On the Silver Oxide Positive of the Alkaline Accumulator. I.

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The alkaline accumulator composed of the silver oxide positive and copper negative was already described by E. W. Jungner. The fundamental chemical reactions involved in the discharge of this accumulator are said to be the followings:

$$Ag_2O_2 + 2\,KOH + 2\,Cu = Ag_2O + 2\,KOH + Cu_2O \qquad (1),$$
$$Ag_2O + 2\,KOH + 2\,Cu = 2\,Ag + 2\,KOH + Cu_2O \qquad (2).$$

The terminal voltages of the cell corresponding to the reaction (1) and (2) were reported to be 0.93 volt and 0.65–0.7 volt respectively. In 1927 F. Jirsa⁽¹⁾ studied the cell of the form Ag/OH′/Fe. He prepared the silver oxide electrodes of the cell by pressing powdered silver oxide or iron on the suitable wire gauze.

The author prepared the silver oxide positive of the alkaline cell in powdered and in pasted forms, and made some experiments on this positive electrode. The present report is the abstract from the detailed description published in Japanese.⁽²⁾

Silver Oxide Positives Prepared in Powdered Form. At first the electrode was prepared by packing the powdered silver oxide (Ag_2O) into the pocket made of silver wire gauze. The size of the pocket was 9 cm. × 3.5 cm. × 2 cm. The cell was made by combining this positive with a negative electrode of a "Nife accumulator." The negative electrode, therefore, was composed principally of iron. The electrolyte used was 20% KOH solution.

The initial charge of the positive electrode was continued for about 20 hours by the current of 1 ampere. The open circuit voltage was found to be 1.260 volts. Eleven cycles of charge and discharge were undertaken and the results obtained are tabulated in Table 1. The characteristic curves of discharge are shown in Fig. 1, the number of cycle being indicated by the figure from 1 to 11.

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(1) Jirsa, *Z. Elektrochem.*, **33** (1927), 129.

(2) Kinoshita, *Toyoda Kenkyu Iho*, **3** (1935), 88; *ibid.*, **4** (1936), 96.

Table 1.

Number of cycles	Discharge current (milliamp.)	End point voltage (volts)	Discharge capacity (a. h.)
1	200-600	0.92	3.10
2	1000	0.0	5.42
3	1000	0.0	4.13
4	1000	0.0	3.43
5	1000	0.57	2.83
6	500	0.49	4.09
7	700	0.0	5.32
8	600	0.0	4.67
9	600	0.0	5.05
10	600	0.36	5.30
11	700	0.0	5.23

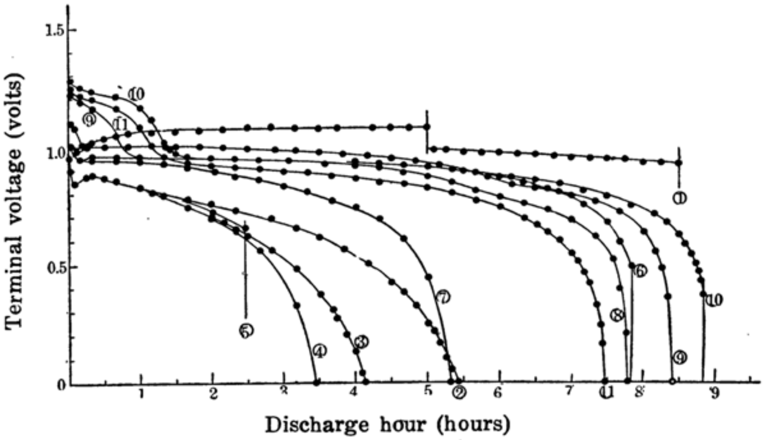

Fig. 1.

In the course of these experiments, as was already noticed by Jirsa, peptization of the active material of the positive electrode took place. As seen from Fig. 1 the forms of the curves for the last three cycles, i.e. 9, 10, and 11th cycle, differ remarkably from the other one. The terminal voltage of the cell falls in two steps, 1.2 volts and 1.0–0.9 volt, and then finally it drops to zero volt. This fact may be interpreted in the following manner.

The active material of the positive plate at the first discharge may be Ag_2O, but this will be then oxidized to Ag_2O_2 in the course of repetition of the cycles of charges and discharges. As the results of this electrolytic oxidation of the active material, the chemical reactions accompanied by the process of discharge may proceed in two stages as shown in the following equations.

$$Ag_2O_2 = Ag_2O + {}^1/_2\,O_2 \qquad (3),$$

$$Ag_2O = 2\,Ag + {}^1/_2\,O_2 \qquad (4).$$

The higher terminal voltage at the beginning is considered to be the result of reaction (3), and the lower terminal voltage reaction (4).

