Studies on the Mechanism of the Electrolytic Formation of Perchlorate.* I.

By Kiichiro SUGINO and Shigeru AOYAGI

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Introduction and Outline of the Research

Preparation of peracids is the typical electroprocess which can not practically succeed by any other method. Especially, the production of perchlorate or persulphate is one of the most important electrolytic processes now operated in the world.

Anodic potential of the formation of perchlorate has been considered to be very high and this electrolytic preparation has been successfully accomplished only by the use of smooth platinum anode which has the highest oxygen overvoltage. One of the authors has already developed a new electrolytic process of this production using lead peroxide anode instead of platinum. In this case, in order to increase the oxygen overvoltage of lead peroxide anode, a small amount of sodium fluoride must be added in the electrolyte. The reason for these devices is that even if the anodic potential of the formation of perchlorate is very high, it can not proceed unless at the lower potential than that of oxygen evolution. But the anodic potential of the formation of perchlorate has not yet been accurately determined and the variation of it with the concentration of chlorate has also remained unknown. Therefore, the present study seeks to measure the anodic potential of perchlorate formation accurately and at the same time to present the most probable mechanism of this anodic process.

Twenty five years ago, the polarographic method was proposed by Heylovský and Shikata and the electrolytic reduction potential of organic compounds which is lower than that of hydrogen evolution at the dropping mercury cathode and the variation of it with the concentration of the depolariser can now be measured very easily by that method. So the authors tried to apply the same method to the anodic process of peracid formation to determine the potential at which the reaction occurs. If the anodic potential of perchlorate formation is lower than that of oxygen evolution at platinum anode, a typical anodic polarogram will be obtained by a platinum micro-anode, just the same as the cathodic polarogram of the reduction process described above. The resulting polarogram assumed is shown in Fig. 1.

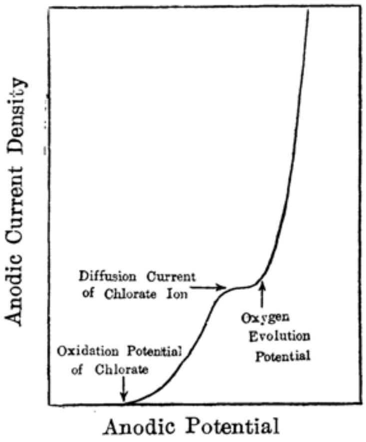

Fig. 1.

And the variation of the anodic potential with the concentration of chlorate will be approximately represented by the following formula.

$$E=\frac{RT}{2F}\ln\frac{K}{C_{\mathrm{ClO_3^-}}\cdot a^2_{\mathrm{OH^-}}}$$

where $C_{\mathrm{ClO_3^-}}$ is the concentration of chlorate having a definite value and K is a constant. If these assumptions are verified by the experiments, the formation of perchlorate must be expressed by the following mechanism; (1)

$$2\mathrm{OH}^- - 2e \rightarrow 2\mathrm{OH} \rightarrow \mathrm{O} + \mathrm{H_2O}$$

$$\mathrm{ClO_3}^- + \mathrm{O} \rightarrow \mathrm{ClO_4}^-$$

Upon these assumptions, the current-

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[*] This papar was already given in the lecture at the general meetings of the Electrochem. Soc. of Japan held on May 1949, April 1950 and April, 1952.

(1) Bennett and Mack, *Trans. Electrochem. Soc.*, **29**, 323 (1916).

potential curves of the electrolytic oxidation of chlorate were measured polarographically under various conditions. The nature of the polarogram thus obtained was quite different from that of the usual oxidation-reduction process as shown in Fig. 1 and from the polarogram, it was pointed out that the anodic potential of the oxidation of chlorate might be higher than that of oxygen evolution. And even the phenomenon which was probably the limiting current of the discharge of OH^- ion could also be seen in the polarogram. These results were not able to be completely explained by the usual mechanism described above. In order to explain the results more suitably, the authors proposed an alternative mechanism, in which the discharge of chlorate ion and the subsequent combination and hydrolysis of ClO_3 were assumed.(2)(3) This mechanism has already been proposed by other investigators, but no experimental verifications were found in the literature of the subject.

