Experimental Studies on the Electrochemical Polarisation Produced in the Cylindrical Mass of Litharge. I.

By Takewo TIKU.

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Introduction. It is well known that the oxides of lead in pasted state applied to the metal grid of lead or lead-antimony alloy are electrolytically transformed into the positive or negative active materials of the lead storage cell in dilute sulphuric acid solution. The above procedure is called the formation of pasted plates. As the negatives are grayish and the positives dark-brown or black, while litharge is yellow, the paste at the initial or final stage of the formation can be easily distinguished. In the intermediate stage of the formation of plates, it is observed that the paste in grids consists of two parts of different colours, displayed by litharge and by the positive or the negative material. The boundary between the two parts is to be regarded as the front of the formation. In the case of the negatives the front progresses from near the surface of the paste, but in the case of the positives it starts from comparatively deep portion of the paste and reaches the surface at the end. From these features of the progress of the formation, the existence of some definite distribution of the electrochemical condition should be expected in the mass of litharge in the electrode plate.

The author intended to study the electrochemical polarisation in the mass of pasted litharge applying the direct electric potential through it, without using any metal electrodes attached to it.

Method of Producing Polarisation in the Mass of Litharge. In order to produce the positive and negative polarisations of the same kind as in the lead storage cell, the pasted mass of litharge must be placed in dilute sulphuric acid solution between two electrodes leading direct electric current. But, if the two electrodes are bridged with the electrolyte in any way, the portion of electric current passing through the mass of litharge shall be very small and the polarisation can hardly occur in it. In order to avoid this difficulty, a glass tube of moderate length was stuffed in its middle position with the pasted mass of litharge and the cavities at both sides of the mass were filled with dilute sulphuric acid solution, as is shown in Fig. 1. The pasted mass of litharge in the glass

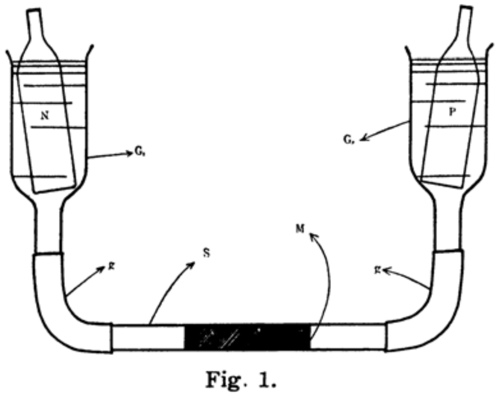

Fig. 1.

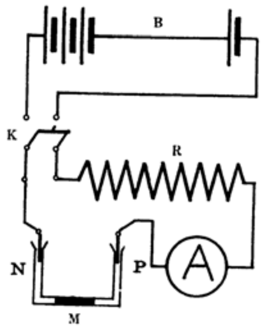

Fig. 2.

tube has a cylindrical form, its two bases being perpendicular to its axis. The length of the cylindrical mass was varied in the range of several centimeters.

In Fig. 1, S is the glass tube mentioned above, which was horizontally supported. M is the pasted mass of litharge. G_1 and G_2 are also glass tubes, supported nearly vertically, and connected to the both ends of S with rubber tubing g. Dilute sulphuric acid was poured into G_1 and G_2 and the small battery plates P and N were introduced as electrodes. The mass M is thus sandwiched by the electrolyte. Direct electric potential was applied between P and N in the manner as shown in Fig. 2. B is a high tension battery, the voltage (v) of which is applied through the ohmic resistance R (8400 ohms) and the ammeter A when the key K is closed.

The pasted mass was made by mixing litharge powder and distilled water, the water being dropped on the powder till the paste attained the desired degree of stickiness. The consumption of the water was about 10% of the litharge in weight in every case. The litharge was put into the glass tube (the inner diameter about 0.7 cm.) as soon as possible and then the potential was applied. Density of the electrolyte used was about 1.20 at ordinary temperature. The value of v was about 66 volts.

After several hours application of v, chemical changes were observed to develop as follows. Around the positive end of the cylindrical mass several spots of grayish colour appeared in the field of buff colour and then the spots grew to be connected into each other. About this time dark brown and rather diffuse spots appeared at the negative side certain distance apart from the above. Then dendroidal figures began to grow from the former toward the latter and the latter proceeded to spread toward the more negative side. A typical appearance of patterns thus obtained are as drawn in Fig. 3. In Fig. 3, B is the former figure and

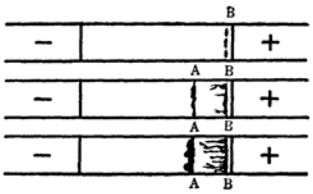

Fig. 3.