Silver Oxide Positives Prepared in Pasted Form. The experiments have been undertaken, then, on the silver oxide positives prepared in the pasted form. The powdered silver oxide was made into paste by mixing with NH_4OH or KOH solution and applied to the grid in the same manner as the ordinary pasted type electrodes of the lead acid cell. The grid was prepared by plating silver on the ordinary grid of lead-antimony alloy. The size of the grid was about 6.0 cm. × 1.5 cm. × 0.3 cm.

The paste was made by adding 1.7 c.c. of 20% KOH or 1.5 c.c. of 5N NH_4OH solution drop by drop to 10 g. of Ag_2O. After pasting the grids were left to dry in the room temperature for about 72 hours, and then were formed into the positives in 20% KOH solution by the current of 40–60 milliamperes.

The silver oxide positives thus prepared was combined with the Nife's negative in 20% KOH solution. The results of charges and discharges obtained on the positive electrode are tabulated in Table 2. The amount of Ag_2O pasted in this grid was 5.21 g.

Table 2. Results from an Electrode.

Discharge current 500 milliamp.

Number of cycles	Discharge capacity (a. h.)	Discharge capacity per 1 g. of Ag_2O. (m. a. h./g.)	Coefficient of utility (%)
1	2.285	439	94.8
2	1.642	315	68.1
3	1.666	320	69.1
4	1.576	303	65.4
5	1.642	315	68.1
6	1.616	310	67.0
7	1.576	303	65.4
8	1.542	296	64.0
9	1.550	298	64.3
10	1.550	298	64.3

The discharge current, in this case, was 500 milliamperes and the end point voltage of the cell was taken to be zero volt against Nife's negative. The 3rd column of Table 2 shows the capacities per one gram of Ag_2O, and the 4th column the percentage ratio of the actual capacity of the plate to the theoretical one. The theoretical capacity was calculated assuming the fundamental chemical reaction for discharge, for 4F of the electricity, to be

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

The ratio thus obtained may be considered to represent the coefficient of utility of the active material in the plate. As seen from this table very large discharge capacity was obtained at the first cycle of discharge, the utility coefficient of which amounting to 94.8%. From the 2nd cycle of discharge onwards the utility coefficient falls to about 60–70%. This particularity of the 1st discharge was noticed in all silver oxide positives other than exemplified in Table 2.

Characteristic curves of the electrodes in charge and discharge are shown in Fig. 2, Fig. 3, and Fig. 4.

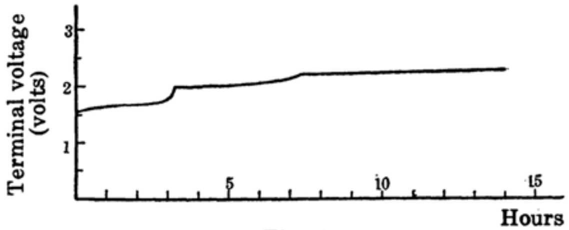

Fig. 2.

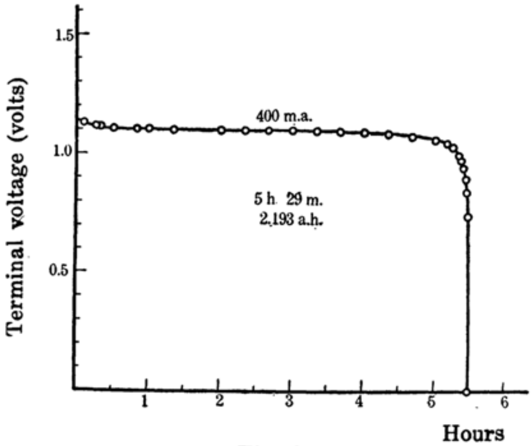

Fig. 3.

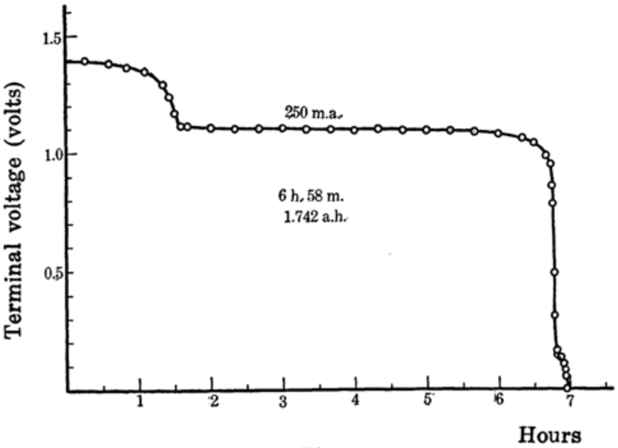

Fig. 4.

