89. *The Anodic Oxidation of Platinum at Very Low Current Density.*

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The results of various workers on the variation of the anode potential with the quantity of electricity passed when the platinum electrode is forced from hydrogen to oxygen evolution, as well as on the type of oxides formed on the surface of the metal before oxygen evolution, have been clarified by carrying out the anodic oxidation of platinum in acid, neutral, and alkaline solutions at very low current density by the direct potentiometric method, using a special cell and constant current unit.

A limited amount of work has previously been carried out on the anodic oxidation of platinum. Bowden (*Proc. Roy. Soc.*, 1929, *A*, **125**, 446) showed that the change of the anode potential with the quantity of electricity passed occurring when the platinum electrode is forced from hydrogen to oxygen evolution was linear save for a slight break which was attributed to the formation of PtO_2 on the electrode. Butler and his co-workers (Butler and Armstrong, *ibid.*, 1932, *A*, **137**, 604; Armstrong, Himsworth, and Butler, *ibid.*, 1933, *A*, **143**, 89; Butler and Armstrong, *J.*, 1943, 743; Butler and Drever, *Trans. Faraday Soc.*, 1936, **32**, 427; Pearson and Butler, *ibid.*, 1938, **34**, 1163), on the other hand, distinguished stages for the ionisation of free and adsorbed hydrogen, the charging of a double layer, and finally the deposition of an adsorbed layer of oxygen. The results of Erschler, Frumkin, and their co-workers (Slygin and Frumkin, *Acta Physicochem. U.S.S.R.*, 1935, **3**, 791; 1936, **4**, 911; 1936, **5**, 819; Erschler and Proskurnin, *ibid.*, 1937, **6**, 195; Erschler, *ibid.*, 1937, **7**, 327; Erschler, Deborin, and Frumkin, *ibid.*, 1938, **8**, 565; *Trans. Faraday Soc.*, 1939, **35**, 464) are in general conformity with those of Butler *et al.* Recently Hickling (*Trans. Faraday Soc.*, 1945, **41**, 333), using his oscillographic method, showed that only PtO is formed on the surface of the anode before oxygen evolution begins. On the other hand, Altmann and Busch (*ibid.*, 1949, **45**, 720), using an undulant current, found by chemical analysis that the product was practically pure PtO_2,nH_2O.

In the present paper this point is clarified by studying the anodic oxidation of platinum in acid, neutral, and alkaline solutions at very low current density by the direct potentiometric method, using a special cell and constant current unit. By using an electrode of large surface area and a small current, a considerable time is required for the electrode to pass from the hydrogen- to the oxygen-evolution values and thus equilibrium potentials can be measured at each stage of the polarisation. From such a study it is shown that PtO is first formed over the surface of platinum, followed by PtO_2, before oxygen evolution occurs. The latter oxide is unstable, decomposing to PtO. The results have also been confirmed oscillographically.

EXPERIMENTAL

The Direct Potentiometric Method.—The circuit used in obtaining the variation of the potential of the anode with the quantity of electricity passed employed a pentode valve as a constant-current device, so the current passing was largely independent of changes in the back-e.m.f. of the electrode system. The current was supplied from a 240 v dry battery.

The electrolytic cell used was of Pyrex glass without rubber connections. It consisted of a vessel of *ca.* 500-ml. capacity provided with 5 openings. Three of these, which had mercury-sealed covers, were for the cathode compartment, the anode compartment, and the compartment for the syphon of the reference electrode respectively. These compartments were plugged with fine sintered-glass plugs to prevent contamination of the anolyte. The other openings were for gas-inlet and -exit tubes, the latter being fitted with a Bunsen valve.

The platinum anode was prepared by platinising a platinum foil of 1·8 sq. cm. with spongy platinum black. This was carried out in 1% platinum chloride solution at a high current density (30 milliamps./sq. cm. for 3 minutes). The spongy platinum deposited did not form a very thick layer and thus could be easily cleaned. The electrode was washed several times in conductivity water and then with the solution in which it would be studied before it was introduced in its compartment in the electrolytic cell. Each experiment was carried out with a freshly prepared electrode. The cathode was a platinum spiral which was placed in its compartment far enough from the anode to ensure uniform distribution of the polarising current at the anode surface.

