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

By Kyôji KINOSHITA.

(Received July 15th, 1937.)

The author reported some experimental investigations on the general features of the silver oxide positives of alkaline accumulator.(1) The present report describes the further experiments, the detailed description(2) being published in Japanese.

In the previous paper, the author pointed out that the chemical reactions corresponding to the discharge of the positives are

$$Ag_2O_2 \rightarrow Ag_2O + \frac{1}{2}O_2 \rightarrow 2Ag + \frac{1}{2}O_2 \qquad (1).$$

It has also been found that the coefficient of utility of the active material and the capacity of the positive electrode are higher than those of the

---

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

(2) Kinoshita, *Toyoda Kenkyu Iho*, **4** (1936), 116-141.

lead peroxide positive of the lead acid cell. In order to bring out the cause of these special features of the silver positive, further experiments have been done, especially on the charging characteristic of the positive.

Experimental. (a) Amount of Oxygen Fixed in the Active Material, and the Discharge Capacity of the Positive. Silver oxide positives were prepared by applying silver oxide paste to the grid as stated in the previous paper. The grid was made of iron plated with silver, the size being about 5.8 × 1.6 × 0.25 cm. "Formation" of the positives was continued for about 17–21 hours by a current of 60 milliamperes.

Fig. 1 shows the construction of the cell. A is a glass vessel of H-shape, P a silver oxide electrode, and N a negative electrode of the "Nife" accumulator. The amount of gas evolved at the positive P was measured by collecting in a glass cylinder G through the tube B. The total amount of electricity, K', passed for charging the cell was measured by means of a copper coulombmeter connected in series to the cell. Nine cycles of discharges were made on the cell. The results are summarized in Table 1.

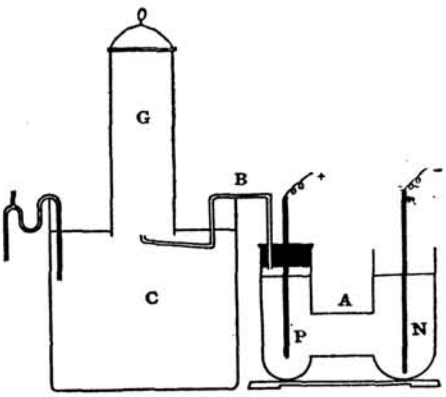

Fig. 1.

Table 1. Comparison of K and C.

Number of cycle	Total amount of elect. used for charging (K') (A.H.)	Volume of gas evolved (0°C., 1 atm.) (c.c.)	Amount of elect. as a loss (K'') (A.H.)	$K = K' - K''$ (A.H.)	Discharge capacity (C) (A.H.)
1					2.080
2	9.30	1506	7.21	2.09	2.030
3	7.80				2.115
4	3.17	394	1.89	1.28	1.260
5	1.89	170	0.81	1.08	1.065
6	1.60	93.7	0.45	1.15	1.149
7	1.72	105	0.50	1.22	1.200
8	1.80	140	0.67	1.13	1.125
9	1.69	122	0.58	1.11	0.949

In the 3rd and 4th columns of the table, the total volume of the gas evolved at P and the amount of electricity (K'') corresponding to the volume of gas are tabulated respectively. The values $K = K' - K''$ in the table are considered to represent the amount of electricity consumed in oxidizing the active material in the positive. The values of K are in good coincidence with the discharge capacity C in the succeeding discharge. This may lead to the consideration that the entire amount of oxygen fixed in the active material of the positive in the charge, may be consumed in the succeeding discharge.

In the case of the 1st discharge in Table 1, for example, K' amounted to 9.30 ampere-hours, and if K' be used only for the electrolysis of water, the amount of oxygen which will be evolved at P is calculated to be 1946 c.c. at 0°C. and 1 atm. So that the volume of oxygen which was fixed in the active material in the charge will be

$$1946 \text{ c.c.} - 1506 \text{ c.c.} = 440 \text{ c.c.} \ (0°\text{C., } 1 \text{ atm.}).$$

On the other hand, the electrode used contains 5.08 g. of Ag_2O as an active material, accordingly, the amount of oxygen in the electrode may be as follow:

$$22400 \times (5.08 \times O_2/2\,Ag_2O) \times (1/O_2) = 245 \text{ c.c.} \ (0°\text{C., } 1 \text{ atm.}).$$

The amount of oxygen which is expected to exist in the positive considering the charged active material to be Ag_2O_2 will be $245 \times 2 = 490$ c.c. (0°C., 1 atm.). From these calculations, it can be concluded that the active material of the plate, in charged state, is composed of a silver oxide of a higher degree of oxidation than Ag_2O. The same result was already described in the preceding paper.

