

# The Electrolytic Formation of Persulphate. Part III. Study of the Electrodes.

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The anode plays a very important part in electrolytic oxidation. Selection of the anode material, its treatment and other conditions are limited especially in the case of electrolysis which involves strong acid solutions as in the present one. Platinum is the anode material which can be used exclusively in such a case, and an alternative to it has been long sought in vain.

The influence of igniting a Pt-anode previously to electrolysis was studied in Part II<sup>(1)</sup> of this investigation, and several other treatments of the anode are subsequently dealt with in this paper. The length of the Pt-wire cathode is also changed to see the influence of the cathodic current density, but nothing remarkable is found to take place.

**Experiment 1. Influence of the Cathodic Current Density.** The anode consists of a spiral of Pt-wire which is 0.05 cm. in diameter and 20.7 cm. in length, and the cathode also of Pt-wire as thick as the anode, which is wound spirally against the wall of the electrolytic vessel. Three different lengths of the cathode are employed, i.e., 20, 45, and 107 cm. 130 c.c. of 15 N sulphuric acid are electrolysed with these electrodes at 15°C. without diaphragm. Current efficiency (to be abbreviated as C.E. hereafter) for different current densities is shown in Table 1 and Fig. 1 and 2, the same amount of electricity being supplied in each case.

Table 1. Current Efficiency with the Length of the Cathode varied, the Electrolyte being 15 N Sulphuric Acid.

The length of the cathode		The current (amp.)	0.163	0.325	0.650	0.975	1.30	1.95	2.60
The Caro's acid C.E.	20 cm.		22.8%	34.2	38.0	34.3	30.4	28.4	27.0
	45		20.0	24.1	24.1	23.5	24.8	25.5	24.1
	107		4.8	33.4	31.5	28.4	25.8	19.2	15.7
The total C.E.	20		31.0	49.1	65.6	74.8	77.7	76.0	75.6
	45		25.5	40.0	58.7	67.3	71.7	74.0	65.5
	107		14.1	38.5	57.1	70.0	70.9	70.9	70.1

(1) This Bulletin, 11 (1936), 650.

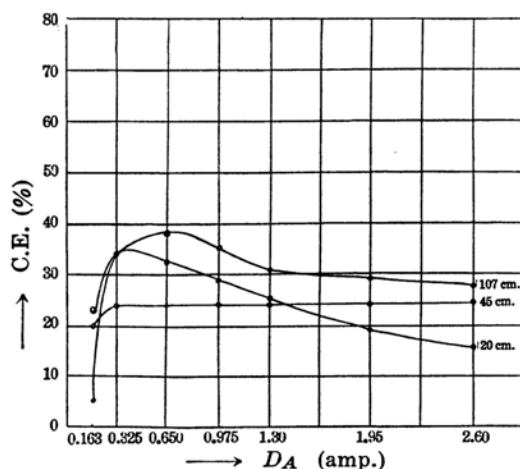


Fig. 1. Caro's Acid C.E. with Various Lengths of the Cathode.

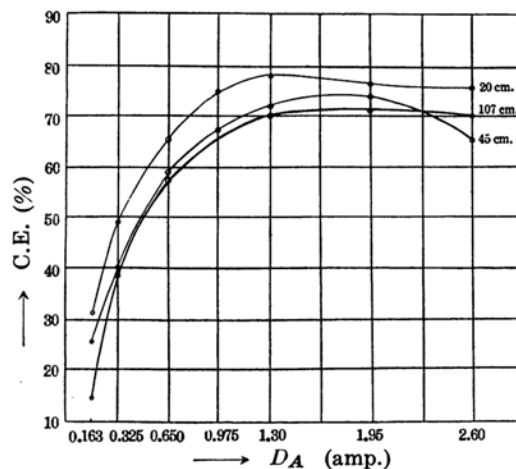


Fig. 2. The Total C.E. with Various Lengths of the Cathode.

The total C.E. is greater, the shorter the cathode: therefore a longer cathode is evidently more effective in reducing the peroxidic anodic products in spite of its smaller cathodic current density, because the influence of the cathode on C.E. probably consists merely in reducing the anodic products.

The greater the total C.E., in this experiment, the smaller the C.E. as to Caro's acid, which was the case also in Experiment 3 of Part II in which 15 N sulphate solutions containing various amounts of ammonium sulphate and sulphuric acid were electrolysed. In the latter case the fact was explained by means of the difference of sulphuric acid concentration. In the present case, however, the reason must be attributed to the condition of the cathode or something connected with it, because both the electrolyte and the anode are similar. Although it is not clearly known why, it seems likely that firstly Caro's acid is formed in greater amount when the cathode is longer, and secondly Caro's acid is reduced more easily than persulphuric acid when it comes near, or in contact with, the cathode irrespective of the magnitude of the cathodic current density.

**Experiment 2.  $\text{PbO}_2$ -anode.**  $\text{PbO}_2$ -anode was studied by several investigators, e.g., its preparation from lead nitrate solution by Y. Kato and K. Koizumi<sup>(2)</sup> and that from lead tartrate solution by G. Angel and H. Mellquist<sup>(3)</sup>. Both of these methods are examined in their adoptability

(2) *J. Electrochem. Assoc. Japan*, **2** (1934), 309.