Measurements have been carried out mainly with three electrolytes: 0·1N-sulphuric acid, 0·2M-KH_2PO_4 + 0·2M-Na_2HPO_4 buffer mixture of approx. pH 6·8, and 0·1N-sodium hydroxide, all prepared from " AnalaR " materials and conductivity water. The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen to remove any dissolved oxygen.

The current used was 30 microamps. per electrode. In each solution three studies were carried out on each electrode—the anodic polarisation, the cathodic polarisation, and the anodic decay. In the case of the anodic polarisation, the electrode was first polarised cathodically until hydrogen was evolved and a constant potential recorded, so as to ensure the reduction of any oxide already present on the surface of the electrode during its preparation. The current was then reversed to start the anodic polarisation, and the potential of the anode was recorded as a function of time. The cathodic curves were obtained after the electrode had been anodically polarised until oxygen was evolved; the current was then reversed and the potential of the working electrode measured at suitable time intervals. In case of the anodic decay experiments, the electrode was polarised anodically until oxygen was evolved; the current was then interrupted and the potential was measured after various times. All the experiments were carried out in an atmosphere of pure nitrogen.

The reference half cell was a saturated calomel electrode prepared according to the directions of Harned and Owen ("The Physical Chemistry of Electrolytic Solutions," 1943, p. 321). The electrolytic cell as well as the reference half cell were kept in an air-thermostat at 25° ± 0·01°. The e.m.f. was measured with a calibrated metre bridge and an Onwood mirror galvanometer having a sensitivity of 190 mm. per microamp.

The Cathode Ray Oscillographic Method.—Work with this method was carried out by one of us (El Wakkad) during a visit to Dr. A. Hickling (University of Liverpool) to whom the authors are greatly indebted. The circuit used was on the same principle as that previously used by Hickling and others (Hickling, *Trans. Faraday Soc.*, 1945, **41**, 333; 1946, **42**, 518; Hickling and Spice, *ibid.*, 1947, **43**, 762; Hickling and Taylor, *Faraday Soc. Discuss.*, 1947, **1**, 277; *Trans. Faraday Soc.*, 1948, **44**, 262; El Wakkad and Hickling, *ibid.*, 1950, **46**, 820); it records the variation of potential with the quantity of electricity passed prior to oxygen evolution. The anode used was a platinum wire sealed into a glass tube and mounted vertically; it had an apparent area of 0·1 sq. cm. and was approx. 1 cm. in length. Before use, it was cleaned with hot concentrated hydrochloric acid, hot concentrated nitric acid, and water, and finally heated to redness. The cathode was a platinum spiral of approx. 0·5 sq. cm. in area. Observations were made in an atmosphere of pure nitrogen in the solutions used in the direct potentiometric method. All experiments were carried out in a hut the temperature of which was constant at 25° ± 0·1°.

FIG. 1.

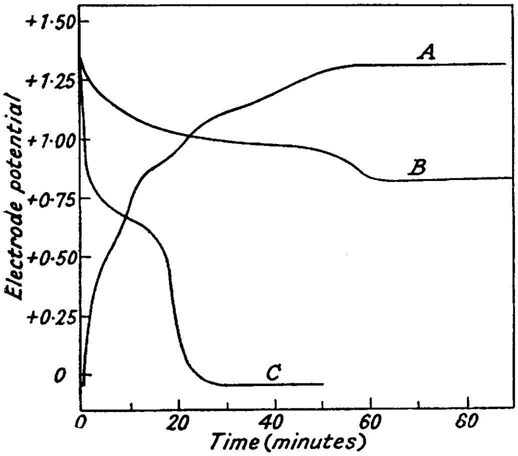
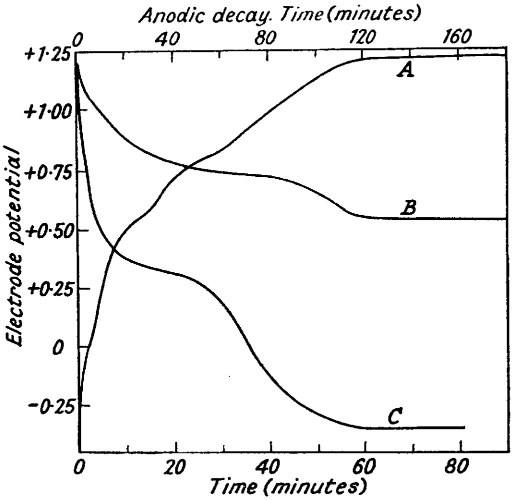


FIG. 2.