The research has been further continued to confirm the above results. For this purpose, the electrolysis of chlorate solution at definite anodic potential was carried out and the anodic current density and the current efficiency of perchlorate formation at that current density were plotted against the anodic potential applied. A current-potential curve like the polarogram was obtained from these experiments and it was observed that the current efficiency of perchlorate formation increased with increasing current density due to the increase of anodic potential applied. And in spite of no perchlorate formation in the electrolysis of a very dilute aqueous solution of chlorate, it was also observed that when the same amount of chlorate dissolved in a concentrated perchlorate solution was electrolysed (this is the case of practical perchlorate cell), perchlorate was formed in a fair current efficiency. In addition to this, perchlorate solution itself gave an analogous polarogram as chlorate in which the discharge potential of perchlorate ion was observed at higher value than that of oxygen evolution. From these experiments, it was made clear that the first step of perchlorate formation was probably the discharge of chlorate ion. And it may be supposed that the reason for the possibility of discharge of chlorate ion is not only the high oxygen overvoltage of special anodic materials, but also the lack of water in the neighbourhood of the electrode surface due to the extraordinarily high salt concentration of the electrolyte and also to the strong hydration power of existing ions. (The latter was verified by further experiment.) These results will be reported successively. In this paper, only results obtained from the measurement of anodic polarogram of the electrolysis of chlorate and a possible mechanism based upon the polarogram were given.

(Part I) Anodic polarogram of the Electrolysis of Chlorate by a Platinum Microanode

Measurement of Current-potential Curves

A micro-rotating platinum electrode and a smooth platinum plate of sufficiently large area were used as the anode and the cathode respectively. The details of the cell design and the measurement circuit are shown in Fig. 2-b and Fig. 2-a.

(1) **Electrolytic Cell.** — The section of the platinum wire of 0.3 mm. diameter sealed in a glass tube was used as the anode, the area of which was about $10^{-3}\sim10^{-4}$ cm^2. The cathode was a platinum plate of 10 cm^2. Throughout the following electrolysis, the current being less than 7×10^{-4} amp., the potential drop across the electrolyte did not amount to 10 mv. which was the limit of accuracy of our potential measurement. The stem of the anode—a glass tube—was rotated at 1000 r. p. m.. Although the significance of this rotation is not very important, it prevents the accumlation of oxygen gas on the surface of the anode and maintains the thickness of the anodic diffusion layer unchanged during the measurement and so a better reproducibility in the measured current-potential curves may be expected.

(2) **Polarograph.** — The sensitivity of the galvanometer used was 3.5×10^{-6} amp./mm./m..

(3) **Apparatus for the cathodic potential measurement.**—Since the cathode has a large area and the current is very small, the polarisation at cathode is generally considered to be very small. But in our case, it was found that it amounted to about 500 mv. for the cathodic current density of 3.5×10^{-3} amp./cm^2.. Thus, the cathodic potential must be measured continually throughout the current-potential curve measurement. For this purpose, the simple apparatus illustrated in Fig. 2-a was sufficient and also very convenient, the sensitivity of which was 3 mv., and the range of measurement, -450 mv.$\sim$ $+450$ mv..

(4) **Temperature.** — The electrolytic cell and the calomel electrode were immersed in a thermostat regulated at 17°C±0.02°.

