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

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It is a difficult matter to construct, in a laboratory, an electrode of the ordinary alkaline storage cell reproducibly under same condition, owing to its very complicated mechanical structure. This fact may be a principal cause of the difficulty to study the properties of the cell.

The present author has succeeded previously in constructing positive electrode of the alkaline storage cell in pasted form,[1] using silver oxide as its active material. By the use of this pasting method, it becomes comparatively easy to study the electrochemical properties of various metallic oxide as an active material of the alkaline storage cell.

Bismuth oxide is very difficultly soluble in acid, excepting nitric acid, and in alkalies, so it has a possibility to be used as an active material for the storage cell. In this connection, the author studied some electrochemical properties of the oxide by using above cited pasting method.

**Experimental.** (1) *Results from the electrodes in the pasted form.* Ordinary yellow bismuth oxide, $Bi_2O_3$, has been used in the experiment. Take necessary amount of the oxide, and add suitable electrolyte solution from a burrette, drop by drop, with constant stirring, and make up into paste. Then the paste is applied to a grid which was prepared by plating silver on the ordinary grid of lead antimony alloy in the same manner as the ordinary pasted type electrodes of the lead acid storage cells. The size of the grid used was about 6.0 cm. × 1.5 cm. × 0.3 cm..

The electrolyte solutions, for preparing the paste, were chosen to be 20% KOH, 5N $NH_4OH$, and 5N $NH_4Cl$. Three different kinds of electrodes were prepared, the details of which are given in Table 1.

(1) K. Kinoshita, this Bulletin, **12** (1937), 164-172.
K. Kinoshita, this Bulletin, **12** (1937), 366-376.

Table 1.

| Plate | Amounts of oxide pasted in the plates $w$ in grams | Pasting liquid |
|---|---|---|
| A | 4 95 | 20% KOH |
| B | 3.83 | 5N $NH_4OH$ |
| C | 4.52 | 5N $NH_4Cl$ |

The values of $w$ in Table 1 were calculated as the difference of the weight of the pasted grid after drying and the weight of the grid used. So that the values of $w$ may be considered to be the weight of $Bi_2O_3$, which was pasted in the grid. Then the pasted plates were dipped into 20% KOH solution, and negatively electrolized (technically called as "formation") by the current of 100 milliamperes for 47 hours. During the process of "formation" changes in colour of the paste (from yellow to brownish black) was discernible.

The plate B, the paste of which being prepared by mixing 5N $NH_4OH$ solution, could not be formed into the negative, for its paste fell to the bottom of the vessel as soon as the formation has begun.

After the "formation" the plates A and C were subjected to charge and discharge for four cycles, the results of these discharges are tabulated in Table 2.

Table 2.

| Number of discharge | Discharge current $i$ (in milli-amperes) | Plate A | | Plate C | |
|---|---|---|---|---|---|
| | | Discharge hour $t$ (in hours) | Discharge capacity $C$ (in ampere hours) | Discharge hour $t$ (in hours) | Discharge capacity $C$ (in ampere hours) |
| 1 | 100~200 | 9.250 | 1.030 | 9.033 | 1.006 |
| 2 | 150 | 6.116 | 0.917 | 3.500 | 0.525 |
| 3 | 150 | 5.550 | 0.832 | 3.100 | 0.465 |
| 4 | 150 | 4.833 | 0 725 | 3.000 | 0.450 |

At the first cycle of discharge, the discharge current was taken, at first, to be 100 milliamperes for 6 hours, but the capacity of the plates were found to be unexpectedly large, so that the discharge current was increased to 200 milliamperes. From the second cycle of discharge, thenceforth, the discharge current was taken to be 150 milliamperes.

As can be seen from Table 2, the capacities of the plates decreased cycle by cycle, and this tendency is especially remarkable in plate C. Some discharge characteristic curves of the plate A are shown in Fig. 1.

The numbers I, II, etc. in the figures correspond to the number of cycle of discharge. From the above figures, it can be noticed that the form

of the discharge characteristic curve changes its form with the progress of the number of cycle. Thus (1) the fall of the terminal voltage for about 1 hour from the biginning of discharge, becomes gradual and (2) discharge characteristic curve changes its nature abruptly at a point denoted by the letter a in Fig. 1.

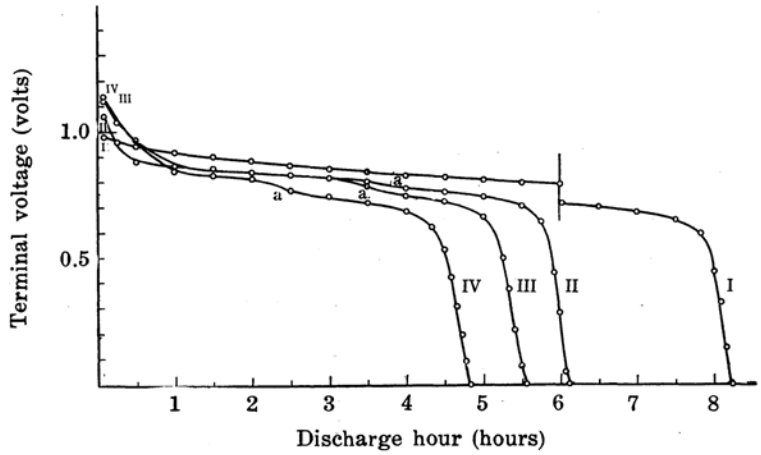


Fig. 1.

