Studies on Sealing of a Cu-PbO₂ Storage Battery

Shin'ichi FURUMI and Toshimichi KUBO

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya

Received Aug. 12, 1964

A storage battery utilizing a cation reversible metallic electrode was studied, and features and behaviors of a Cu-PbO₂ battery, which was designed as an example by exchanging the negative pole of a lead-acid battery for a Cu plate, has been investigated.

This battery has many merits relative to the original lead battery, yet has some serious defects as reported formerly. To overcome these defects, the best countermeasure may be to seal this battery. It was found possible to use it without danger in the sealed state, provided the current source is previously adjusted, so as to indicate the maximum voltage below 1.9 V during the charging process.

Now it has been proved by experiments, that for this battery the decomposition voltage of water exceeds the voltage of the charging reaction by 0.4~0.6 V, at the end of its charging course; this voltage difference is affected by the concentration of Cu²⁺. Therefore the two reactions can be separated by manipulating the terminal voltage, and the liberation of gases can be avoided.

Regarding a lead battery, the separation of these two reaction is hardly possible, due to its high electromotive force, which allows above mentioned both reaction voltages coincide at half-way of the charging process. Thereupon when the current is reduced, the charging reaction is also stopped insufficiently. Hence it is actually impossible to apply sealing to the lead battery, expelling gases anyhow in charging.

1. Introduction

Both electrodes of an existing storage battery are anion reversible. The active material, being an insoluble ionic compound, possesses an extremely high electrical resistance³⁾. In order to create an extensive contact between electrode and solution, the former is made of porous material. Hence stagnating the solution absorbed, its porous structure impedes the diffusion and the transfer of the reacting ion, and causes extreme polarization of its active material when c.d. is raised.

Whenever the battery is charged or discharged, particles of the active material of these electrodes change their crystal structure and volume. This causes their binding force to relax. Hence increasing

their resistance and polarization, the function of these electrodes is lowered, and their reversibility is receded. Reversible electrode reaction is the most essential and fundamental feature of a storage battery, its electrodes should conserve their reversibility as surely as possible, in order to endure the lasting use repeating charges and discharges.

A cation reversible metallic electrode inherently sustains its new surface, depositing and dissolving whenever it is charged or discharged, thus eliminates the need for making it porous artificially. In addition its resistance is by far smaller than that of an anion reversible one. If made of a noble metal it preserves almost perfectly its reversibility even in the presence of

other cations, provided the concentration of this reacting cation in the solution is kept enough. But the dissolution and deposition of this reacting cation create other deficiencies.

To build a storage battery by using both cation reversible electrodes is technically difficult, so a Cu-PbO₂ battery was designed using cation reversible one as the cathode

only¹⁾. Pb of the lead battery was exchanged for Cu. To eliminate the main defects of this battery, sealing it may be the most adequate countermeasure^{1),2)}. It was found possible to safely charge this battery, without a burst of expelled gases in a sealed state, when the applied voltage is limited to values below 1.85 V.²⁾ The behavior of this battery around this limiting

(a), (b) The maximum applied voltage has been 1.9 V. In the voltage curve, a slight "step" appears near the end, then it reaches the maximum, while the current is reduced to zero.

(c) The maximum applied voltage has been 1.6 V. The "step" of the voltage curve almost vanishes, and the current is reduced gradually to zero.

(d) The maximum applied voltage has been 2.2 V. The "step" grows, but without arriving at its maximum value, the electrode reaction is changed to the decomposition of water, though its current is very weak.

The applied voltage is expressed by o and the current strength by x.

Fig. 1 Charging of a Cu-PbO₂ battery of 48 A.hr capacity, without regulating the circuit at half-way of an experiment, by arranging previously.

voltage has been investigated and the results are reported herewith.

2. Experimental

2.1 Charging Curve of Both Batteries

The rectifier is pre-regulated, so as the terminal voltage of its output side to assume a value below 1.9 V at its maximum. This battery of 48 A. hr is then charged by connecting it directly to this output terminals. At first a current of 1.5 V and 1.8 A approximately is sent through the battery, and as the charging proceeds terminal voltage of the battery increases by slow degrees up to its final value, while the current intensity diminishes gradually until it is finally reduced to zero.

