Properties of Mercury Oxide as an Active Material of Positive Electrode in Alkaline Storage Cell.

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(1) *Experiments with red mercury oxide.* The author has reported that the positive and the negative electrode plates of the alkaline storage cell can be prepared with silver oxide⁽¹⁾ and bismuth oxide⁽²⁾ respectively in pasted form. In the present paper, the results of similar experiments with mercury oxide will be reported.

When red mercury oxide is mixed with 5NNH_4OH solution, a paste-like material will be obtained such as we get in kneading lead oxide with dilute sulphuric acid. We shall call this material "paste" throughout the present report. The electrode plate was prepared by applying this paste to the grids made of nickel plated lead antimony alloy (the size of the grid being about 6.0 cm. × 1.5 cm. × 0.3 cm.) which can also be used for preparing the lead accumulator plate. When the plate thus prepared was dipped into 20% KOH solution a small amount of the active material fell off from the surface. This seemed to happen owing to the poor cohesive power of the active material made of mercury oxide. Similar experiments were undertaken therefore, with the electrode plate which was made by the paste produced by mixing silver oxide and red mercury oxide.

Table 1 shows the properties of the plate used for the experiments.

Table 1.

Number of electrode plate	Amount of active material w (in gram)	Composition of Paste		Weight of grid (in gram)
		Amount of Ag_2O mixed (in gram)	Amount of HgO mixed (in gram)	
6	9.63	—	10.00	15.26
8	5.22	4.00	2.00	15.98
9	6.20	3.75	3.75	16.04
10	6.98	2.00	6.00	16.66

After the paste was applied to the grids, they were left to dry for about 72 hours, then they were dipped into 20% KOH solution. There was no falling off of the active material in any electrode plate.

Electrolytical "formation" of the pasted plate thus obtained were undertaken in 20% KOH solution by the current of 80 milliamperes for

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(1) K. Kinoshita, this Bulletin, **12** (1937), 164, 366.
(2) K. Kinoshita, this Bulletin, **15** (1940), 59.

about 90 hours. With the completion of the formation, the positives were combined with the negative electrode of the Nife's accumulator which had already been fully charged, and were subjected to four cycles of charges and discharges by the current of 250 milliamperes. Table 2 shows the results of the experiments.

Table 2.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	Discharge hour (in hour)	Capacity C. (in ampere-hours	Discharge hour (in hour)	Capacity C. (in ampere-hours	Discharge hour (in hour)	Capacity C. (in ampere-hours)
1	7.266	1.817	7.833	1.958	8.216	2.054
2	5.500	1.375	6.333	1.583	6.166	1.542
3	5.183	1.296	6.466	1.617	5.633	1.408
4	5.166	1.292	6.500	1.625	5.916	1.479
mean		1.445		1.696		1.621

The voltage of the accumulator No. 6 has fallen to zero at fifteen minutes after the starting of the discharge, so that it was left out from discharging afterwards.

As shown in Table 2, the discharge capacity is comparatively large for each accumulator in the first discharge, but falls remarkably in the second discharge, then it tends to fall continuously.

Fig. 1 shows the discharge characteristic curve in the first discharge.

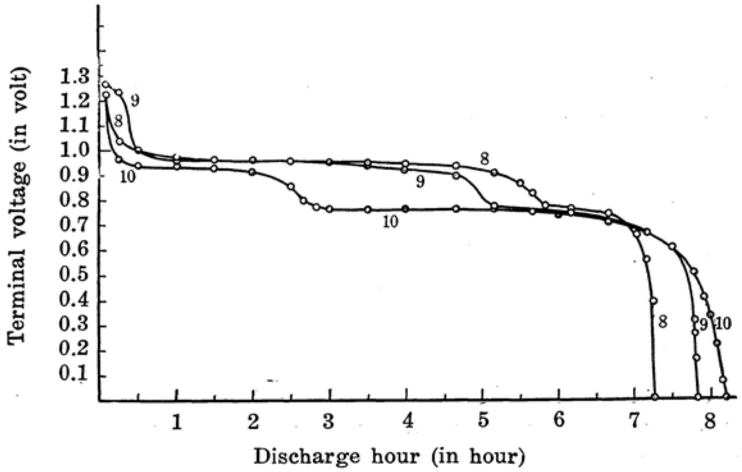

Fig. 1.

As shown in the figure, the voltage falls in two stages the first stage being about 0.95 volt and the second about 0.75 volt. The cell No. 9 gives at the beginning of discharge, the value of over 1.2 volts. Now, the whole discharge capacity C, is devided into two parts C_1 and C_2, at the inflexion points of the voltage curve between these two stages. The results are given in Table 3.

