

## SURFACE OXIDES ON PLATINUM AT HIGHER ANODIC POTENTIALS IN SULPHURIC ACID SOLUTIONS\*

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The phase oxide II is formed on a platinum anode at potentials in the region from 2.1 to 2.5 V\*\* only; its rate of formation reaches a maximum at 2.3 V and diminishes with increasing concentration of sulphuric acid. At constant potential its growth obeys a parabolic law. A discussion of the observed phenomena is presented.

The behaviour of the platinum electrode at higher anodic potentials, *i.e.*  $>2.0$  V\*\* is of great theoretical and practical importance with regard to a number of technological electrolytic processes (production of peroxydisulphates, perchlorates, or hydrocarbons by Kolbe synthesis). Although the surface oxide layers on platinum formed in solutions of acids and their salts in that potential range have been studied extensively in recent years, our knowledge in this respect is still insufficient. It is known that during polarization of a platinum electrode at potentials higher than 2.1 V in sulphuric acid solutions, two types of surface oxides are formed. The first one (type I) is reduced in a broad potential range of 0.3–0.8 V in a single step which may split into two *e.g.* when the rate of change of potential is very large<sup>1,2</sup>. The amount of this oxide attains a limiting value at about 2.2 V independent of the concentration of the acid<sup>2-7</sup>. The conditions of formation of this surface oxide and its properties have been dealt with extensively in the literature<sup>8-12</sup>. The type II surface oxide formed at high anodic potentials on platinum<sup>13-17</sup> is reduced in a narrow range of potentials. For example, Obručeva<sup>13</sup> found a distinct delay at about 0.39 V during reduction with a constant current of  $6.1 \cdot 10^{-7}$  A/cm<sup>2</sup>, similarly as Shibata<sup>15</sup> with  $10^{-5}$  A/cm<sup>2</sup>, whereas Kozawa<sup>16</sup> and James<sup>17</sup> obtained in voltammetric reduction with scanning rate of  $-3$  mV/s a sharp peak at about 0.2 V. The composition of the type II oxide was found by electron diffraction as PtO<sub>2</sub> (private communication of Shibata<sup>17</sup>). Besides formation of a surface oxide film, the atomic oxygen evolved anodically penetrates into the platinum electrode<sup>18</sup> forming a "dermasorbed" layer of oxygen<sup>19</sup> or a solid Pt-O alloy<sup>20</sup>.

Even the work of James<sup>17</sup> published after the substantial part of our work was finished does not give sufficient information about conditions of formation and existence of the type II surface oxide. The results of our investigation of this problem, performed as a part of the study of electrolytic production of peroxydisulphates<sup>21,22</sup>, are the subject of this work.

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\*\* All potential values are referred to hydrogen electrode in the same solution.

## EXPERIMENTAL

*Apparatus.* The measurements were performed in a three-compartment cell made of Sial glass. The studied electrode, pure Pt wire of 0.5 or 1 mm in diameter (0.1 or 0.31 cm<sup>2</sup> surface area) sealed in glass at both ends, was in the middle compartment, while in the other two were two platinized Pt counter electrodes of 2 cm<sup>2</sup> surface area, connected in parallel. A hydrogen reference electrode was dipped into the solution of the same composition as in the measuring compartment; all potential values given in the text are referred to this electrode. The measured electrode 1 (Fig. 1) was connected by lead 2 to current source and by lead 3 and mercury mantle 4 to grounded socket of emitter follower 10, from which the signal is fed to an oscilloscope. Haber-Luggin capillary 5, joined firmly with electrode 1, connects it through salt bridge 6 with reference electrode 7. Auxiliary platinized Pt reference electrode 8 located in the salt bridge served for detecting potential changes during switching on or off the current pulse. This electrode, unlike a similar one used by Bewick and coworkers<sup>23</sup>, was not saturated with hydrogen, thus eliminating possible diffusion of hydrogen to the measured electrode 1. With an input resistance of the emitter follower of 100 k $\Omega$ , the change of potential of electrode 8 is only several mV/s so that its stability in the course of microseconds is very good. To eliminate errors due to induced voltage from the polarizing circuit, the electrode 8 is screened by a grounded mercury mantle. The loop formed by the circuit of the auxiliary reference electrode has an area of several cm<sup>2</sup> and is oriented perpendicularly to the interrupted current circuit so that the mutual inductance of both circuits is minimalized<sup>24</sup>. To determine exactly the potential of the measured electrode even at large current densities (up to 5 A/cm<sup>2</sup>), the ohmic potential drop between the Haber-Luggin capillary and the measured electrode was found from the drop of potential of the latter immediately after interrupting the polarizing current by means of a transistor interrupter of own construction<sup>24</sup>. This enables to interrupt currents larger than 1 A during 0.1–0.3  $\mu$ s, the oscillographic curve being free from disturbing oscillations.