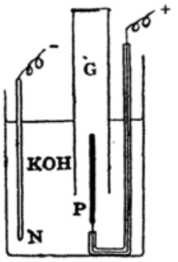

Fig. 2.

In the above experiments the grids made of iron were used for the preparation of the positive. By the use of such a grid, however, the discharge capacity of the positive diminishes gradually as the cycles of discharge are repeated. So in the following experiments the grids of lead-antimony instead of iron was used. In this case the positive P was fixed in a large vessel A, as shown in Fig. 2. N is a negative electrode, and G a glass cylinder for collecting the gas evolved at P. The results are tabulated in Table 2. The same conclusion can be obtained from this table as from Table 1.

Table 2. Comparison of K and C.

Number of cycle	Total amount of elect. used for charging (K') (A.H.)	Volume of gas evolved (0°C., 1 atm.) (c.c.)	Amount of elect. as a loss (K'') (A.H.)	$K = K' - K''$ (A.H.)	Discharge capacity (C) (A.H.)
1					2.242
2	3.363	330.2	1.58	1.78	1.780
3	2.376	142.2	0.68	1.70	1.634
4	2.450	144.0	0.69	1.76	1.750
5	2.750	204.0	0.98	1.77	1.759
6	2.708	178.9			

(b) Changes of the Rates of Gas Evolution in the Course of Charge. Rates of gas evolution at a silver oxide electrode in the course of charges were measured. Fig. 3 shows an example of the results obtained. In the figure the ordinate indicates the velocity of gas evolution (c.c./min.) or the terminal voltage of the cell (volts), and the abscissa the time of charge and discharge (min.). The curve represented by circlets shows the evolved gas, and the curves represented by black dots are the characteristic curves of the cell in charge and discharge, the current being taken as 500 milliamperes. The terminal voltage of the cell in charge rises abruptly at about 75 min., accompanied by a slow evolution of gas. The rate of gas evolution rose slowly, and at last it reached nearly 1.74 c.c./min. The value 1.74 c.c./min. coincides with theoretical rate of gas evolution at the positive electrode in the electrolysis of water by the current of 500 milliamperes. So that the curve is considered to indicate the change of rate of propagation of oxidizing reaction at the electrode, and the reaction proceeds no more when the rate of gas evolution reached 1.74 c.c./min.

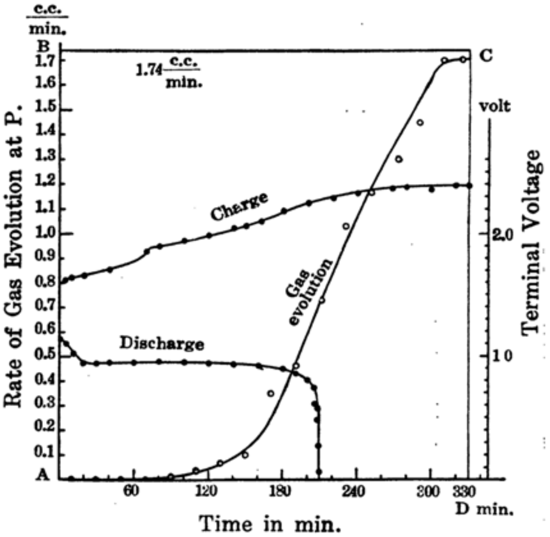

Fig. 3.

The area ABCD in Fig. 3 corresponds to the total amount of gas which will be evolved at the positive in the case of electrolysis of water by the current of 500 milliamperes in 330 min. The area surrounded by the straight lines AB and BC, and the gas evolution curve, corresponds to the amount of oxygen, which was fixed in the active material of the plates, and the rest, which lies on the right side of the curve indicates the amount of gas evolved at the positive as a loss.

(c) Proceeding of Oxidizing Reaction at the Electrode and the Amount of Electricity Used for Charging the Cell. Now, a very interesting special feature of the silver oxide positive was observed. The silver oxide positive in the pasted form could be discharged before applying any electrolytic treatment, i.e., "formation". The discharge capacity of the positive, in this case, almost coincides with those expected from the amount of silver oxide pasted in the positive and from the following chemical reaction:

$$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2 \qquad (2).$$

The calculated and the observed capacities are compared in Table 3. As seen in the table the coefficient of utility reaches from 90 to 97%. In this case the capacity S of the electrode may be considered to be the in-

Table 3. Comparison of Discharge Capacity at First Discharge with the Calculated Value.