Table 3.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)
1	1.417	0.400	1.242	0.717	0.667	1.388
2	0.983	0.392	0.875	0.708	0.317	1.225
3	1.000	0.296	0.908	0.708	0.292	1.117
4	0.863	0.429	1.008	0.617	0.333	1.146
mean	1.066	0.379	1.008	0.688	0.402	1.219

By examining more closely the discharge characteristic curve of Fig. 1, we know, that the variation in the terminal voltage is much like that of silver oxide positives in the pasted form, which the author has previously noticed.(1) When the silver oxide plate combined with the negative electrode of the Nife accumulator was discharged in 20% KOH solution with the same rate of the discharge current, the terminal voltage of about 0.95–0.99 volt was obtained.

Moreover, the terminal voltage of about 1.2 volts at the beginning of the discharge for the cell No. 9 in this experiments was also observed in the case of the silver oxide electrode. This is understood as the discharge capacity obtained by the chemical changes of silver peroxide into silver oxide. The discharge capacity shown in Fig. 1, C_1, therefore, may be resulted from the discharge of the silver oxide which has been mixed in the active material of the electrode.

The following shows the amount of the silver oxide and the mercury oxide in the active material of the electrode, which has been calculated from Table 1.

Number of the electrode plate...	No. 8	No. 9	No. 10
Amount of silver oxide (g.) ..W_s	3.48	3.10	1.74
Amount of mercury oxide (g.) W_m	1.74	3.10	5.24
Total ....w	5.22	6.20	6.98

The values of C_1/W_s have been calculated assuming that the discharge of the first stage is resulted from the discharge of silver oxide, and are shown in Table 4. In this table the values of C_2/W_m are also shown for comparison.

This table shows that the value of C_1/W_s is the same as, or a bit smaller than, that of the alkaline storage cell in the pasted form consisting of silver oxide alone, which was determined previously by the author.(1)

Table 4.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	C_1/Ws in ma. h./g.	C_2/Wm in ma. h./g.	C_1/Ws in ma. h./g.	C_2/Wm in ma. h./g.	C_1/Ws in ma. h./g.	C_2/Wm in ma. h./g.
1	414	230	401	231	383	265
2	284	225	282	228	182	234
3	287	170	294	228	168	213
4	248	246	325	199	191	219
mean	311	218	326	222	231	233

The value of C_1/W_s decreases as the amount of HgO increases, while the value of C_2/W_m does not change so much with the variation of the content of Ag_2O.

Now, plotting C_1 or C_2 in ordinate (in amperehour) and W_s or W_m in abscissa (in gram) we obtain Fig. 2 and Fig. 3.

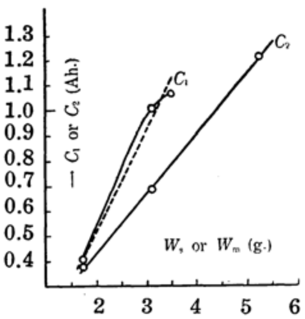

Fig. 2.

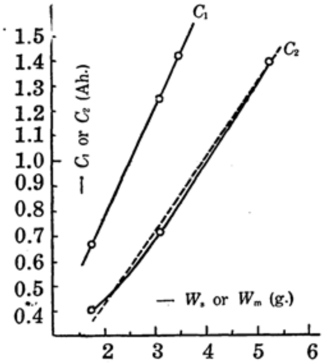

Fig. 3.

In Fig. 2 the average value of the four discharges is used for each of C_1 and C_2, and in Fig. 3 the result of the first discharge is used for each of C_1 and C_2. As can be seen from Fig. 2, there is a linear relation between C_2 and W_m, while no such relation between C_1 and W_s. From Fig. 3, both C_1 and C_2 may be presumed as linear. However, all these have only three measuring points and the relation cannot accurately be brought out.

In calculating the value of C_1, in the case of such electrode as No. 9 which shows the characteristic curve that seems to result owing to the reaction $Ag_2O_2 \rightarrow Ag_2O$, should be left out from the calculation.

(2) *Experiments with yellow mercury oxide.* Similar experiments as above were undertaken on the yellow mercury oxide. The grid used for the experiments were made of lead antimony alloy plated with nickel as in the previous case. Four electrode plates were prepared having different constitution of the paste, which are shown in table 5.

Table 5.