Fig. 2 is the charging curve of the positive electrode of a cell. The terminal voltage of this cell in charge rises abruptly at two points, namely at about 3.25 hours and 7.25 hours.

Fig. 3 and Fig. 4 show the discharge curves of another positive at the 1st discharge (discharge current 400 milliamperes) and the 8th discharge (discharge current 250 milliamperes) respectively.

At the first cycle of discharge, the silver oxide electrode always shows a curve of the form like Fig. 3. After repeating a few cycles of discharge the curve transforms to the form like Fig. 4. An overcharged Nife's negative was always used as the auxiliary electrode for the measurement of the terminal voltage of the electrode.

The above described change of form of the discharge curve, therefore, is considered to be due to the special feature of the silver oxide electrode.

The form of the discharge characteristic curve shown in Fig. 4 may be understood by considering that the fundamental chemical reactions (3) and (4) are involved in the electrode.

Comparison of the Silver Oxide Electrode with Lead Peroxide Positives. As already shown in Table 2 the utility coefficient of the silver oxide positive amounts to extraordinary high value in comparison with that of the positive of the lead acid cell. The coefficient of utility of the positive electrode of the lead acid cell is said to be about 25%–50% in 5 hour rate of discharge.

The capacities per 1 gram of the active materials of silver oxide and lead peroxide electrodes are plotted against the magnitude of discharge

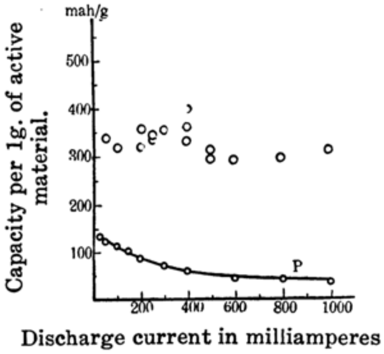

Fig. 5.

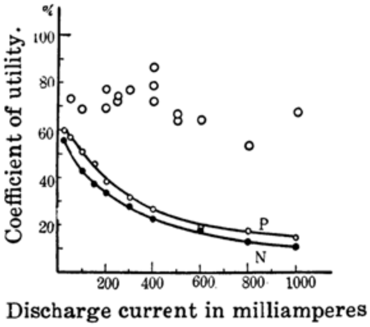

Fig. 6.

current in Fig. 5. The coefficient of utility of the active materials of these electrodes are plotted against the discharge current in Fig. 6. The points indicated by the circlets are the values for the silver oxide electrode.

The curves marked with P are the results of the positive electrodes, and the curve marked with N is the results of the negative electrode of the lead acid cell respectively.

These figures show that the capacities and the utility coefficients of the silver oxide positives are practically independent of the discharge current, and that this electrode has much higher utility coefficient than that of the electrode of lead accumulator.

The watt-hour output of the silver oxide cell and the lead acid cell are compared in Table 3. As seen in this table the watt-hour output of the silver oxide positive is greater than that of the lead peroxide positive so much as about 50%.

Table 3.

	PbO_2 electrode	Ag_2O electrode	
		Example 1	Example 2
Concentration of electrolyte	**28% H_2SO_4**	**20% KOH**	**20% KOH**
Discharge current	**200 m. amp.**	**200 m. amp.**	**200 m. amp.**
Discharge capacity	**0.567 a. h.**	**1.580 a. h.**	**1.653 a. h.**
Coefficient of utility	**38.1%**	**75.2%**	**78.7%**
Mean terminal voltage	**1.908 volts**	**0.984 volts**	**0.991 volts**
w. h. output	**1.082 w. h.**	**1.555 w. h.**	**1.637 w. h.**
Weight per unit w. h. output	**6.24 g./w. h.**	**3.12 g./w. h.**	**2.96 g./w. h.**