In Table 3 the discharge capacities per one gram of $Bi_2O_3$ are tabulated.

Table 3.

| Number of discharge $n$ | Discharge current $i$ (in milliamperes) | Plate A $C/w$ $\left(\text{in}\frac{\text{milliampere hour}}{\text{gram}}\right)$ | Plate B $C/w$ $\left(\text{in}\frac{\text{milliampere hour}}{\text{gram}}\right)$ |
|---|---|---|---|
| 1 | 100 ~ 200 | 208 | 223 |
| 2 | 150 | 185 | 116 |
| 3 | 150 | 168 | 103 |
| 4 | 150 | 147 | 100 |

(2) *Results from the electrode in the pocketed form.* As the results of experiment (1), it was found that the bismuth oxide can be used as an active material for the alkaline storage cell, but it seemed to be wanting in sticking property to adhere to the ribs of grid. Thus in the case of electrode B, the active material fell to the bottom of the electrolyte vessel during the "formation."

Thereupon, the electrode in a pocketed form was prepared. A positive tube (pocket) of the Nife's alkaline storage cell was taken out, and the active material in a tube was thoroughly pushed out and rinsed well.

Then powdered bismuth oxide was packed into the empty tube thus obtained and formed into the negative electrode of an alkaline storage cell. The weight ($w$) of bismuth oxide packed in a pocket was found to be 12.65 grams.

"Formation" of the plate was undertaken in 20% KOH solution, by the current of 150 milliamperes for 6 hours and thereafter by the current of 200 milliamperes for 17 hours. After the "formation" it was combined with well charged Nife's positives and was subjected to 13 cycles of charges and discharges.

The discharge capacities ($C$) thus observed, and the capacities per one gram of bismuth oxide ($C/w$) are tabulated in Table 4.

Table 4.

| Number of discharge $n$ | Discharge current $i$ (in milliamperes) | Discharge hour (in hours) | Discharge capacity $C$ (in ampere hours) | $C/w$ $\left(\text{in}\frac{\text{milliampere hour}}{\text{gram}}\right)$ |
|---|---|---|---|---|
| 1 | 250 | 5.500 | 1.375 | 109 |
| 2 | 250 | 4.000 | 1.000 | 79 |
| 3 | 150 | 6.716 | 1.007 | 80 |
| 4 | 150 | 5.933 | 0.899 | 71 |
| 5 | 150 | 5.433 | 0.815 | 64 |
| 6 | 150 | 5.166 | 0.775 | 61 |
| 7 | 100 | 5.450 | 0.545 | 43 |
| 8 | 150 | 3.000 | 0.450 | 36 |
| 9 | 150 | 3.333 | 0.500 | 40 |
| 10 | 150 | 3.250 | 0.488 | 39 |
| 11 | 150 | 3.366 | 0.505 | 40 |
| 12 | 150 | 3.016 | 0.453 | 36 |
| 13 | 150 | 2.500 | 0.375 | 30 |

We know from these tables that the values of $C/w$ in Table 4 are very small in comparison with those in Table 3. These facts may be considered to be due to the effects of separation of the active material

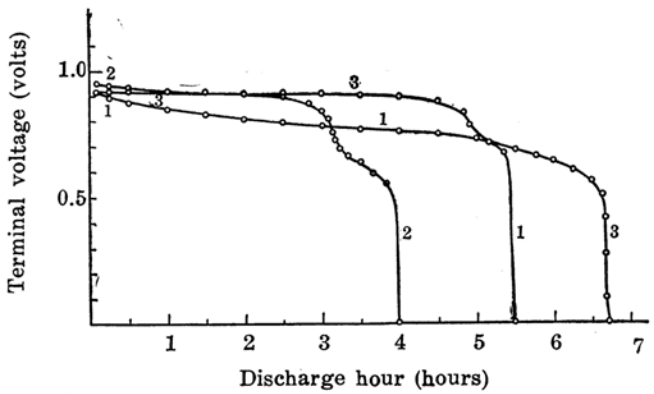


Fig. 2.

and the electrolyte solution with the metallic diaphragm, which composes the metallic pocket, and the results of the poor electrical conductivity of bismuth oxide.

The discharge characteristic curves of the first three cycles can be seen in Fig. 2.

The curve for the first cycle indicates the monotonous fall of terminal voltage, while the curves of the 2nd and the 3rd cycles proceeded in two stages.

(3) *Experiments with the active material mixed with graphite powder.* It was pointed out in the preceeding paragraph that the low values of $C/w$ in experiment (2) may be attributed to the poor electrical conductivity of bismuth oxide. So that, bismuth oxide mixed with 20% of graphite powder was used as an active material, in order to increase the electrical conductivity. The construction of the electrode was the same with that in the case of experiment (2). The amount of the active material packed in a tube was found to be 15.37 grams, accordingly the amount of bismuth oxide ($w$) contained in it was 12.30 grams. "Formation" was undertaken in 20% KOH solution by the current of 100 to 150 milliamperes for 38 hours. The results of 13 cycles of discharges are tabulated in Table 5.