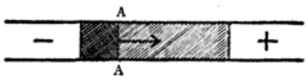

Fig. 4.

A the latter. Materials formed at A and B are ascertained to be lead-peroxide and lead respectively. These changes from litharge are of the same nature as in the formation of positive and negative electrodes of the lead storage cell, the electrolysis taking place in the mass itself.

Phenomena Observed before the Polarisation Patterns are Formed. In a few minutes after the application of the potential v, it was found that the colour of the negative end region of the mass turns slightly reddish, and this region spreads toward the positive side (Fig. 4). It was easily observed from the displacement of the boundary $\overline{AA}$ between two regions of different colours toward the positive side. The average direction of the boundary $\overline{AA}$ appeared almost perpendicularly to the axis of the cylinder.

The velocity of $\overline{AA}$ diminished with time, and the displacement of $\overline{AA}$ became scarcely observable at the position certain distance apart from the positive end of the cylinder. Soon after, the polarisation patterns began to appear and the positive figure of the patterns appeared at the position of $\overline{AA}$, i.e., A in Fig. 3 is the place where $\overline{AA}$ ceased to move.

The current passing through the mass varied with time though the applied voltage v had nearly a constant value. This is shown in Fig. 5, the ordinate being the current, and the abscissa being the time after the application of v. The current gradually decreased with time at the beginning and reached minimum value within 10–90 minutes. At the next increasing stage, the fluctuation of current was so frequent that secure readings can hardly be obtained. It was during this period when

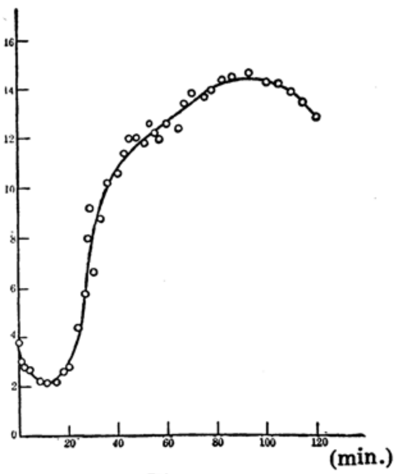

Fig. 5.

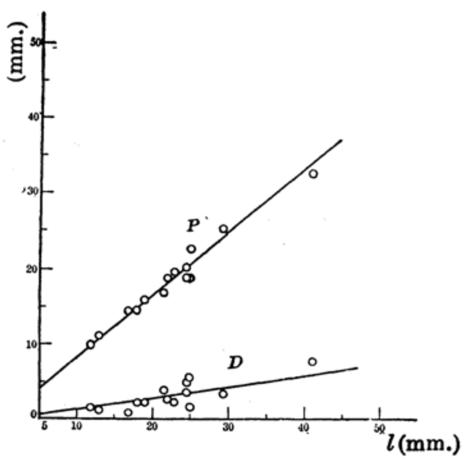

Fig. 6.

the polarisation patterns began to appear. After almost all the patterns shown in Fig. 3 were formed, the current did not change so much and maitained certain values for a while. The order of the currents was about several milliamperes.

On the Polarisation Patterns. It was experimented with several samples of different lengths. Apparent density of the mass in the glass tube before the application of the voltage was about 6.0 in every case. It was found that the position A where the positive figures are formed, was more distant from the positive end of the mass when the length l was larger. While the negative figures were formed at practically same position near the positive end, within the range of a millimeter. The relative position of A with respect to l, can be known from Fig. 6. Here, P is the distance of A from the negative end of the mass, and D is the distance between A and B in Fig. 3. From the figure, it may be recognized that points showing P and D respectively distribute on a straight line. The inclinations of the lines for P and D are 0.83 and 0.14 respectively. These are the average values of P/l and D/l which are independent of the length. The above fact shows that the relative position where the positive figure of the polarisation pattern is formed is definite amount apart from the both ends of the cylindrical mass.

The type of the development of positive and negative patterns of the polarisation already described was observed to be similar to that of the Lichtenberg figure. But the dendroidal development of the positive Lichtenberg figure was observed in the negative patterns in our case and the positive patterns were alike the negative Lichtenberg figure. The dendroidal development of the negative patterns corresponds to the phenomenon observed in the negative deposition of metals in electrolysis.

