt 30%.

Lasting time of discharge increase with increasing cobalt content within this range. As seen in Fig. 6 (a), (b), when cobalt solutes in solid state, it is considered that crystals become unstable and charging becomes easy due to the increase of activity and therefore the availability of active material increases. At cobalt 50%, the availability was maximum, probably because two phases of active solid solution and $\text{Co}(\text{OH})_3$ exist, but the potential remarkably drops owing to the addition of cobalt. At cobalt 100%, the potential of discharge curve drops suddenly and it is considered that $\text{Co}(\text{OH})_3$ already grows in discharged state and therefore active material stays unchanged by charging.

On the durability tests of the sample prepared along the method shown in Table 2 A, the capacity drop begins after 300 cycles about the one containing no cobalt and the capacity

keeps almost constant value after 500 cycles in case of containing cobalt.

At 2000 cycles, the capacity difference between the plates is remarkable. On the other hand, according to the X-ray diffraction diagram (Fig. 5), the growth of diffraction line decreases with decreasing capacity drop. In the case of the sample prepared by the method shown in Table 2 (B), the effect of cobalt appears after 1000 cycles. Compared with (a), (b) and (d) in Fig. 6, the drop of capacity decreases with decreasing strength of line and with increasing diffusion of line. The drop of capacity decreases with increasing addition of cobalt. When cobalt solutes in active material, the activation of active material rises and cobalt continues this behavior.

According to Fig. 3, initial capacity drop is remarkable and it is probably because stabilization and coaguration of active material happens to occur by heating after impregnation. On the contrary, at cobalt 10%, initial drop is little, because cobalt prevents these action.

In Fig. 4, charging becomes easy due to the activation of active material by cobalt solid solution, therefore capacity drop is considered small by low rate charge.

4. Conclusion

The availability of active material of sintered-type alkaline storage batteries increases by the addition of cobalt. Also, charge and discharge potential drops are both small. Capacity decrease by charge-discharge for a long period is prevented only by 5% cobalt addition. And also, capacity drop by low rate charge is decreased. It is considered that these phenomena are attributed to the activation of crystals by the formation of cobalt solid solution in active material and by the dispersion of crystals originated from activation.

The author wishes to acknowledge in particular the assistance in X-ray analysis by Mr. Masao Fukui, University of Kyoto Polytechnic and Textile. He is also grateful to Mr. Y. Yamamoto, Mr. M. Ozasa and Mr. K. Hayashi

for their co-operation in this investigation.

Literature :

- 1) T.A. Edison, U.S. Pat. 678,722 (1901); U.S. Pat. 1,083,356 (1914).
- 2) S. Januszkiewicz, *Proceedings of Annual Power*

Source Conference **13**, 75 (1959).

- 3) D. Yamashita, Y. Takeuchi, *Denki-kagaku* **29**, 162 (1961).
- 4) D. Yamashita, Y. Yamamoto, Y. Takeuchi, *Kōgyō Kagaku Zasshi* **65**, 10 (1962).