Properties of Cobalt Oxide as an Active Material of Negative Electrode in Alkaline Storage Cell.

By Kyôji KINOSHITA.

(Received February 26, 1940.)

The author has reported previously, that the electrode plates of the alkaline storage cell could be made by using the metallic oxides such as silver oxide,(1) bismuth oxide,(2) and mercury oxide,(3) in the pasted form.

It was found recently, that cobalt oxide can be made into the negative electrode plate of the alkaline storage cell in the pasted form, just like other metalllic oxides mentioned above. The present paper describes the results of the experiments dealed with cobalt oxide.

(1) **Experimental.** (a) *Preparation of the cobalt oxide.* Three kinds of the oxides of cobalt having the compositions, CoO, Co_2O_3 and Co_3O_4 are known. In preparing the electrode plate in the pasted form, it becomes a matter of question that, which oxide out of these three should be chosen as the material of the paste.

In the preparation of the electrode plate of the lead acid storage cell, oxides such as Pb_2O (lead suboxide), and PbO (litherge) are preferred as the material of the paste, and the oxide of higher degree of oxidation seemed to lack cohesive power to be used as the material for the paste. From the analogy of this fact CoO, which is low in degree of oxidation, was chosen as the cobalt oxide for the experimental purposes.

The CoO which was used for the experiments was prepared by heating pure $CoCO_3$ in an electric furnace under the reduced atmospheric pressure to red heat and decomposing $CoCO_3$ by the reaction of

$$CoCO_3 \rightarrow CoO + CO_2 .$$

Changes in weight in the course of above reaction show that, the above mentioned decomposing reaction proceeds stoichiometrically. In this manner an oxide of greenish brown in colour could be obtained.

(b) *Experiments on the electrode plates in the pasted form.* CoO thus prepared was made into paste mixing with 5N NH_4OH, or 5N NH_4Cl, and then the paste was applied to the grid made of silver plated lead antimony alloy. The size of the grid used was about 6.0 cm. × 1.5 cm. × 0.3 cm.. As the pasting liquid, solution of NH_4Cl seemed to be more suitable than NH_4OH, because the cohesion of the cobaltous oxide paste was found to be excellent in this case.

The plate which had been applied with the paste of cobaltous oxide by the above method was negatively electrolyzed in 20% KOH solution

---

(1) K. Kinoshita, this Bulletin, **12**, (1937), 164, 366.

(2) K. Kinoshita, *ibid.*, **15**, (1940), 59.

(3) K. Kinoshita, *ibid.*, **15**, (1940), 82.

and was converted into the negative electrode plate of the alkaline storage cell (process of "formation").

That is, the "formation" was undertaken by the current of 50 milliamperes in 20% KOH solution. But with the starting of the "formation" violent evolution of gas was observed at the electrode, thereby it was supposed that the progress of the electrolytical reducing reaction of the active material at the electrode do not proceed properly.

The "formation" process was continued for about 30 hours and then the electrode plate thus formed was combined with positive electrode plate of Nife alkaline accumulator, and dipped in 20% KOH solution. The open voltage of the cell was found to be 1.564 volts, but when the discharge was started by the discharge current of 200 milliamperes the terminal voltage fell to about 1.1 volts and in 30 minutes it reached zero volt, that is, its discharge capacity was 0.1 amperehours. Then after a full overcharge by the charge current of 200 milliamperes, the cell was discharged by the discharge current of 200 milliamperes. This time its discharge capacity was found to be 0.074 amperehours.

It was thought, from the above results, that the active material which consists of CoO alone seemed wanting in electrolytical reversible nature to be used as an active material in storage cell. The fact that the violent evolution of gas in the process of "formation" may be accounted for as one evidence of this. The poor electrical conductivity of the oxide may be the principal cause of this irreversible nature.

In order to improve the electrical conductivity, therefore, a little amount of graphite powder was added to CoO. The cobalt oxide, CoO, which was produced by the thermal decomposition of $CoCO_3$ was mixed with graphite powder amounting 20 to 30%, and was made into paste with 5 N NH_4Cl solution, and then finished into two electrode plates. The constitutions of these two plates are shown in Table 1.

Table 1.