The electrochemical patterns already described are not a superficial phenomenon occurring at the boundary between the mass and the glass tube. The cylindrical sample was cut perpendicularly to the axis and the sectional surface was examined. The results are as follows. (1) In the parts of $\overline{\mathrm{AA}}$ and $\overline{\mathrm{BB}}$ in Fig. 3, the positive or negative formation was completed over the whole sectional surface. (2) In the part between $\overline{\mathrm{AA}}$ and the positive end, the polarity of the formation was positive or negative, and the pattern of either dull-grayish or dark-brown colour was found as spots in the sectional surface. In many cases, the positive was only of single big spot, while the negative was of several small ones. (3) In the part between $\overline{\mathrm{AA}}$ and the negative end, no polarisation was found.

Observations with Different Kinds of Litharge and under Varied Conditions. Further experiments on the effects of the modification of litharge, the diameter of the mass, and the terminal voltage V upon the value of P/l were undertaken. The same experimental arrangement as before was used, and in addition to this a voltmeter (resistance 10000 ohms) was shunted between the electrodes to know the value of V. Estimation of P was made as follows in this case. After the polarisation patterns appeared, thin cerophane paper was fastened just around the glass tube and perspective figures of the patterns were drawn on the paper. Then the paper was taken off, spread in a plane and the average value of P was determined by rounding off the irregularities around the mass.

It was noticed that the value of P/l was not always 0.83, but it varied in wide range under the same experimental conditions, according to the sample used. Litharge is found at ordinary temperature in red, yellow and buff modifications,[1] intermediate ones being often met with in commercial samples. Five different samples were examined in the experiment and the results obtained with them are as shown in Table 1.

Table 1.

Symbols for the different kinds of litharge	Colour of the powder	P/l	Remarks
(D), (C)	light greenish yellow	0.9	
(E)	yellowish red	0.2	
(A)	yellowish brown	0.6	for the battery use
(K)	yellow	0.8	" Bleioxyd—Kahlbaum zur Analyse "

The length and sectional diameter of the pasted cylindrical mass were about 23 mm. and 7 mm. respectively, the applied potential v was 110 – 120 volts. In pasting, 10 g. of the samples were taken and the necessary quantities Q of mixing water dropped into were as follows; 0.7 – 0.8 c.c. for (D) and (C), 1.15 c.c. for (E), 0.85 c.c. for (A), and 1.10 c.c. for (K). The room temperature was about 17 – 20°C. and the relative humidity about 70%. At the above compositions[2] the pastes attained the same degree of stickiness.

The apparent densities of them in the glass tube before the formation were about, 6.5 – 7.0 for (D) and (C), 6.5 for (E), 6.8 – 7.3 for (A), and 6.2 for (K) respectively.

From Table 1 it is known that the value of P/l is comparatively large with rather yellowish litharge, and small with reddish one. And this means that the boundary $\overline{AA}$ does not reach so near the positive end of the mass in the case of the reddish litharge, as for yellowish one. The samples (D) and (C) could not be distinguished by their appearance. The values of P/l for them were roughly 0.9 as shown in the Table 1. Precisely, the value for (C) was about 0.89, for (D) about 0.93, and the polarisation patterns in (C) appeared more elegantly than in (D). The sketches of the figures are shown in the next page.

(1) J.A. Smythe, " Lead," 234, (1923).

(2) In the previous work Q was 10% of the litharge, and the sample was rather reddish or brown.

The differences in the values of P/l for different samples will be considered to be the combined effect of the size of the particle, crystal form, purity and so on.

With the sample (C) described in Table 1, the polarisation phenomena were examined at different lengths and diameters of the mass and at varying series resistances. The composition of the paste was 10 g. of litharge and 0.7–0.85 c.c. of water. Applied voltage v was 110–120 volts.

(1) *Length.* Nineteen specimens of different lengths, 7.5–5.10 mm., were submitted to formation. Glass tubes for them were so chosen as the inner diameters were about 7.0 mm. The apparent densities were about 7.0.