The electrode was polarized with constant or linearly increasing potential by means of a Wenking 61 RS or 68 TA type potentiostat combined with a current integrator of own construction. The current was measured with a laboratory amperemeter

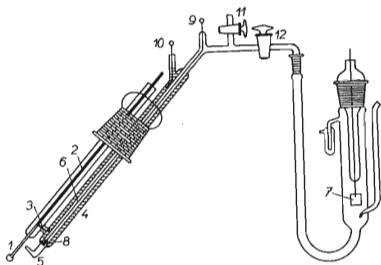


FIG. 1

Scheme of Measured and Reference Electrodes with Salt Bridge for Potential Measurement

or milliamperemeter of the type Metra DLi. Voltammetric curves were recorded by an  $x-y$  recorder of the type Endim 2200 (Meßapparatewerk Schlottheim, GDR) or with an oscilloscope of the type Tesla BM 430. The voltage between the measured and reference electrodes was fed to the input of a d.c. amplifier of the type MV 8 (Clamann and Grahner, GDR) connected with a laboratory voltmeter of the type Metra DLi.

*Preparation of the electrode and electrolyte.* Prior to measurement, the electrode was either ground with an emery paper No 4/0 and 6/0, wiped with a filter paper and rinsed with distilled water, or heated for several seconds in an oxidizing propane-butane flame to yellow glow.

The electrolyte was 1, 5 or 10N- $H_2SO_4$  prepared by diluting concentrated reagent grade acid with distilled water. For comparison, an electrolyte free from possible organic impurities was prepared by boiling the concentrated acid with a small amount of hydrogen peroxide<sup>25</sup> and diluting with triply distilled water. However, cathodic voltammetric curves due to reduction of surface oxides were in both electrolytes the same.

*Method of measurement.* The electrode under study, heated as mentioned above, was polarized anodically in the mentioned electrolyte at constant potential for a chosen time interval. Afterwards the surface layer was analyzed voltammetrically, *i.e.* by measuring the current during polarization with a linearly decreasing voltage. To avoid possible reduction of oxygen or  $S_2O_8^{2-}$  ions which might have been formed during preceding anodic polarization, the solution from the middle compartment of the electrolytic cell was quickly replaced by fresh electrolyte of the same original composition from which oxygen had been removed by bubbling nitrogen or argon. The electrolyte was changed within 15 s in currentless state while the electrode potential was in the region 1.0–1.5 V and the surface layers remained practically unaffected. The voltammetric curves were recorded beginning from the potential of 0.9–1.0 V. The electrode potential was changed according to the scheme in Fig. 2. The temperature of measurement was  $15 \pm 0.1^\circ C$ .

## RESULTS

In Fig. 3 are shown some of the voltammetric curves obtained with the ground platinum electrode prepolarized at  $2.14 \pm 0.01$  V for various time intervals in 1N- $H_2SO_4$ . All show a distinct wave with a broad maximum at 0.46–0.53 V. This wave is due to reduction of type I surface oxide. Owing to a relatively slow potential decrease ( $-0.05$  V/s) during recording the  $i-E$  curve, the oxide I is reduced in most cases in a single wave. In some cases its reduction proceeds in two waves. Curves 1–3 corresponding to 1–5 min prepolarization at 2.14 V show two adsorption waves of atomic hydrogen in the range of 0.03–0.4 V. Curves 4–7 corresponding to 20 min

or longer prepolarization at 2.14 V show a wave with a sharp maximum at 0.12–0.13 V, the area of which increases markedly with prolonged anodic prepolarization. We attribute this wave to the reduction of the surface oxide II in accord with other authors<sup>16,17</sup>; at the given scanning rate it lies in the same potential region as the second wave of hydrogen adsorption, which is thus masked. At a lower scanning rate, the maximum of the reduction wave of oxide II is shifted to more positive potentials, e.g. at  $-0.005$  V/s to 0.17–0.18 V.