(5) **Electrolyte.**—1$\sim$6 mol./l. aqueous solutions of sodium chlorate were used. It is seen that the use of such a high concentration of the

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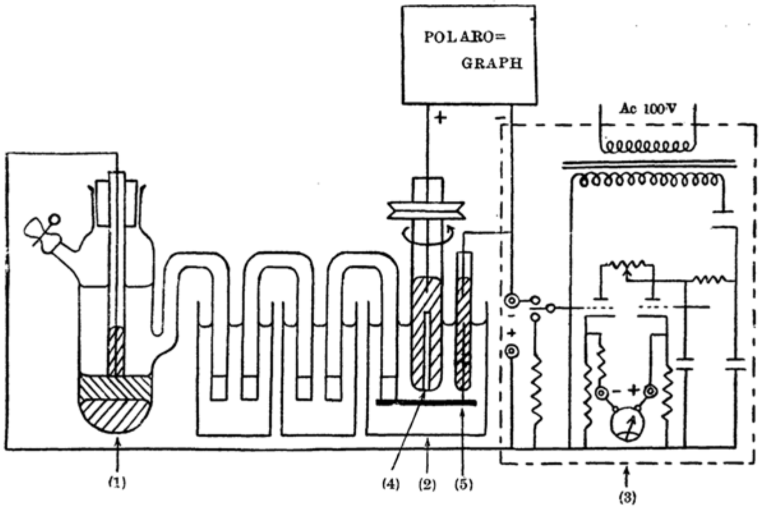
(2) Oechsli, *Z. Electrochem.* **9**, 807 (1903).

(3) Knibbs and Palfreeman, *Trans. Faraday Soc.*, **16**, 402 (1920).



Eig. 2 a.—(1) Calomel Electrode (Saturated KCl Type)
(2) Electrolytic Cell, (3) Valve Voltmeter,
(4) Anode. (5) Cathode.

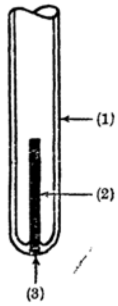


Fig. 2 b.—(1) Glass Tube
(2) Platinum Wire
(3) Anode Surface

electrolyte, together with the relatively large anodic current density mentioned above, makes the condition of our current-potential curve measurement deviate from that of the ideal polarographic method. But it was confirmed that for wellknown anodic processes (which occur at lower potential than that of oxygen evolution), usual polarograms were always given by the use of the same apparatus and under the same measuring conditions as described later.

Results and Discussion

The polarograms for various concentrations of sodium chlorate solutions are shown in Fig. 3. The abscissa corresponds to the anodic potential (the numerical values of which were obtained by subtracting the cathodic potential from the cell voltage and by referring to the hydrogen scale). The ordinate corresponds to the apparent anodic current density in amperes per dm². Its value, however, was not so reliable in consequence of the obscurity of the true apparent area of the anode.

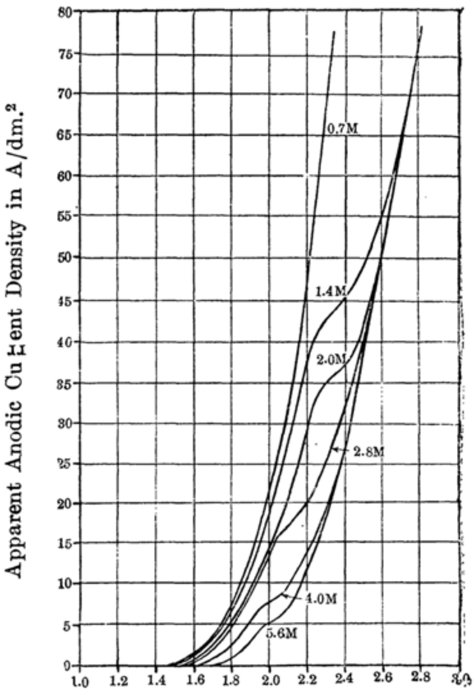
The potentials of the second stage were seen to be:

about 2.1 V for 5.6 M solution
2.1 〃 〃 4.0 〃
2.2 〃 〃 2.8 〃
2.4 〃 〃 2.0 〃
2.4 〃 〃 1.4 〃

Some characteristics of the polarograms obtained may be summarized as follows:

(1) In a moderately concentrated solution of chlorate, two stages of potential were definitely observed, as shown in Fig. 3.