The polarisation figures drawn on cerophane papers are shown in Fig. 7. Numerals in the nineteen figures are the lengths for themselves. The upside of each figure is the positive side. So the upper patterns are of negative and the lower zigzag patterns are of positive in each figure,

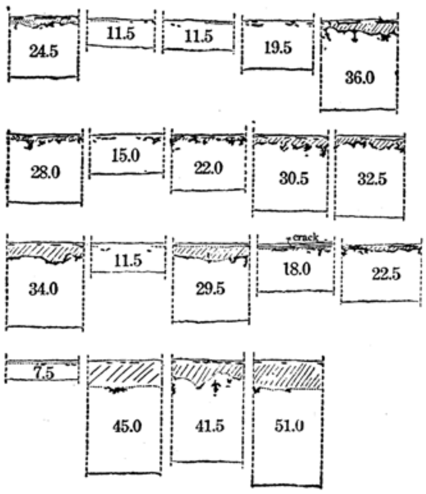

Fig. 7.

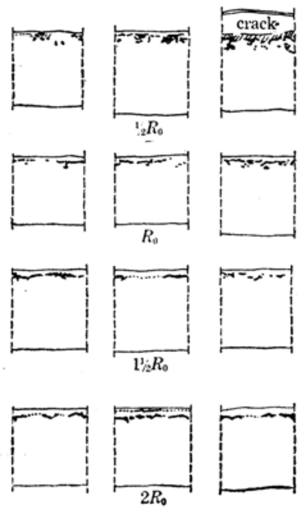

Fig. 8.

and dotted lines are the boundary $\overline{AA}$ where the patterns did not yet appear. The average values of P in these figures are plotted against the length l in Fig. 9. There exists a linear relationship for most points between P and l, which is represented by the straight line (1) in the figure. Several points, however, may be connected with the other straight line (2) also shown in the figure. The above straight lines pass through the origin. P/l estimated from (1) is 0.87, and from (2) is 0.78.

(2) *Thickness.* Thirteen kinds of the glass tube, the inner diameters of which were varied in 2–10 mm., were used to examine the effect of the thickness of the sample. The preparation of the specimens was the same as above. The length was about 25 mm. The value of P/l was about 0.9 or less in the average, and it showed a slight tendency to decrease with diminishing diameter. It would be the effect due to the fact that the apparent densities of the mass were found to diminish with

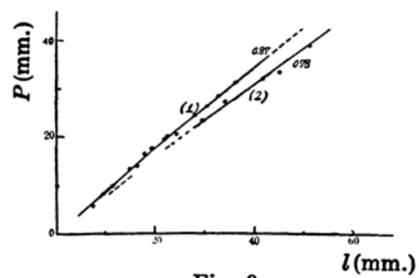

Fig. 9.

Table 2.

Value of series resistance	Time at maximum V (min.)	Maximum value of V (volts)
$^1/_2\ R_0$	5–10	80
R_0	15–25	62
$1^1/_2\ R_0$	20–30	50
$2R_0$	30–50	40-45

increasing diameter. P/l may be affected by the hardness of the mass.

(3) *Series resistance.* Terminal voltage V and the current through the mass are changed by the value of the external series resistance R. R was 8400 ohms in the above experiments. The four cases when R was $\frac{1}{2}R_0$, R_0, $1\frac{1}{2}R_0$, and $2R_0$ (R_0=8400 ohms) were tested. The lengths and the diameters of the samples were 26–32 mm. and 6.5–6.7 mm. respectively. P/l took nearly the same value, about 0.9, in four cases. The polarisation patterns, however, grew rather finely as seen in Fig. 8 which was drawn in the same manner as Fig. 7 and their progress became slower at higher resistances. It would be due to the lowering of the field in the mass. The characteristic between V and the time changed with the series resistance as shown in Table 2.

Summary.

Litharge powder was mixed with distilled water and turned to pasted form. This was stuffed in glass tubes of moderate length at their middle portions, and direct electric current was passed through the mass. Positive and negative patterns due to electrolytic polarisation was produced in the mass facing each other at definite positions in the axial direction of the cylindrical mass, the position of the negative being near the positive end of the mass. The ratios of the distance P of the positive position from the negative end to the length l of the mass were found to be independent of the length in the average.

The value of P/l is affected by the modification of litharge, but not by the diameter, the length of the mass and the terminal voltage.

In conclusion, the author wishes to express his hearty thanks to Prof. M. Katayama of the Tokyo Imperial University for the interest in this work and the encouragement through the course of the experiment, and to Asst. Prof. D. Nukiyama of the University for his kind advices on this investigation.

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