The Chemical Reaction Involved in Discharging the Silver Oxide Positive. The discharge characteristic curves of silver positive become in two stages as have already been shown in Fig. 1 and Fig. 4. This can be interpreted by the fact that the chemical reactions of the electrode proceed in two stages expressed by (3) and (4). In order to bring out this fact more clearly, the chemical analysis was made of the active material of electrode in charged state. The electrode which had been subjected to a few cycles of charge and discharge was now fully charged by the current of 200 milliamperes for 72 hours. It was, then, rinsed thoroughly with water in order to be freed from alkali, and the active material was taken out of the grid and made to powder. The sample thus obtained was dried in a deccicator for about 72 hours. The dried sample was dissolved in a small amount of dilute nitric acid and the solution was diluted to 500 c.c. and then was titrated with NH_4CNS solution according to Volhard's method.(3) The results were as follows. Dried sample taken: 5.9745 g. Content of Ag, found: 5.204 g. Ag calculated, assuming the sample to be Ag_2O_2: 5.204 g. Ag calculated, assuming the sample to be Ag_2O: 5.562 g. From this results, we see that the active material of the silver oxide positive in charged state is Ag_2O_2.

The weighed sample of the active material was heated to 120°C. until the weight becomes constant. In the process of this heating the sample changes its colour from bluish black to brown. This corresponds to the decomposition of Ag_2O_2 to Ag_2O and O_2. The brown powder was then heated to dull red heat. The colour now changes readily to silver white. These reactions are expressed by the followings.

$$Ag_2O_2 \xrightarrow{\text{above } 100^\circ\text{C.}} Ag_2O + {}^1\!/_2\, O_2 \xrightarrow{\text{above } 300^\circ\text{C.}} 2\,Ag + {}^1\!/_2\, O_2$$

The results of the chemical analysis are given in Table 4.

Table 4.

Heating bluish black sample to 120°C.	Sample taken		1.9174 g.
	Decrease of weight	Calculated	0.1238 g.
		Found	0.1126
	Content of Ag_2O_2 calculated from the decrease of weight		90.95%

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(3) Treadwell, "Lehrbuch der analytische Chemie," II, (1927), 612.

Table 4.—(*Concluded*)

Heating brown sample to dull red.	Sample taken		1.3869 g.
	Decrease of weight	Calculated	0.0957 g.
		Found	0.1029 g.
	Content of Ag_2O calculated from the decrease of weight		107.5%
Heating bluish black sample to 120°C.	Sample taken		3.0008 g.
	Decrease of weight	Calculated	0.1937 g.
		Found	0.1925 g.
	Content of Ag_2O_2 calculated from the decrease of weight		99.33%
Heating brown sample to dull red.	Sample taken		1.3957 g.
	Decrease of weight	Calculated	0.0964 g.
		Found	0.0987 g.
	Content of Ag_2O calculated from the decrease of weight		102.4%

We will consider the relation between the chemical reactions and the utility coefficient of the electrode. Table 5 gives the utility coefficient of an electrode assuming the chemical reaction to be

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

and

$$Ag_2O \rightarrow 2\,Ag.$$

The values always exceed 100% if they are calculated from the latter equation, while less than 100% from the former one. We know, therefore, that the active material of silver positive in charged state is composed of some higher oxide than Ag_2O.

In conclusion the author wishes to express his hearty thanks to Prof. Sameshima of the Tokyo Imperial University, and Dr. Tiku of the Toyoda Research Laboratory, for their valuable advice on this experiments.

Table 5.

Number of cycle	Discharge hour (h. m.)	Discharge capacity (a. h.)	Coeff. of utility considering chem. reaction to be $Ag_2O_2 \rightarrow 2\,Ag$	Coeff. of utility considering chem. reaction to be $Ag_2O \rightarrow Ag$
1	8.36	2.146	96.4%	192.8%
2	6.08	1.533	68.8	137.6
3	5.39	1.413	63.4	126.8
4	5.50	1.458	65.5	131.0
5	6.38	1.658	74.5	149.0
6	6.43	1.678	75.4	150.8
7	6.46	1.692	76.0	152.0
8	6.35	1.646	74.0	148.0
9	6.17	1.572	70.6	141.2
10	7.06	1.775	79.8	159.6
11	6.49	1.703	76.5	153.0
12	6.28	1.617	72.6	145.2
13	6.12	1.550	69.6	139.2
14	6.10	1.542	69.3	138.6

Summary.

(1) A cell was constructed from the silver positive and iron negative in KOH solution, and the charge and discharge curves of the positive were examined.

(2) It was known that the discharge curve runs in two steps in general, which can be interpreted by assuming that there occurs the following consecutive chemical reactions.

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

(3) The chemical analysis of the active material of charged silver positive supports the above consideration.

(4) The coefficient of utility of the active material of the silver positive is much higher than that of the lead peroxide positive of the lead acid cell.

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