Number of electrode plate	Constitution of paste (amount of graphite) %	Amount of paste applied to grids (in grams)	Amount of CoO applied to grids w (in grams)
1	20	3.71	2.97
2	30	3.87	2.72

The "formation" of these plates were undertaken in 20% KOH solution by the current of 100 milliamperes for about 70 hours. Immediately after the "formation" the plates were combined with the positive electrode plates of Nife accumulator and subjected to discharge by the current of 100 milliamperes for five times in 20% KOH solution. The results of experiments are shown in Table 2.

As seen in Table 2, the discharge capacity C of cell No. 1 at any cycles of discharge gradually decreases from the value of C in preceeding cycle. The discharge capacity of cell No. 2 does not fall so markedly.

In the case of cell No. 1 appreciable amount of the active material fell off from the surface of the electrode plate, in the course of charges

Table 2.

Number of discharge n	Discharge current milli-amperes	Number of electrode plate			
		No. 1		No. 2	
		Discharge hour in hours	Discharge capacity C in ampere hours	Discharge hour in hours	Discharge capacity C in ampere hours
1	100	5.500	0.550	4.000	0.400
2	100	5.083	0.508	3.500	0.350
3	100	4.433	0.443	3.000	0.300
4	100	3.733	0.373	3.000	0.300
5	100	2.250	0.225	3.250	0.325

and discharges. In the cell No. 2 the active material fell off more or less, though not so much.

The discharge characteristic curves of the storage cell No. 1 are shown in Fig. 1.

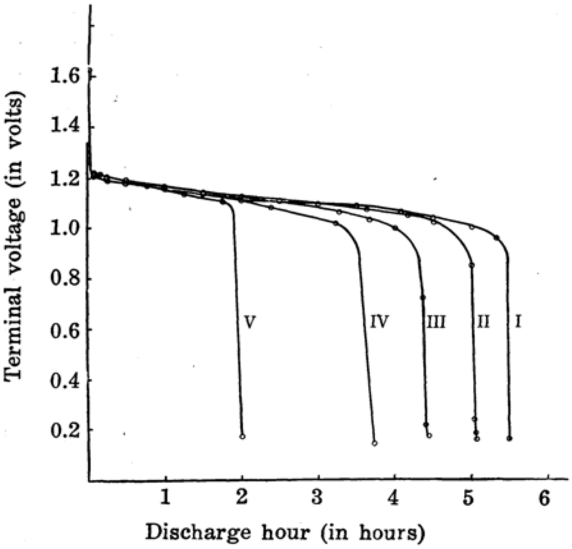

Fig. 1. Discharge characteristic curves of the cell No. 1. Numbers I, II,—V, correspond to the number of cycles.

Similar discharge characteristic curves can be obtained in the case of cell No. 2. The open voltage of the cell was about 1.5 volts or 1.6 volts. When discharged by the current of 100 milliamperes, the current density being about 5.5 milliamperes/cm^2., the terminal voltage lowered at first to about 1.2 volts, then kept on decreasing gradually, and then it dropped rather abruptly to zero volt at the last period of the discharge.

The type of this discharge characteristic curve is analogous in form to that of the lead acid storage cell, and it is noteworthy that the terminal voltage of cobaltous oxide cell is found to be comparatively high as an alkaline storage cell.

Table 3 shows the discharge capacity per one gram of cobaltous oxide (C/w) which has been applied to grids.

(c) *Experiments on the plates in the pocketed form.* As described in the preceeding paragraph the author has succeeded in making the electrode plates of alkaline storage cell with CoO, in the pasted form,

Table 3.

Number of discharge n	Discharge current milliamperes	Number of electrode plate	
		No. 1	No. 2
		Capacity per one gram of CoO C/w in $\frac{\text{milliampere hour}}{\text{gram}}$	Capacity per one gram of CoO C/w in $\frac{\text{milliampere hour}}{\text{gram}}$
1	100	185	147
2	100	171	129
3	100	149	110
4	100	126	110
5	100	76	120

but the discharge capacities of the electrode plates thus prepared tended to decrease gradually. This tendency seemed to arise from the falling off of the active material. Therefore, the similar experiment was undertaken with an electrode which was prepared in the pocketed form.

The mechanical structure of the ordinary pocketed type electrode plate of alkaline accumulator is very complicated and is very difficult to reproduce in a laboratory, thereupon the author made use of the positive pocket of the Nife accumulator.