With prolonged anodic prepolarization, the cathodic current in the potential range of hydrogen adsorption (0.03–0.4 V) increases as follows from comparison of curves 1–3 (Fig. 3). Similarly, the voltammetric curves recorded during increasing potential (curves 2' and 3') immediately after the curves 2 and 3 are shifted towards the region of cathodic currents with prolonged anodic prepolarization. Hence, in the range 0.03–0.4 V another cathodic current is superposed on the current due to adsorption or desorption of hydrogen. This cathodic current corresponds to reduction of oxygen formed and dissolved during the anodic prepolarization in the electrode<sup>9,10</sup> as evidenced below; it is more distinct on voltammetric curves obtained after the electrode was freed from oxide layers by a short-termed reduction. In con-

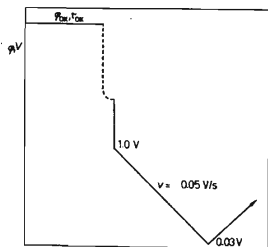


Fig. 2.

Scheme of the Program of Potential Changes of the Measured Electrode

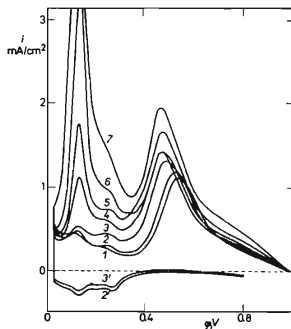


FIG. 3

Voltammetric Curves of Ground Platinum Electrode Prepolarized in 1N-H<sub>2</sub>SO<sub>4</sub> at 2.14 ± 0.01 V

Duration of polarization: 1 1 min; 2 3 min; 3 5 min; 4 20 min; 5 30 min; 6 50 min; 7 60 min. 2' and 3' voltammetric curves measured at increasing potential immediately after 2 and 3.

trast to the layers of oxides I and II which are reduced quantitatively by a single voltammetric pulse in the range 0.03–0.9 V, the oxygen dissolved in the electrode is reduced entirely only by multiple consecutive voltammetric pulses in the mentioned potential range where further dissolution of evolved oxygen in the electrode does not take place. In Fig. 4 are shown such consecutive voltammetric curves measured after the platinum electrode was prepolarized at 2.1 V for 1 hour and then freed from surface oxides by a short cathodic pulse at 0.2 V; it is seen that the cathodic current begins to flow at 0.8 V although adsorption of hydrogen takes place at less than 0.4 V. Owing to the partial reduction of oxygen dissolved in the electrode during the first cycle, the subsequent voltammetric curves 2 and 2' are less shifted towards the side of the cathodic currents in comparison with curves 1 and 1' as shown in Fig. 4. After one hour of further polarization at 0.3 V, this oxygen is reduced practically quantitatively so that curves 3 and 3' are nearly symmetrical to the  $x$  axis and correspond mostly to adsorption or oxidation of adsorbed atomic hydrogen. Since the voltammetric curves in the presence of oxygen dissolved in platinum in the region 0.03–0.4 V differ only by a shift along the  $y$  axis, it follows that under these

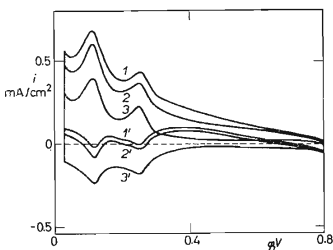


FIG. 4

Voltammetric Curves of Ground Platinum Electrode Prepolarized for 1 h in 1N- $H_2SO_4$  at 2.14 V and Reduced with a Pulse at 0.2 V for 0.5 s

1 and 1' descending and rising voltammetric curves immediately after reduction; 2 and 2' descending and rising voltammetric curves recorded after 1 and 1' in the range 0.8–0.03 V; 3 and 3' descending and rising voltammetric curves of electrode reduced for 1 h at 0.3 V.

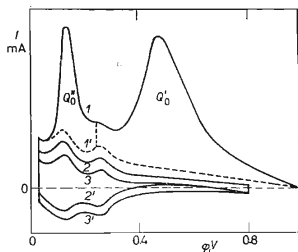


FIG. 5

Method of Evaluating the Charges  $Q_0^I$  and  $Q_0^{II}$

1 Voltammetric curve of electrode with surface oxides; 2, 2', 3, 3' cyclic voltammetric curves following after 1; 1' extrapolated voltammetric curve due to processes on the electrode during recording curve 1 without reduction of surface oxides I and II.

conditions the rate of oxygen reduction is independent of electrode potential and is controlled by diffusion of oxygen from the bulk of the electrode to its surface.

From the above considerations, the following method of evaluating the charge consumed in reduction of the surface oxides of both types was deduced (Fig. 5). The charge was determined from the area between the voltammetric curve of the oxidized electrode and the curve obtained by extrapolation of the consecutive curves to the first pulse without surface oxides (Fig. 5, curve 1'). In the presence of both surface oxides the charge for their reduction was found on the basis of the assumption that the current minimum between the reduction waves of both oxides I and II separates the reduction of oxide I from oxide II.