Actual aspects of the charging process of this battery are seen in Fig. 1. (a) and (b) stand for charging under a final voltage of 1.9 and 1.8 V respectively. Near its final value the voltage rises creating a small "step", and at the same time the current decreases somewhat steeply. This step falls and finally disappears completely, when the applied voltage is lowered, as can be seen in (c), in which the value of the final voltage was 1.6 V.

Many gaps and fluctuations are seen in these curves. Gaps arise when the measurement is interrupted till next day, and they are increased according to the advance of the polarization of the active material, i.e. near the end of both the charging and discharging processes. Fluctuations are more promoted on the current curves than on the voltage ones, though their values are the same order when measured in volt and ampere units. The aspect of the fluctuations is different on every curve showing the condition of each electrode experimented with.

The internal resistance of this battery considerably varies according to the state of electrodes; at a fairly charged state it was 0.1~0.3 Ω . This value is by one order

of magnitude lower than that calculated from the values of the applied voltage V and current intensity A , employing Ohm's law $i=E/R$; hence they seem to contradict each other. However E must stand for the real electric force required to drive the current. Thus the difference between the applied voltage and the battery's e.m.f., and not the terminal voltage as indicated by the voltmeter should be employed.

When the applied voltage is fully balanced by the e.m.f. of the battery, a voltmeter set in the circuit does not indicate zero, despite the fact that no current can be sent through the circuit. Hence E of Ohm's law means the actual electric force required to drive the current, which may be about one order of magnitude smaller than the value indicated by the voltmeter, (i. e. the voltage applied in the experiment). This may be the reason, why the fluctuations of the voltage curve are mild compared with those of the current intensity curve.

Fig. 1 (d) shows the behavior of the curve when the final voltage is raised to 2.2 V, using the same battery by which curve (a) was obtained, but inserting a resistance of about 0.2 Ω in series to the battery. The step of the voltage near the end of the charging process and the corresponding decrease of the current intensity are larger than in (a) and (b), but the final current intensity of (d) does not diminish to zero causing some decomposition of water and liberation of a small quantity of gas.

If the same experiment is carried out with a lead battery, a curve shown in Fig. 2 (a) is obtained. It resembles the one in Fig. 1 (c) of the other battery, but the current ceases to drop at a certain value, and the electrode reaction is succeeded by the decomposition of water accompanying a vigorous liberation of gases. If the applied voltage is lowered the current

does drop, but the charging process is also restrained and stops at half-way of its course. It is difficult to separate the two reactions by manipulating the voltage.

Fig. 2 (b) represents the discharging curve following the charging of the lead battery. Both terminal voltage and current intensity are measured in the same way as in the charging experiment. The net energy accumulated is by far smaller than that put into the battery, showing it has a poor efficiency. While the Cu-PbO₂ battery proves to possess an outstanding efficiency, combined with the low tendency for gas expulsion. However concerning the capacity for storing energy, the latter is much inferior to the former due to its low e. m. f.

If this battery is charged restricting the output voltage of the electric source below 1.9 V, current density amounts to only 0.2 A/dm² and about 35 hours may be needed to complete the charging. But as the reaction proceeds, the current is reduced to zero and stops completely when saturation is reached. This fact points out the possibility of applying sealing to the battery²⁾. Actually this can be proved to be

(a) Charging, with 2.5 V as the maximum voltage value. The electrode reaction changes smoothly to the decomposition of water.

safe. To investigate the feature about this critical voltage, the following experiments were performed.

2.2 Voltage Difference of the 2 Reactions

Regarding a lead battery of 48 A. hr capacity, a voltage equal and opposite to its e. m. f. is applied, by regulating the electric source at the end of its charging cycle. As this is an equilibrium state, no current is passed through the circuit. Then the voltage is raised by slow degrees, measuring this voltage value and the corresponding current intensity, and then this voltage is slowly lowered back continuing the measurements. Fig. 3 illustrates the actual behavior of this battery, showing a nearly linear relationship between the applied voltage and the current intensity.

The linearity of this relationship has been tested up to a current of 7 A, and has been found to hold continuously throughout this range. In Fig. 3 the applied voltage was plotted as ordinate and the current

(b) Discharging, following the above charging process. The fact that its accumulated energy is small compared with that put in, shows the low efficiency of this battery.