Electrode	Amount of Ag_2O pasted (g.)	Discharge capacity (calc.) S (A.H.)	Discharge capacity (obs.) S' (A.H.)	Coefficient of utility (%)	Capacity per 1 g. of Ag_2O (mA.H./g.)
6 a	4.61	1.066	1.038	97.3	225
6 b	4.66	1.078	1.050	97.4	225
6 c	4.91	1.146	1.100	95.9	224
6 d	4.72	1.092	1.058	96.8	224
6 e	4.84	1.119	1.038	92.8	215
6 f	4.89	1.130	1.050	93.0	215
6 g	4.82	1.115	1.038	93.1	215
6 h	4.90	1.134	1.050	92.6	214
7 a	4.97	1.150	1.075	93.4	216
7 b	4.84	1.121	1.033	92.1	214
7 c	5.13	1.188	1.104	92.8	215
7 d	5.33	1.235	1.150	94.1	216

herent capacity of the electrode, which is to be determined by the amount of Ag_2O pasted in the grids.

In the following experiments the relation between the progress of the oxidizing chemical reaction at the electrode, and the amount of electricity used for charging the cell was examined. The degree of the oxidizing reacton at the electrode in charge can be measured from the discharge capacity of the cell in the succeeding discharge.

Four silver oxide electrodes were subjected to charge and discharge by the current of 250 milliamperes, and the values of K (which was measured from C in the succeeding discharge) was estimated, the values of K' being varied at the same time.

In Fig. 4 the values of C of the electrodes are taken in ordinate, and the K' in abscissa. As seen in the figure, if K' be smaller than 1.5 S_m(3), it is nearly equal to C in the succeeding discharge. In this case, therefore, we can forecast the end of the discharge by dividing K' by the magnitude of discharge current in the ranges of a few minutes. If K' be greater than 1.5 S_m, C becomes constant and nearly equal to 1.5 S_m.

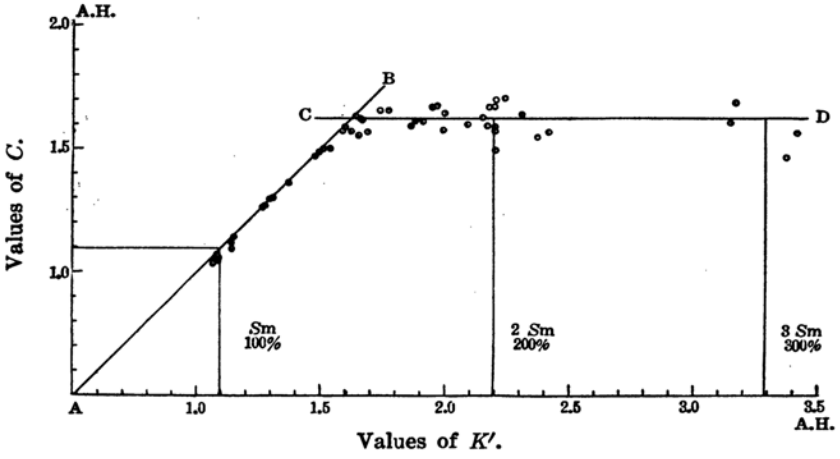

Fig. 4.

The inherent capacity of the electrode S is the theoretical one, the fundamental chemical reaction of the electrode being assumed to be (2). Accordingly, it may be expected that the total capacity of the electrode will increase to as much as $2S$, if the active material of the electrode

---

(3) S_m means the mean inherent capacity of the four electrodes used in the experiments.

be oxidized into Ag_2O_2, as the result of repeating the cycles of charge and discharge.

Relations between K' and K (or C) were examined by varying the magnitude of the charging current. The results obtained are diagramatically represented in Fig. 5 and Fig. 6, which correspond to the data obtained by the charging current of 500 milliamperes and 1000 milliamperes respectively.

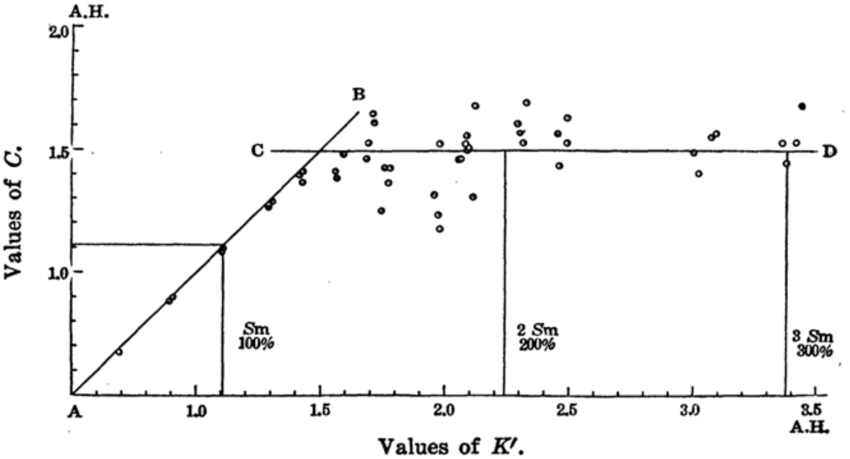

Fig. 5.