To determine the number of oxygen atoms in oxide I bound to one Pt atom on the surface, the ratio  $Q_0^I/2Q_H$  was evaluated, where  $Q_0^I$  denotes charge consumed in reduction of surface oxide I and  $Q_H$  charge for coverage of the electrode with a monolayer of adsorbed hydrogen. The latter quantity cannot be found directly from the voltammetric curve since a current due to evolution of molecular hydrogen (dissolving in the electrolyte not saturated with hydrogen) is added to the current of hydrogen adsorption at potentials more negative than 0.1 V. We therefore calculated the  $i-E$  curve for evolution of molecular hydrogen using the known diffusion coefficient<sup>26</sup> of hydrogen in sulphuric acid solutions. This curve was subtracted from the  $i-E$  curve measured on the electrode containing no dissolved oxygen to obtain the charge  $Q_H'$  corresponding to the true adsorption of atomic hydrogen in the potential range 0.4–0.068 V (the latter value corresponds to the current minimum of the  $i-E$  curve). As it is known<sup>27</sup> that at 0.068 V the surface coverage with adsorbed hydrogen is only 0.84, the charge  $Q_H$  for full monoatomic adsorption is given by the relation  $Q_H = Q_H'/0.84$ .

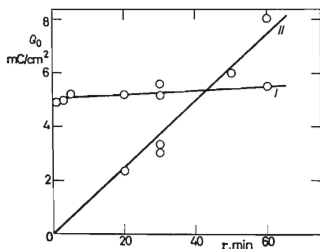


FIG. 6

Dependence of the Charges  $Q_0^I$  (I) and  $Q_0^{II}$  (II) on Duration of Electrode Polarization in 1N- $H_2SO_4$  at 2.14 V

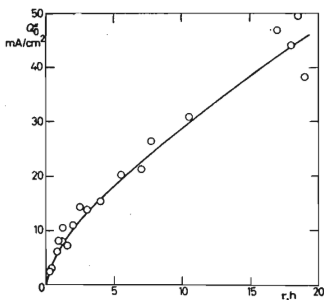


FIG. 7

Dependence of the Charge  $Q_0^{II}$  on Duration of Electrode Polarization in 1N- $H_2SO_4$  at 2.14 V

In the described manner, the voltammetric curves of platinum electrodes in 1, 5 and 10N-H<sub>2</sub>SO<sub>4</sub> prepolarized at 0.9–3.0 V for various time intervals of 1 min to several tens of hours were evaluated. Special attention was paid to the potential range of 2 V and higher. It follows from the *i*-*E* curves measured on the ground platinum electrode in 1N-H<sub>2</sub>SO<sub>4</sub> that the surface oxide I is formed in the whole potential range studied, *i.e.* 0.9–2.2 V. The latter limit could not be surpassed since at 2.2 V the current density was already 2–3 A/cm<sup>2</sup> resulting in an ohmic potential drop (*IR*) between the electrode and the tip of the Haber–Luggin capillary of about 0.5 V (in 1N-H<sub>2</sub>SO<sub>4</sub>); at still higher currents the necessary accuracy of potential measurements of ±5 mV (after correction for *IR*) could not be preserved.

The amount of surface oxide I formed during anodic polarization after a certain time increases with potential up to 1.9–2.0 V attaining a limit corresponding to  $Q_0^I = 5.0\text{--}5.4\text{ mC/cm}^2$  of geometric surface. The ratio  $Q_0^I/2Q_H$  was determined as  $2.04 \pm 0.13$ . The limiting amount of oxide I depends only little on duration of anodic polarization if the latter is longer than 1 min, *e.g.* at 2.14 V the value of  $Q_0^I$  does not increase by more than 10% in the range 1 min–1 h (Fig. 6).

In 5 and 10N-H<sub>2</sub>SO<sub>4</sub> it was possible to polarize the platinum electrode more positively than in 1N-H<sub>2</sub>SO<sub>4</sub> since the currents in the more concentrated acid were smaller than in the diluted one at the same potential<sup>28–31</sup>; in 5N-H<sub>2</sub>SO<sub>4</sub> the measuring range was 1.9–2.6 V and in 10N-H<sub>2</sub>SO<sub>4</sub> 2.1–3.0 V. Here the amount of surface oxide I was independent of potential in the whole range studied and of time for times

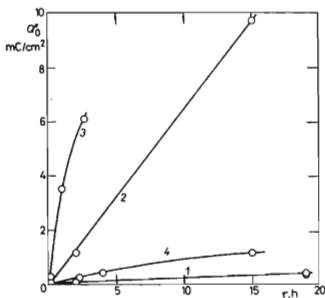


FIG. 8

Dependence of the Charge  $Q_0^{II}$  on Duration of Electrode Polarization in 5N-H<sub>2</sub>SO<sub>4</sub>

Electrode polarized at: 1 2.1 V; 2 2.2 V; 3 2.35 V; 4 2.47 V.