Fig. 2 Charging and discharging of a lead battery of 48 A.hr capacity, without regulating the circuit at half-way of the experiment as related in Fig. 1.

Data of the forward course (voltage is raised gradually) are expressed by O, and those of the backward course (voltage is lowered gradually) by X.

Fig. 3 Testing of electrode reaction of a charged lead battery, by measuring the applied voltage and the current strength, and by observing the aspect of gas expulsion from both electrodes.

intensity as abscissa. The upper couple of lines represents data obtained from a battery, immediately after its electrodes have been fully overcharged; while the lower couple illustrates the behavior of a battery, which has been charged and then

(a), (b) Measurement on a battery, the anode reaction is unsaturated still, while Cu^{2+} left in the solution presents a little quantity. Charging only takes place below the steep slope range, while above it, it occurs together with the decomposition of water.

left for some days to stabilize its e. m. f.

The forward and backward curves of the two couples nearly coincide, proving their condition of electrode reaction to be sustained invariably during the one couple of processes. Evolution of gas is noticed on both electrodes from the beginning and grows appreciably as the current increases. This evolution of gas increases on the upper couple more vigorously than on the lower one. Hence regarding a lead battery, the voltage of charging and that of water decomposition may overlap, causing both reactions to occur side by side, beginning from half-way of the charging cycle.

Fig. 4 and Fig. 5 represents the results of similar experiments carried out on the Cu-PbO₂ battery. Curves (a) and (b) of Fig. 4 were obtained from a battery whose electrodes still reserve some capacity, but the Cu^{2+} concentration in the electrolyte remains small as illustrated by the loss of color of the solution. Measuring the forward process, at first the terminal voltage increases slowly, but soon it begins to rise making a "steep slope", and then resumes

(c), (d) Measurement on a battery, the anode reaction is saturated and a little Cu^{2+} is present in the solution. Readings at the steep slope range stray about requiring a while to settle.

(e) Measurement performed at similar conditions as in the above case, but at a slow pace allowing the readings to settle down. A quadrilateral is formed between the forward and the backward curves.

(f) Measurement performed as in (e), but 30 cm^3 of saturate CuSO_4 solution has been added, before the backward course is started. The quadrilateral is distinctly contracted in width.

Fig. 4 Testing of electrode reaction of a charged Cu-PbO₂ battery, by measuring the applied voltage and the current strength, and by observing the aspect of gas expulsion from both electrodes.

its slow slope again, corresponding to the constant increase of the current intensity. Then reversing the course, the backward process is measured, its curve behaves so similarly as to coincide with the forward one.

Curves (c) and (d) of Fig. 4 show the ensuing measurements of the previous battery, in the case the battery is charged to full capacity as far as both electrodes and solution are concerned. The concentration of Cu^{2+} was lowered from (c) to (d), because the current was sent continually without making up for the loss of this ion. In this case readings at the steep slope range of the forward course became unsteadily straying for a while, and the slope itself grew so steep as to rise up vertically. However the grade of steep slope portion of the backward was almost identical to those of (a) and (b).

Liberation of gas occurs at the PbO_2 anode from half-way of the steep grade portion, and begins also at the Cu cathode from the outset of the upper slow grade, while on the returning course it behaves in the reverse order. This liberation of gas seems to behave more accurately on the forward course, in case the steep grade part becomes vertical. This steep grade portion changes its place according to the Cu^{2+} concentration as described later, but the above observation regarding the liberation of gases holds, independently of the shift of the steep grade portion.

Henceforth Fig. 4 (d), measurements of the backward course were commenced after a pause of 30 minutes finishing the forward course, so the two curves forward and backward are detached at their upper ends too. Besides henceforth Fig. 4 (e), data were measured at a slow pace intentionally at the vertically rising range, waiting to calm down the straying of readings. This time the steep grade portions of both curves are separated, forming a

quadrilateral as can be seen in (e) and (f) of Fig. 4 and in Fig. 5.

This quadrilateral area seems to be growing, probably because of changes in the battery's conditions, caused by the prolonged driving of current through it. Anodic reaction being saturated already, thus almost no chemical changes may occur in the active material merely expelling O_2 . Cathodic reaction is restrained by the lack of Cu^{2+} in the solution, and as this lack grows rapidly, it may affect the battery's condition, hence in (f) 30 cm³ of saturate CuSO_4 solution had been added before the backward was commenced. The area of the quadrilateral is clearly reduced comparing with (e).