Table 5.

| Number of discharge $n$ | Discharge current $i$ (in milliamperes) | Discharge hour $t$ (in hours) | Discharge capacity $C$ (in ampere hours) | $C/w$ $\left(\frac{\text{milliampere hours}}{\text{gram}}\right)$ |
|---|---|---|---|---|
| 1 | 150 ~ 300 | 19.600 | 3.215 | 261 |
| 2 | 400 | 6.016 | 2.405 | 196 |
| 3 | 300 | 8.666 | 2.600 | 211 |
| 4 | 400 | 5.183 | 2.074 | 169 |
| 5 | 400 | 4.750 | 1.900 | 155 |
| 6 | 400 | 4.500 | 1.800 | 146 |
| 7 | 400 | 4.400 | 1.760 | 143 |
| 8 | 300 | 6.650 | 1.995 | 162 |
| 9 | 300 | 6.483 | 1.945 | 158 |
| 10 | 300 | 6.433 | 1.940 | 158 |
| 11 | 300 | 6.316 | 1.895 | 154 |
| 12 | 300 | 6.033 | 1.810 | 147 |
| 13 | 300 | 6.233 | 1.880 | 153 |

As can be seen in Table 5 the values of $C/w$ are 261–143 milliamperehour/gram and show remarkable increase in value compared with the results of experiment (2), and are comparable to the values tabulated in Table 3. In Fig. 3 the values of $C/w$ in experiment (2) and

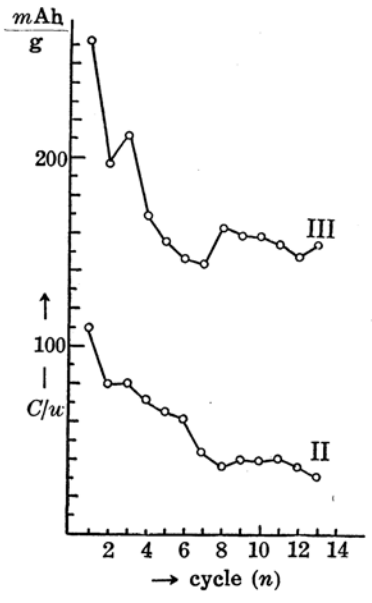

Fig. 3.

(3) were plotted against the number of cycle of discharge ($n$), the curves denoted by the letter II and III are the results of experiments (2) and (3) respectively.

It may be considered, from the result of Fig. 3 that the low values of $C/w$ observed in the case of experiment (2) are the effects of the poor electrical conductivity of bismuth oxide, and the effect of adsorbed electrolyte around the carbon particles, and the increase of porosity of the active material by the mixing of carbon particles must be taken into considerations.

Some of the discharge characteristic curves obtained in experiment (3) are shown in Fig. 4.

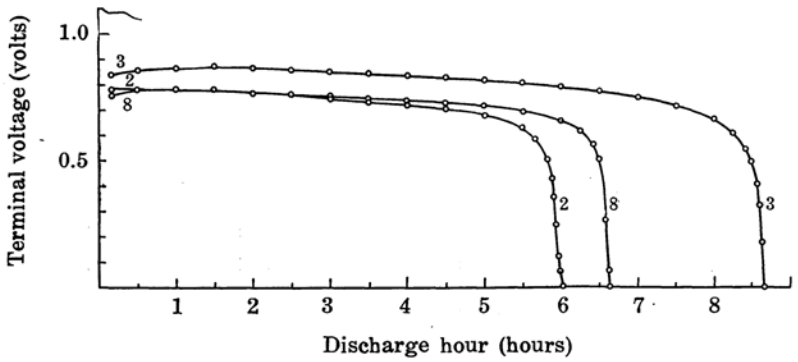


Fig. 4.

It is noteworthy, that in the case of experiment (3) the terminal voltage of the cell does not change in two stages as was seen in the case of experiments (1) and (2).

**Conclusions.** As the results of the experiments above described it is evident that the bismuth oxide can be used as an active material for the negative electrode in the alkaline storage cell, in pocketed or in pasted forms. But the output of the bismuth oxide alkaline cell seems to be limited by the poor electrical conductivity of bismuth oxide for some extent. It is very curious that the discharge characteristic curve changes its form in two staged type or in monotonous one staged type according to the conditions of the electrodes. These facts may have some connection with the above described electrically resistant nature of the bismuth oxide.

## Summary.

(1) Negative electrode of the alkaline storage cell can be prepared using bismuth oxide as an active material, in pasted form or in pocketed form.

(2) The capacity of the electrode is improved greatly by mixing graphite powder to the active material, amounting the value 261 milliamperehour at highest per one gram of the oxide.

(3) It is thought to be probable, therefore, that the electrochemical properties of the electrode prepared from bismuth oxide, seems to have close connection with electrically resistant nature of the oxide.

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