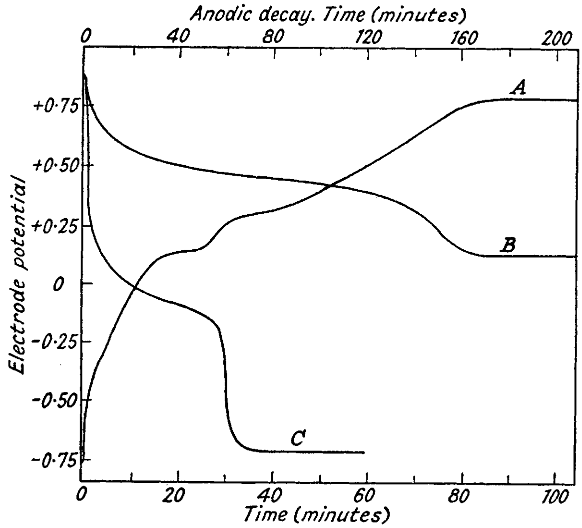
The results are shown as photographed oscillograms in which the ordinates represent potentials and the abscissæ are proportional to quantities of electricity passed. Suitable horizontal reference lines at intervals of 0·25 v were photographed immediately after the polarisation tracks, so that significant potentials can be read directly from the oscillograms. All potentials quoted are on the hydrogen scale. The quantity of electricity passed at any stage in the polarisation is obtained from the known capacity of the condenser in the circuit and the horizontal displacement which is governed by the voltage to which the condenser is charged. Suitable vertical lines at intervals of 10 v are shown, when necessary, to enable the quantity of electricity passed during the polarisation process to be calculated. In all cases a 5-μF condenser was convenient for the exhibition of a suitable polarisation track.

RESULTS AND DISCUSSION

Curve *A*, Fig. 1, is the characteristic anodic polarisation curve of platinised platinum at 25° with a polarising current of 30 μA, in 0·1N-sulphuric acid. Curve *A* of Fig. 2 is the same anodic polarisation curve in phosphate buffer of pH 6·8, and curve *A* in Fig. 3 is the anodic polarisation curve in 0·1N-sodium hydroxide. From these curves, which show the variation in the potential of the platinum anode with quantity of electricity passed, it can be seen that at first there is a rapid initial build-up of potential [ascribable to the charging of the double layer (Hickling, *loc. cit.*)] which is followed by two well-defined arrests before oxygen evolution. Measurements from a large number of polarisation curves in 0·1N-sulphuric acid gave an average value of double layer capacity of $\sim$18 000 μF per apparent sq. cm. of our platinised platinum electrode. In phosphate buffer solution the average value was of the same order as in 0·1N-sulphuric acid while in 0·1N-sodium hydroxide the average value was $\sim$30 000 μF. The first arrest appears to start at a potential of 0·82 v in 0·1N-sulphuric acid, at 0·50 v in the phosphate buffer, and at 0·12 v in 0·1N-sodium hydroxide. The second arrest appears to start at potentials of 1·05, 0·70, and 0·30 v in the three solutions respectively.

Figs. 4, 5, and 6 give the characteristic oscillograms for the anodic polarisation of platinum at 25° in 0·1N-sulphuric acid, phosphate buffer of pH 6·8, and in 0·1N-sodium hydroxide with a polarising current density of 100 μA/sq. cm. The spots on the extreme left of each photograph show the steady hydrogen and oxygen evolution potentials at the same current density. From these oscillograms it can be seen that before oxygen evolution there are the following three stages : (1) a rather short period of constant potential, followed by a slow and somewhat irregular but reproducible rise of potential; (2) a rapid build-up of potential; and (3) a somewhat slow rise of potential accompanied by two steps, which are well-defined in 0·1N-sulphuric acid, but comparatively ill-defined in neutral or alkaline solution.

Fig. 3.