At the measurements of (e) and (f), the solution was somewhat thicker than in (a)~(d) presuming from the tinge of Cu^{2+} in the solution. Interpreting from the variation of the concentration of Cu^{2+} between forward and backward courses, the growth of this quadrilateral area seems to exceed the expectation, for the consumption of Cu^{2+} in the forward process must be fully recompensed, by the addition of the saturate CuSO_4 solution prior to the backward process. Hence the growth of the area of this quadrilateral is not understood well enough.

Hitherto it has been made clear from experiments, that the steep grade portion is shifted to the left side, when Cu^{2+} of the solution runs short, and to the right in case Cu^{2+} is supplied. Experiments illustrated in Fig. 5 confirm this point. In (a) this fact was tested with rich electrolyte; the vertical portion of the forward course is shifted to the right side, corresponding to 2.5 A of the abscissa. Anyhow the quadrilateral is contracted both in width and in length, and simultaneously shifted to the upper and righthand side as a whole.

In (b) and (c) of Fig. 5 Cu^{2+} was added

Fig. 5 (a) Measurement on a battery, the anode reaction is saturated, but Cu^{2+} ion is present abundantly in the solution.

The quadrilateral shrinks in length and width, and is moved to the right upward side as a whole.

Fig. 5 (b), (c) Experiments performed at conditions similar to those (e) and (f) of Fig. 4, 40 cm^3 of saturate CuSO_4 solution were added at half-way of the steep grade, both in forward and backward courses. An abrupt shift to the right down side appears corresponding to this addition.

at half-way of the forward and the backward courses. A solution having a light tinge of Cu^{2+} at the beginning showed a slight increase in color at the end of the run, after a double addition of 40 cm^3 of saturate CuSO_4 solution. Whenever this addition is performed at the steep grade portion, the curve is shifted abruptly to the right and downward direction. This time also the vertical portion of the forward course is shifted to 2.5 A of the abscissa as in (a), in spite of the fact that the solution is by far poorer in Cu^{2+} than in the previous case. But it does not contract so much in length.

On the backward course, besides the similar abrupt shift to the right and downward direction as is seen on the forward

one, the inclination of this steep slope is further lessened, and obviously this portion is moved to the left as a whole, despite the fact that the concentration of Cu^{2+} is increased in comparison with the forward course. The saturation of the active material of the charged anode may affect these phenomena; anyhow it seems that they are more emphasized, whenever the measurements are made during a longer period of time.

A paste type PbO_2 electrode of $48 \text{ A}\cdot\text{hr}$ capacity of a lead battery, consisting of 4 leaves, was utilized as the anode; and a common Cu plate of 1 mm thickness, produced by an electrolytic procedure, was adopted as the cathode forming a 5-plates unit. A glass cell of a dissected lead

battery was utilized for the vessel, and it contained about 1.1 l of electrolyte solution.

The concentration of the solution were as follows: for the experiments illustrated in (a) (d) of Fig. 1, saturate CuSO_4 solution was diluted to 1/200, for those illustrated in (e) and (f) of Fig. 4 and (b) and (c) of Fig. 5, the same solution was diluted to 1/20~1/50, while for the experiment of (a) of Fig. 5, the dilution was 1/2. Of course they contained also no small quantity of H_2SO_4 , produced because of the preparative charging reaction.

2.3 Discussion of Experimental

The concentration of the reacting ion in the vicinity of the electrode on which this ion reacts, controls the equilibrium potential of the electrode, hence this concentration may affect the aspect of the experimental curve, especially when it is low. The lower the concentration is, the more rapidly it varies corresponding to a given amount of electricity sent through the cell. From this viewpoint Cu^{2+} ion may have the most significant influence, because its concentration diminishes at a steady pace at the closing of the charging process.

Therefore as the charging proceeds, the electrode reaction of the charging is restrained due to the shortage of Cu^{2+} depositing on the cathode, and as the current strength being decreased and the electrode potential being raised, the reaction is necessarily changed to the decomposition of water. Hence the steep slope portion of the backward course must shift to the left upper side forming the quadrilateral, the area of which may be developed deservedly, if data are taken deliberately over a time driving the current.