The positive pocket of the Nife alkaline accumulator was taken away from the electrode plate, and the active material packed in it was thoroughly removed, and then rinsed well. Then the mixture of CoO and graphite (percentage of graphite being 20) was sealed in an above cited empty tube, and made into electrode plate. Two electrode plates were thus prepared the constitution of which being as follow.

Number of plate	Amount of active material packed in (grams)	Amount of graphite %	Amount of $C_0\,O$. (w) (grams)
A	8.96	20	7.17
B	8.82		7.06

The "formation" was undertaken by the current of 100 milliamperes for 59 hours in the case of No. A, and the same current for 35 hours in the case of No. B. The electrode plates A and B were combined with the positive electrode plates of Nife alkaline accumulator and dipped in 20% KOH solution, and then were subjected to discharges for nine cycles. Tables 4 shows the results of the experiments.

Cell A was discharged, in the second cycle, by the current of 100 milliamperes for 7 hours and then discharged again by the current of 200 milliamperes for 52 minutes, while cell B was discharged throughout by the current of 100 milliamperes. In the ninth cycle, both cells were discharged by the current of 160 milliamperes. In other cycles both cells were discharged by the current of 150 milliamperes and charged by the current of 100 milliamperes for about 18 hours.

Table 4.

Number of discharge n	Discharge current milli-amperes	Number of electrode plate			
		A		B	
		Time of Discharge hour (in hours)	Discharge capacity C in ampere hours	Discharge hour (in hours)	Discharge capacity C in ampere hours
1	150	5.450	0.818	3.700	0.555
2	100∼200	7.866	0.873	5.700	0.570
3	150	5.900	0.885	3.500	0.525
4	150	6.183	0.936	3.333	0.500
5	150	5.833	0.875	3.166	0.475
6	150	5.916	0.887	2.800	0.420
7	150	5.883	0.882	2.666	0.400
8	150	6.100	0.915	2.883	0.433
9	160	5.400	0.854	2.633	0.421

As shown in Table 4 the value of C differs considerably notwithstanding the value of w is almost equal in both electrode A and B. This seems to have its cause in the fact that it is difficult to make the electrode plates in the pocketed form of the same conditions. Probably some insignificant difference in conditions in preparing the electrode plate, such as difference of compressed condition of active material or the different condition of "formation" may leave serious influence upon the discharge capacity of the electrode. Though there is a considerable difference in the value of C between the cell A and B, it does not vary so much according to the number of discharge in one cell.

With respect to the electrode A and B the discharge capacity per one gram of CoO (C/w) is calculated and tabulated in Table 5.

Table 5.

Number of discharge n	Discharge current milliamperes	Number of electrode plates	
		A	B
		Capacity per one gram of CoO C/w in $\frac{\text{milliampere hour}}{\text{gram}}$	Capacity per one gram of CoO C/w in $\frac{\text{milliampere hour}}{\text{gram}}$
1	150	114	79
2	100∼200	122	81
3	150	124	74
4	150	131	71
5	150	122	67
6	150	124	59
7	150	123	52
8	150	128	61
9	160	119	60

The discharge characteristic curve is very similar to that which was shown in the case of the plates in the pasted form. The open voltage before the discharge was about 1.5 volts or 1.6 volts, then lowered to about 1.2 volts in the first period of discharge, and then it falls continuously in the vicinity of 1.1 volts and finally reaches the nearly zero voltage showing the end of discharge. After the sudden fall of the terminal voltage at the end of discharge, the lowering seemed to stop for a while at the point of about 0.3 volts and show a uniform voltage for a time, but this point was not touched in this experiment.

(2) Conclusions. The negative electrode plate of the alkaline storage cell can be prepared with CoO both in pasted and in pocketed forms.

Considerable discharge capacity can be obtained from these electrode plates, when combined with the positive electrode plate of Nife alkaline accumulator and dipped in 20% KOH solution.

The discharge characteristic curve shows about 1.5 volts in the open condition before the discharge, and during the discharge (the discharge current density being about 5.5 milliamperes/cm.^{2})⁽⁴⁾ it shows an average voltage of about 1.1 volts, and falls gradually, and then at last ends in the sudden fall of the terminal voltage.

In conclusion the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University, for his valuable advice on these experiments.

Toyoda Research Laboratory,
Imperial Invention Society,
Shimomeguro Tokyo.

---

(4) In the experiments on the plates in the pocketed form, material for calculting the exact current density are lacking. But it is considered to be nearly the same as that in the case of pasted form.