(3) *Z. Elektrochem.*, **40** (1934), 702.

for the present purpose. Lead dioxide is deposited electrolytically on a Pt-anode from lead nitrate solution, whose compositions are varied as follows: 5 to 39 g.  $\text{Pb}(\text{NO}_3)_2$ , 1 to 10 c.c. conc.  $\text{HNO}_3$ , 0 to 1 g. gelatine, 90 to 95 c.c. water.

The Pt-anode is the same as used in Experiment 1 and the cathode is one of 45 cm. in length described above. The current is varied 0.04 to 3.0 amp., the temperature  $50^\circ$  to  $80^\circ\text{C}.$ , and the time of electrolysis 1 to 30 minutes. It is found that the deposition of lead dioxide is the hardest, the most uniform and adherent when the solution contains 39.0 g.  $\text{Pb}(\text{NO}_3)_2$ , 1.0 c.c. conc.  $\text{HNO}_3$ , 90 c.c. water and 1 g. gelatine, and the temperature  $77^\circ\text{C}.$ , the current 0.5 amp., and the time of electrolysis 30 minutes. A solution which is 3 and 4 N respectively as regards ammonium sulphate and sulphuric acid is electrolysed without diaphragm at  $15^\circ\text{C}.$  with the  $\text{PbO}_2$ -anode prepared under the best conditions as mentioned above. Three different intensities of current, 1.30, 1.95 and 2.60 amp., are applied for the electrolysis, the amount of electricity being the same, i.e., 1170 coulombs in each case. The total C.E. remains 3.0 to 3.1% for all the three intensities of current. When 15 N sulphuric acid is electrolysed under the same conditions as above, the total C.E. is even less than 3.0%. The  $\text{PbO}_2$ -anode prepared from lead nitrate solution under the other conditions is proved unavailable for the electrolysis, since the  $\text{PbO}_2$ -layer comes off partly or entirely during electrolysis.

Angel and Mellquist<sup>(3)</sup> say that they succeeded in preparing a  $\text{PbO}_2$ -anode by depositing lead dioxide on iron, steel or copper from lead tartrate solution, and the deposition of the same on platinum is here examined. A 13% KOH solution containing 17.7 g. lead tartrate in 100 c.c. is electrolysed at  $14^\circ$  to  $17^\circ\text{C}.$  by a current of 1.30 amp. for 15 minutes with the same anode and cathode as used in the previous case, and lead dioxide is deposited on the anode. While a solution which is 3 and 4 N respectively as regards ammonium sulphate and sulphuric acid is being electrolysed with the  $\text{PbO}_2$ -anode thus prepared and a Pt-cathode by a current of 1.30 amp. at  $15^\circ\text{C}.$ , it is found that lead dioxide comes off entirely from the Pt-base.

**Experiment 3. Carbon-anode.** An anode is made of gas carbon which is of rectangular section 4 mm.<sup>2</sup> and 3 cm. in length. The cathode is the Pt-one as used in previous cases. Three electrolyses are tested with these electrodes at  $15^\circ\text{C}.$  without diaphragm: 10 N sulphuric acid with a current of 2.6 amp., 6 N ammonium sulphate solution with 0.163 amp., and 6 N ammonium sulphate solution containing ammonia with 0.163 amp. The

carbon-anode is found, in each of these cases, partly to disintegrate, therefore its use is not promising.

**Experiment 4. Various Treatments of the Pt-anode.** 130 c.c. of 15 N sulphuric acid are electrolysed without diaphragm for 30 minutes at 15°C. with an anodic current density of 20 amp./dm.<sup>2</sup> Both the anode and cathode which is 45 cm. long are as described in Experiment 1, and the former, however, is subjected, immediately before use, to various heat treatments as follows.

When hydrogen and acetylene are used as the fuel for the treatments, each of these is led to a blast lamp and burned with air whose amount is so controlled as to keep the temperature of the Pt-anode which is put in the blast just to white heat. The temperatures to which the anode is heated are kept as near as possible throughout the treatments.

Table 2. Various Treatments of the Pt-Anode.

	Caro's acid C.E.	The Total C.E.
Coal gas flame <sup>(1)</sup>	24.1%	58.7%
Hydrogen flame	17.0 18.9 mean 18.0	50.0 46.1 mean 48.1
Acetylene flame	16.1 16.2 mean 16.2	63.0 60.5 mean 61.8
D.C. (downwards)	18.3 19.5 mean 18.9	50.2 58.7 mean 54.5
D.C. (upwards)	17.4 17.7 mean 17.6	53.5 54.4 mean 54.0
A.C.	20.9 21.1 mean 21.0	63.8 64.4 mean 64.1

Though it is not clear what takes place in the Pt-anode as the result of its heat treatments, more or less differences of C.E. are seen to occur according to the kind of treatment. Among the three kinds of flame

acetylene gives the best total C.E., hydrogen the poorest, and coal gas comes between them. Therefore the presence of hydrocarbon in the combustible gas or its combustion seems favourable to improve the anode activity.

The electrical treatment in which D.C. is flowed from the top of the anode to its lower end is denoted in the table as D.C. (downwards) and the reversed case as D.C. (upwards). There is no considerable difference between the influences of these two on C.E. The A.C. treatment, however, is superior to the D.C. treatment in increasing C.E. and gives the greatest total C.E. of all.

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