The discontinuous shift as seen in (b) and (c) of Fig. 5, when Cu^{2+} is added, may also be due to the same reason. In

this case, as the concentration of the reacting ion is increased by its sudden addition at half-way of the steep grade, relaxing the shortage of Cu^{2+} , and thus favoring the main electrode reaction, the current intensity may be increased while the applied voltage may be lowered, i. e. the curve may promptly be compelled to shift to the right down side, irrespective of the course forward or backward.

Probably the reason, that the steep slope portion of the forward course rises vertically, and that of the backward one makes a gentle slope, may also be the same. That is, as the solution runs short of Cu^{2+} , readings on the steep slope tend to be moved to the left upward, forcing the deposition of H^+ instead that of Cu^{2+} . Hence at the steep portion of the forward course, the higher the readings are situated, the later they are measured and the more they are shifted, causing the slope to become steeper still. Similarly lower readings are moved to a larger extent at the steep portion of the backward course, making the slope gentle.

It is not clear, why the steep slope of the backward course departs from that of the forward, to an extent exceeding any presumption, when measured at slow pace, and why it does not retrace the initial locality of the forward, despite the supply of Cu^{2+} to fill up the shortage is practiced. The operation of the overvoltage may be repressed, by the inertia of the continuous and vigorous liberation of gases on the backward course; or may be due to the porous structure of the anode, obstructing the diffusion and the transfer of the reacting ion in the solution, which had permeated among this structure.

However the most probable reason may be the saturation of the PbO_2 anode. This electrode is saturated from the beginning as related formerly, but when the battery

is reposed, some capacity may be regained in the active material by local currents and self-discharges, averaging the change and expelling the excess over its surface. Hence it may absorb oxygen at the start, but will soon be saturated again, and restricted by this saturation, electrode reaction may be urged to shift to the decomposition of water, raising the applied voltage in spite of the existence of Cu^{2+} ion.

The fact, that the vertical portion of the forward course is shifted to 2.5 A unconcerned with the concentration of Cu^{2+} , provided this ion is present in a sufficient quantity, can be seen in Fig. 5. This may also be interpreted by this saturation of PbO_2 . Anyhow the electrode reaction of charging is limited by two factors, i.e. the shortage of the Cu^{2+} reacting ion and the saturation of the PbO_2 active material. In such cases O_2 is expelled at half-way and H_2 is liberated at the upper end of the steep grade, showing that the exchange of the charging for the decomposition of water happens at this steep grade range.

From experiments mentioned above, we arrived at the conclusion, that there are two oblique curves, which are parallel to each other with an interval of about 0.5 V between them, increasing their current intensity as the applied voltage is gradually raised. The upper curve represents the decomposition of water, and the lower curve represents the electrode reaction of charging, showing the feature of this battery.

When the applied voltage is low, the lower reaction occurs adapting its current intensity to this voltage. In case the applied voltage is raised, it is forced to exchange for the upper reaction, again adapting its current intensity to this raised voltage tracing the forward course. It traces reversely changing the reaction from the upper to the lower, when the applied voltage is lowered making the backward course.

Hence the steep grade portion of this

experimental curve undertakes the role to change the electrochemical reaction from one to the other. That is, it serves as a bridge connecting both domains of chemical reactions, the charging of the battery and the decomposition of water. Besides, this bridge moves from right to left along the thresholds of the two domains, as a function of the rate of disappearance of Cu^{2+} ion. The interval between these thresholds is kept at about 0.5 V, in case the concentration of Cu^{2+} is not too high.

3. Behavior of the Sealed Battery

Regarding the lead battery, both reactions are difficult to separate, because they occur at overlapping potentials. Therefore as the charging proceeds, the rate of reaction of water decomposition grows concurring with the charging reaction, so it is difficult to seal expelling gases.

Concerning this battery, due to the low e.m.f., the electrode potential of these two reactions differ by about 0.5 V at the end of the charging process. On the other hand, if the electrolytic formation of active material of the anode is unsatisfactory, O_2 is liberated occasionally at a voltage as low as 1.6 V, but H_2 is never expelled when the applied voltage is below 2.1 V, despite the solution holds acid as described formerly. Hence the sealing is applicable, and this sealed battery has been tested actually in order to investigate the practical remedy for its defects.