Number of electrode plate	Amount of active material w (in gram)	Composition of paste		Weight of grid (in gram)
		Amount of Ag_2O mixed (in gram)	Amount of HgO mixed (in gram)	
1	5.26	4.50	1.50	16.95
2	5.00	4.00	4.00	15.37
3	4.81	2.00	6.00	15.10
4	5.68	—	10.00	15.70

When the paste was applied to the grids, each plate showed considerable stiffness, and seemed to give a satisfactory result. But in dipping in 20% KOH solution, the active materials of No. 3 and No. 4 have dropped off readily. The active material in No. 1 and No. 2 did not fall off so much and could be formed into the positive electrode plate by the current of 100 milliamperes for about 96 hours. Immediately after the "formation," they were charged and discharged for two times.

Table 6.

Number of discharge n	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	4.333	1.083	4.333	1.083
2	3.333	0.833	4.000	1.000
mean	3.833	0.954	4.167	1·042

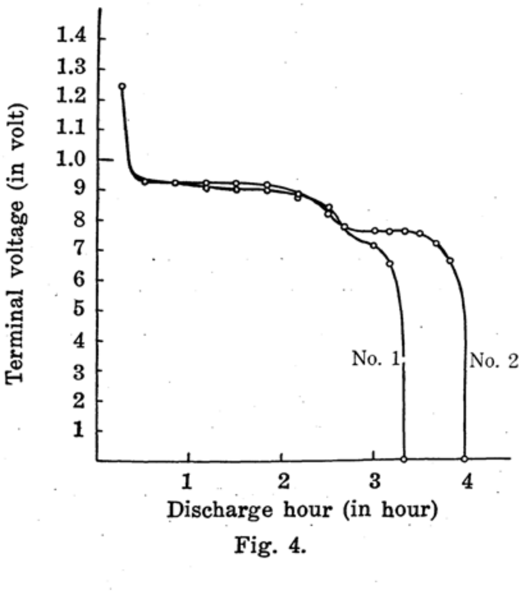

Fig. 4.

The colour of the plate of No. 1 was brown, when the paste was applied in the grids, and that of No. 4 yellow, and No. 2 and No. 3 showed medium colours between brown and yellow according to their constitution. The dischange current was taken to be 250 milliamperes and the charge was undertaken by the current of 200 milliamperes for about 10 hours. Table 6 shows the discharge capacity.

Fig. 4 shows the discharge characteristic curves.

Both No. 1 and No. 2 show the first stage of about 0.92 volt and the second stage of about 0.75 volt. This is just the same as obtained in the experiments with red mercury oxide. The fact that No. 2 which contains more mercury oxide than No. 1 has larger discharge capacity in the second stage, is the same tendency as seen in the red mercury oxide experiment.

(3) *Conclusion.* The positive plate of an accumulator in pasted form can be made by the mercury oxide (both red and yellow) provided that it is given some cohesive power as the active material by mixing with silver oxide.

The discharge characteristic curve has two steps in general, so that the whole discharge capacity can be divided into the two parts C_1 and C_2. The discharge characteristic curve of the first stage resembles much with the curve of the silver oxide positive plate, moreover, C_1 and C_2 stand in proportional relations with W_s and W_m, the quantities of silver oxide and mercury oxide in the active material respectively. This fact proves that C_1 is the result of the activity of silver oxide and C_2 the result of that of mercury oxide.

The appearance of the terminal voltage of about 1.2 volts at the beginning of the discharge, may be accounted for by the formation of silver peroxide. At present, the author will not discuss fully on the discharge characteristics of mercury oxide, but will insist the fact that if we can keep up mercury oxide as the active material of the electrode plate by some proper means, it can be used as the alkaline accumulator positive.

It was not possible to get an electrode plate made of yellow mercury oxide alone and the author can say nothing about it. In the case of red mercury oxide, however, the plate No. 6 which was made of red mercury oxide alone showed a small discharge capacity. This is a notable fact.

All these and the fact that the increasing of mercury oxide decreases the value of C_1/W_s seem to show the poor electrical conductivity of mercury oxide as the active material of electrode plate. It is thought to be probable from the result of experiments that the silver oxide mixed with the mercury oxide gives not only cohesive power but also better electrical conductivity of the active material, for it leaves powdered metallic silver as the result of the discharge.

Summary.

(1) Mercury oxide (both red and yellow) can be used into the electrode plate of the alkaline accumulator in the pasted form by mixing silver oxide.

(2) Its discharge characteristic curve varies in two stages, the first stage being caused by the discharge of silver oxide and the terminal voltage of about 0.95 volt, and the second stage being caused by mercury oxide.

(3) Mercury oxide seems to be a considerably poor substance in the electrical conductivity and the mixing of silver oxide raises its electrical conductivity.

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