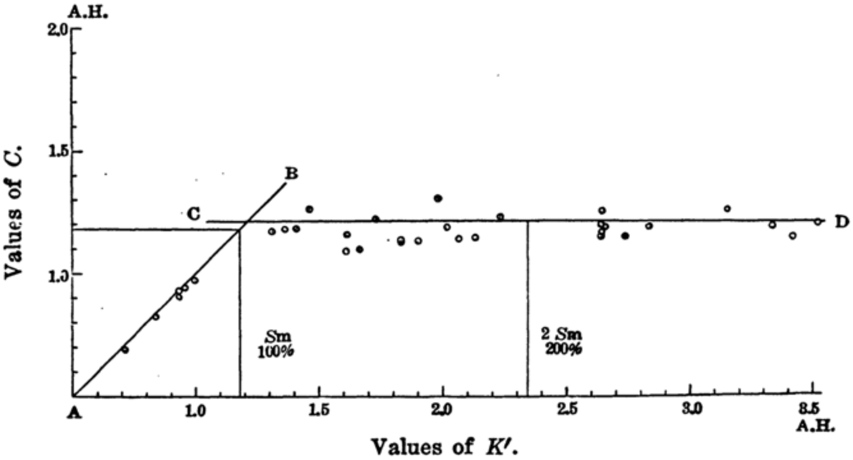

Fig. 6.

(d) Relation between Magnitude of Charging Current and Charged Amount of Electricity. As the result of experiments (c) it may be expected that the amount of electricity actually accumulated in the active material i.e., the amount of electricity consumed for oxidizing the active material of the electrode, changes with the magnitude of the charging current.

The silver oxide positives were charged fourteen times as much as their inherent capacities, the magnitude of the charging current in this case being from 100 milliamperes to 1300 milliamperes. And then they were discharged by a current of 250 milliamperes. The results thus obtained are summarized in Table 4.

Table 4.

Charging current (I) (ampere)	Time of discharge (t) (hours)	Discharge capacity (C) (A.H.)	log I	log t	log t (calc.)
0.100	6.471	1.604	−1.000	0.808	
0.200	5.566	1.392	−0.699	0.746	
0.300	5.750	1.438	−0.523	0.760	0.761
0.400	5.558	1.389	−0.398	0.745	0.744
0.500	5.383	1.346	−0.301	0.731	0.731
0.700	5.142	1.286	−0.155	0.711	0.711
1.000	4.892	1.223	0.000	0.688	0.690
1.300	4.725	1.181	0.114	0.675	0.675

The following tendency can be noticed from the table: the discharge capacities (C) of the electrodes become smaller with the increase of the charging current, but an especially small discharge capacity was observed when the charging current was 200 milliamperes. In the 4th and the 5th columns of the table, the values of $\log I$ and $\log t$ are tabulated. Plotting these values on a $\log I - \log t$ diagram, we obtain a straight line, as seen in Fig. 7. So that the relation can be represented by the following equations;

$$\log t = -n \log I + \log k \qquad (3),$$

$$I^n t = k \qquad (4),$$

where n and k represent constants. The equation (4) is analogous in form to Peukert's formula⁽⁴⁾ which gives the relation between discharge

---

(4) Peukert, *Elektrotech. Z.*, (1897), 287.

hour rate and the magnitude of the discharge current in the lead acid storage cell. Two constants in the equations (3) and (4) were found to be $n = 0.136$, and $\log k = 0.690$. In the 6th column of the table, the values of $\log t$ calculated from the equation (4) are tabulated.