The pressure rises temporarily above 2 atm., when the sealed battery is charged under the above condition, and is lowered sometimes below 1 atm., when it is left to stand after charging. Charging takes as long as 30~40 hr, the current density being about 0.2 A/dm². However this time may be shortened to nearly 20 hr, by repeatedly attending and regulating the termi-

nal voltage, to indicate 1.85 V throughout the charging.

Immediately after the charging, self-discharge of this sealed battery is raised markedly surpassing that of the unsealed one by 2~5 A. hr, yet it calms down after 1~2 days to a low rate similar to that of the unsealed one. Originally self-discharge of this battery advances very slowly amounting only to 12 A. hr during 4 months, which still leaves about 3/4 of the charged electric energy. The high rate self-discharge of the sealed battery immediately after charging may be due to the expulsion of oxygen, which has been absorbed compulsorily in the course of overcharge.

The electrode reaction of charging, when the battery is saturated, may be as follows. Now the anode can absorb no more oxygen, hence

the expulsion of H_2 is restrained when the voltage is limited to a value below 2.1 V, but current flows as long as Cu^{2+} ions are present in the solution

combining both reactions we get

When the battery is sealed, as oxygen cannot be expelled as O_2 gas, it must be forced into the solution. Hence the Cu plate may be oxidized, and reacting with H_2SO_4 this oxide may dissolve into the solution,

combining these two stages into one,

The former overcharging electrode reaction is compensated with the latter oxidizing reaction of Cu, and there occurs no chemical change after all. Actually in such cases the coloration of the solution caused by Cu^{2+} decreases at a slower pace and the evolution of heat becomes eminent.

When the electrode is overcharged, self-

discharge as described above, may serve as the compensating reaction in a sealed battery. Because the anode may yield oxygen, which it has been previously forced to absorb during charging, gradually during discharging. Compensating reaction may be the simultaneous reaction and the self-discharging reaction may be the ensuing one, which repay the overcharging reaction, because the true nature of both reactions is identical, i.e. changing H_2SO_4 to CuSO_4 of the electrolyte and reducing the anode.

Regarding the unsealed battery, irreversible expulsion of O_2 is its main defects, causing to diminish the Cu^{2+} concentration in the solution.^{1),2)} By sealing it, this defect should be overcome, but this defect of Cu^{2+} diminution remains actually in some measure yet. It may be due to irreversible absorption of oxygen by the active material. Each particle of its structure changes the function of its chemical reaction as often as it is served; at some times enhancing its function, it is incorporated into the electric circuit; while at the other times raising its resistance, it is isolated from the circuit, and the absorbed oxygen may be reserved in the anode structure irreversibly.

Because of the short testing time, we are uncertain as to the durability of this battery, but the collapse of the anode by the oxidation of its frame seems to occur much slower than in the case of the original lead battery, even when sealed. Special attention should rather be paid to the cathode, for it is deposited and dissolved repeatedly. To carry out overdischarge until its e.m.f. drops markedly, or to overcharge until Cu^{2+} is exhausted in the solution seems to have a bad effect on both electrodes.

4. Conclusion

In various aspects this Cu-PbO₂ storage battery excels the original lead-acid battery,

while it has some serious defects which were enumerated and discussed previously^{1),2)}. The sealing of this battery may be the most effective means to overcome these defects. The possibility of its application has been confirmed, investigating the ground of its eligibility, as mentioned above.

The e.m.f. of this battery at the charged state is 1.4 V, and it has been verified that, when the applied voltage is regulated below 1.9 V, charging is performed securely and the most of its defects are likely to be cancelled by sealing the battery. Yet ex-

periments must be continued to investigate more precisely and accurately, as to the character and the durability of this sealed battery.

Literature:

- 1) S. Furumi, *Denki-kagaku* **30**, 833 (1962); S. Furumi, H. Sakashita, *This Journal* **30**, 173 (1962).
- 2) S. Furumi, T. Kubo, H. Sakashita, *Denki-Kagaku* **32**, 342 (1964); S. Furumi, T. Kubo, H. Sakashita, *This Journal* **31**, 160 (1963).
- 3) S. Furumi, *Denki-kagaku* **31**, 89 (1963); S. Furumi, T. Kubo, *This Journal* **30**, 179 (1962).