The first stage can be attributed as in previous studies (Pearson and Butler, *loc. cit.*) to the ionisation of free and adsorbed hydrogen; it was not observed by the direct potentiometric method. This may be due to the fact that a platinum electrode subjected to alternate anodic and cathodic polarisation (as in the oscillographic study) is normally in an active state (Bowden, *Proc. Roy. Soc.*, 1929, *A*, **125**, 456), whereas in the direct potentiometric method each experiment was carried out with a freshly prepared electrode. Also there is the possibility that the time intervals in the potentiometric study were too large to record these steps.

The second stage has been ascribed to the charging of the double layer. Measurements of a large number of oscillograms in 0·1N-acid gave an average value for the capacity of $\sim$200 μF per apparent sq. cm. of smooth platinum, which agrees with the values quoted by Pearson and Butler and by Hickling (*locc. cit.*). In phosphate buffer and in 0·1N-alkali the change in potential appears to be less rapid and the capacity in such solutions is between 400 and 500 μF per apparent sq. cm.

The fact that there are two steps in the third stage is of great importance. The first step appears to start at a potential of 0·80 v in 0·1N-acid, at 0·50 v in phosphate buffers, and at 0·15 v in 0·1N-alkali. The second arrest appears to start at potentials of 1·07, 0·75, and 0·35 v in the three solutions respectively.

In the annexed table the starting potentials of the first arrest obtained by the direct potentiometric and by the oscillographic method are compared with the equilibrium potential of the system Pt–PtO in the same solutions. The latter were obtained from Grube's results (*Z. Elektrochem.*, 1910, **16**, 621) after application of the ordinary equation for variation of potential with pH. The agreement between the starting potentials of the first arrest obtained by both methods with the equilibrium potentials of the system Pt–PtO indicates that this step in the anodic polarisation corresponds to the formation of PtO.

FIG. 4.

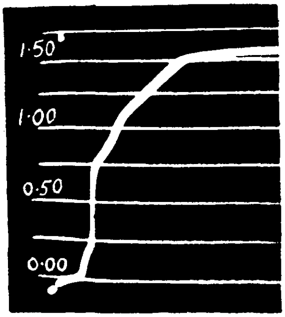


FIG. 5.

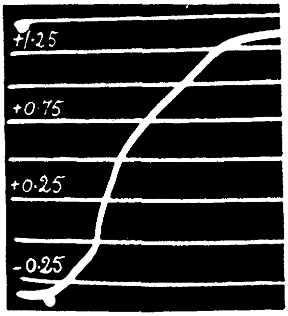
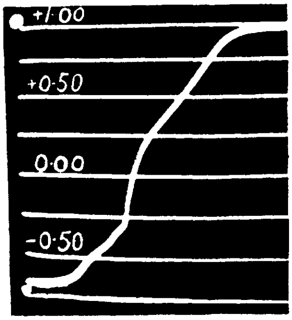


FIG. 6.



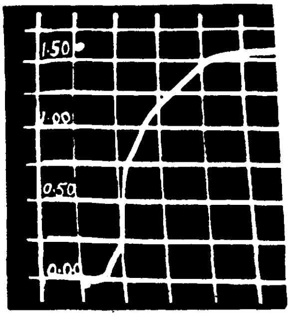


FIG. 7.

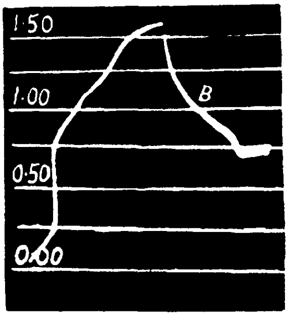


FIG. 8.

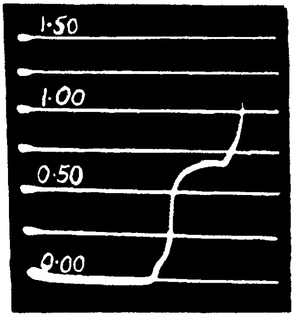


FIG. 9.