(2) In the first or lower stage, the potential has a value of about 1.7—1.9 v. On the other hand, in the second or higher stage, the potential has a higher value than 2.3 v.



Anodic Potential in Volts (Hydrogen Scale).

Fig. 3.

(3) Contrary to the usual polarogram, the height of the wave of the first potential stage was seen to be reversely proportional to the concentration of chlorate. It lowered as the

concentration of chlorate increased.

(4) For a sufficiently dilute solution, this wave height grew so high that it reached beyond the range of the measurement, a simple exponential curve being observed.

If an analogous interpretation would be made for our polarogram to ordinary ones of the cathodic process, the first or lower stage should be the potential of the oxidation of chlorate and the second or higher one of oxygen evolution. This, however, must be decidedly denied by the fact that the height of the wave corresponding to the first stage is reversely proportional to the concentration of chlorate. In addition to this, the value of the potential of first stage was found to correspond to the one of oxygen evolution. (The reversible oxygen potential, E_{O_2/OH^-}, is about 0.8 v. for any solution of pH 7 and estimating about 1v. of oxygen overvoltage of a smooth polainum plate at the current density of 1 amp./dm^2., the actual oxygen evolution potential for any solution concerned amounts to about 1.8 v.) So, among two potential stages mentioned above, the lower one may be supposed, on account of its value of potential, to be a potential corresponding to the electrolysis of water or the evolution of oxygen gas. If the lower stage is regarded as the potential of oxygen evolution, the higher one may be of the oxidation of chlorate. Thus, our polarograms should be classified in another type of current-potential curve from the ordinary one. And it is obviously certain that the oxidation of chlorate occurs at some higher potential than that of oxygen evolution. This fact is not able to be explained by an usual following mechanism.

$$2OH^- - 2e \rightarrow 2OH \rightarrow O + H_2O$$

$$ClO_3^- + O \rightarrow ClO_4^-$$

So an alternative mechanism already proposed by other investigators was adopted by the authors in which the discharge of chlorate ion was assumed. A supposed mechanism may be formulated as follows

$$2ClO_3^- - 2e \rightarrow 2ClO_3$$

$$2ClO_3 + H_2O \rightarrow HClO_3 + HClO_4$$

$$\left\{\begin{array}{l} 2ClO_3^- - 2e \rightarrow 2ClO_3 \\ 2ClO_3 \rightarrow ClO_3-O_3Cl \\ ClO_3-O_3Cl + H_2O \rightarrow HClO_3 + HClO_4 \end{array}\right\} \quad (2)$$

Later, in order to confirm the accuracy of our polarographic method, one of the authors has carried out the measurement of current-potential curves of several typical anodic reactions (electrolysis of KCl, KBr, KI, $NaNO_2$, $Na_2S_2O_3$, Na_2SO_3 etc.) which seemed to occur at lower potential than that of oxygen evolution. In the polarograms thus obtained, the potential stages corresponding to each anodic reaction were observed definitely at lower potential than that of oxygen evolution. These results showed that the polarogram of the electrolytic oxidation of chlorate described above and the proposed mechanism based on the polarogram were both probably correct.

Further, in view of the prospective discussion of the dependence of the discharge of chlorate ion on the mechanism of perchlorate formation, it is necessary to know the true formation of perchlorate at the potential of second stage in Fig. 3. For this purpose, in the following research, the electrolysis of chlorate solution was carried out at a definite anodic potential, corresponding to the second stage in Fig. 3. under various conditions. Many interesting phenomena were observed and from the results obtained, our conclusion based upon the polarogram was seen to increase its appropriateness. These results will be reported hereafter.

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Laboratory of Organic Electrochemistry and
Biochemistry, Tokyo Institute of
Technology, Tokyo