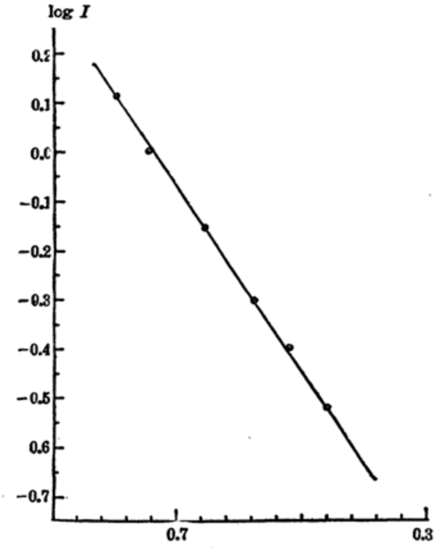

Fig. 7.

(e) On the Peptization of the Active Material at the Electrode. The silver oxide positives, in many cases, dispersed their active material into the solution of electrolyte when they were subjected to charge and discharge, forming a colloidal solution of silver oxide. This phenomenon was already noticed by Jirsa,(5) the author,(2) and Tanaka.(6) The colour of the colloidal silver observed in these experiments(7) was sometimes pink, yellow, brown, bluish brown or black. In order to see the effect of the concentration of the electrolyte upon the formation of the colloid, two electrodes (4H and 4I) were charged and discharged by a current of 100 milliamperes. The result observed at their first charge is summarized in Table 5. As seen in the table the formation of the colloid seems to have some relation to the concentration of the electrolyte. From

Table 5.

Electrode	Conc. of electrolyte	Colour of colloid	Remark
4 H	40% KOH	Pink	Upper part of the electrolyte: pink; lower part: transparent.
4 G	2.5% KOH	Dark yellow	Upper part of the electrolyte: transparent; lower part: dark yellow.

---

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

(6) Tanaka, *J. Electrochem. Assoc. Japan*, **3** (1935), 9.

(7) The photographs showing the formation of the colloids can be seen in the original paper (2).

the second charge onward the formation of the colloid in pink colour cannot be observed even in the case of electrode 4 H.

Positive and negative electrodes of the cell were put into two separate glass vessels, each containing 20% KOH solution, and the vessels were connected with a U-tube, which was also filled with 20% KOH solution. The charging current of this cell was taken to be 100 milliamperes, the peptization of the active material could be noticed only in the electrolyte into which the silver oxide positives were dipped. In discharging the positives, formation of the colloids could also be observed.

Consideration of the Results. The fundamental chemical reactions involved in the charge and discharge of the silver oxide positives will be considered to be as follows:

$$Ag_2O_2 \rightarrow Ag_2O + \frac{1}{2}O_2 \rightarrow 2Ag + \frac{1}{2}O_2 .$$

Of these the decomposing reactions of silver oxide into metallic silver corresponds to the discharge of the cell.

On the other hand, it was noticed, that the reduction of the active material occurred at first at the ribs of the grid, and then propagated into the inner part of the active material. This fact can easily be known from the colour difference between Ag_2O and Ag.(8) The material in discharged part is metallic silver, which is good electrical conductor, so that the discharge reaction will proceed smoothly and completely even in the innermost part of the active material.

In case of a charge, on the other hand, the active material in uncharged state (metallic silver) will be separated from the rib by a layer of charged material (silver oxide) which has small electrical conductivity. Accordingly the charging chemical reaction will not proceed so smoothly into the active material.

The following characteristic properties of the silver oxide positives may be explained from the above considerations: (1) Silver oxide positive gives very high values of coefficient of utility of the active material; (2) discharge capacities and the utility coefficient are not so seriously affected by the magnitude of the discharge current; (3) the oxygen fixed in the active material of the positives in a charged state is

---

(8) The photographs showing the propagation of chemical change at the electrode in discharge can be seen in the paper published in Japanese: Kinoshita, *J. Electrochem Assoc. Japan*, **4** (1936), 27; *Toyoda Kenkyu Iho*, **4** (1936), 108.

consumed completely in the succeeding discharge; (4) the amount of electricity charged in the active material is affected seriously by the magnitude of the charging current.

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

Summary.

(1) Further experimental investigations were made on the charge and discharge characteristics of the silver electrode of the cell which was constructed from the silver positive and the iron negative in KOH solution.

(2) Silver oxide positive gives very high value of the coefficient of utility of the active material.

(3) Discharge capacity and the utility coefficient are not seriously affected by the strength of the discharge current.

(4) The oxygen fixed in the active material in the charged state is consumed completely in the succeeding discharge.

(5) The amount of electricity charged is affected seriously by the strength of the charging current.

(6) These phenomena can well be explained by the following chemical reactions.

$$Ag_2O_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Ag_2O + \frac{1}{2} O_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2\,Ag + \frac{1}{2} O_2 .$$

Toyoda Research Laboratory, Imperial Invention
Society, Shimomeguro, Tokyo.