Solution	pH	Starting potential of first step, potentiometric, v	oscillographic, v	Equilibrium Pt–PtO potential
0·1N-H_2SO_4	1	0·82	0·80	0·82
Phosphate buffer	6·8	0·50	0·50	0·49
0·1N-NaOH	13	0·12	0·15	0·13

In the direct potentiometric method, the quantity of electricity passed from the beginning of the first step to the beginning of the second step was in all solutions about 15 000 μc per apparent sq. cm. This is sufficient for the liberation of about $4·7 \times 10^{16}$ atoms of oxygen; if the diameter of the platinum atom is taken as $2·5 \times 10^{-8}$ cm. (from the specific gravity) there should be about $1·6 \times 10^{15}$ atoms of metal per sq. cm. at a platinum surface. A rather crude estimate of the ratio of the real to the apparent area of our platinised platinum electrode can be obtained from the value of the capacity of the double layer at the electrode in 0·1N-sulphuric acid, compared with that of smooth platinum in the same solution. The ratio of the real to the apparent area at a smooth platinum surface has been previously estimated by different observers as between 1·5 and 3, and the value of 2 is usually taken as an average. If the difference between the capacity of our platinised platinum electrode used in the direct potentiometric method and the smooth platinum electrode used in the oscillographic experiments is assumed to be due to the difference in the true surface areas, the ratio of the real to the apparent area of our platinised platinum electrode will be about 180. This shows that the quantity of electricity passed in the first step corresponds to the formation of less than a unimolecular layer of PtO on the surface of the platinum. The oscillographic results also lead to this conclusion. In this case the quantity of electricity passed at any stage is computed from the known capacity of the condenser used and the horizontal displacement, which is governed by the voltage to which the condenser is charged. Fig. 7 shows the standard anodic track of smooth platinum in 0·1N-sulphuric acid, together with the vertical reference lines at intervals of 10 v. The quantity of electricity passed during the formation of PtO was found as a result of measurements of several oscillograms to be equal to about 250 μc per apparent sq. cm. This is sufficient for the liberation of about 8×10^{14} atoms of oxygen. The ratio of real to apparent area being assumed as 2, the quantity of electricity passed again corresponds to the formation of less than a unimolecular layer of PtO on the surface of the platinum electrode.

In the light of the previous studies of the anodic polarisation of metals (Hickling *et al.*, *loc. cit.*; El Wakkad and Hickling, *loc. cit.*) one would expect the step following the formation of PtO to be due to the formation on the surface of the metal of an oxide higher than PtO, and the potential recorded to correspond to an equilibrium potential between the higher oxide and PtO. From the starting potentials of the two steps as given above, the second step in each solution is seen to be about 0·2 v more positive that than of the Pt–PtO potential in the same solution. The potential of the system, $Pt(OH)_2 = PtO_2 + 2H^+ + 2e^-$, has been estimated to be *ca.* 1·1 v (Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solutions," New York, 1938, p. 196), compared with 0·88 v for the system Pt–PtO. Thus, provided that the ordinary equation for the variation of the oxide potential with pH applies, the equilibrium potential between PtO and PtO_2 will always be about 0·2 v more positive than that of the system Pt–PtO. This suggests that the second step is due to the formation of PtO_2. Further evidence as to the nature of the second step can be obtained from the study of the anodic decay. Curves *B* in Figs. 1, 2, and 3, and section *B* in the oscillogram, Fig. 8, represent such anodic decays. These curves reveal that on interruption of the polarising current when the anode was at oxygen evolution potential, the potential did not drop directly to that of the system Pt–PtO but that it halted first at the PtO–PtO_2 potential, confirming the existence of a higher oxide over the surface of the electrode. However, after a certain time (which varies from one solution to another) the potential dropped further to the Pt–PtO value, indicating that the PtO_2 formed at the surface of the electrode during its anodic polarisation is rather unstable. The quantity of electricity passed in the second step (for the formation of PtO_2) obtained potentiometrically or oscillographically is always of the same order as that passed in the first step. This suggests that in the second step the PtO previously formed is further oxidised to PtO_2.

The existence of the PtO_2, has not, however, been recognised in any of the cathodic polarisation curves obtained either by the direct potentiometric method (curves *C* in Figs. 1, 2, and 3) or oscillographically (Fig. 9). On reversal of the current to make the oxide-covered electrode cathodic, the potential dropped directly and showed only one arrest at about the potential of the system Pt–PtO. This behaviour is not, however, unexpected owing to the unstable nature of the PtO_2 as revealed from the anodic decay curves.

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