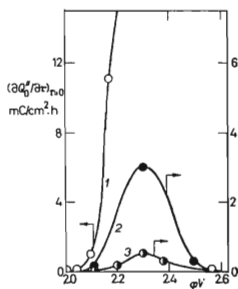


FIG. 9

Dependence of Initial Rate of Growth of Surface Oxide II on Potential

Rate of growth expressed as  $(\partial Q_0^{II}/\partial \tau)_{\tau=0}$ . Electrolyte: 1 1N; 2 5N; 3 10N-H<sub>2</sub>SO<sub>4</sub>.

longer than 1 min. However, this conclusion may be affected by the error in determining  $Q_0^I$ , which is larger when the surface oxide II is formed simultaneously with oxide I. The value of  $Q_0^I$  measured in 5N-H<sub>2</sub>SO<sub>4</sub> was  $3.5 \pm 0.4$  mC/cm<sup>2</sup>, in 10N-H<sub>2</sub>SO<sub>4</sub>  $3.3 \pm 0.4$  mC/cm<sup>2</sup>. The ratio  $Q_0^I/2Q_H$  in 10N-H<sub>2</sub>SO<sub>4</sub> is by 10–20% smaller than in 1N-H<sub>2</sub>SO<sub>4</sub>. Apparently the values of  $Q_0^I$  and  $Q_0^I/2Q_H$  diminish somewhat with increasing concentration of the acid.

On electrodes preheated in an oxidation flame, the surface oxide I is formed in amounts smaller by the factor of 5–6 than on ground ones, but the ratio  $Q_0^I/2Q_H$  is the same. Hence, the different amount of oxide I can be attributed to a different surface roughness factor.

The anodic formation of surface oxide II on platinum electrode is subjected to different laws: it follows already from Fig. 3 that the initial rate of formation of oxide I is much larger than that of oxide II so that after 5 min polarization in the range of potentials where the oxide II can be formed it is possible to detect only oxide I on the electrode (Fig. 3). During further polarization the amount of both oxides becomes equal and after several hours the amount of oxide II can exceed that of oxide I many times. The rate of increase of the oxide II layer (expressed as  $Q_0^{II}$ ) is not constant but diminishes with time (Figs 7 and 8).

The dependence of the formation of the surface oxide II on potential is also other than that of the oxide I as may be seen from Fig. 9 where the initial rate of formation of the oxide II is plotted as a function of potential at various concentrations of sulphuric acid. The initial rate was determined from the plot of  $Q_0^{II}$  against time  $\tau$  (Figs 7 and 8) at  $\tau = 0$  for various potentials and concentrations of the acid. It is apparent from Fig. 9 that the oxide II begins to deposit on the platinum anode at 2.1 V. The rate of its formation increases with increasing potential the more diluted is the acid, the maximum rate being attained at 2.3 V regardless of the acid concentration; at more positive potentials it diminishes until it drops to zero at 2.55 V. At still more positive potentials no formation of the oxide II was observed regardless of the acid concentration. Even the oxide II layer, formed at 2.3 V after a longer time, is destroyed after the electrode was polarized at 2.7 V for 18 hours.

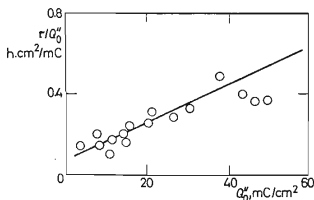


FIG. 10

Dependence of the Charge  $Q_0^{II}$  on Duration of Electrode Polarization

Electrolyte 1N-H<sub>2</sub>SO<sub>4</sub>, potential 2.14 V; equation (1) of parabolic law of growth was used.



On the electrode polarized at 2.5–3.0 V, the oxide II cannot be prepared by decreasing the potential to 2.2–2.4 V, a region favourable for its formation. The oxide II was not formed even when the platinum electrode was after prepolarization in the "persulphate" potential range (2.5–3.0 V) reduced for a long time at 0.1 V and afterwards polarized at 2.2–2.4 V.

The mentioned results are referred to a ground platinum electrode. With a platinum electrode preheated in an oxidation flame to yellow glow, no surface oxide II was formed even after polarization at 2.2–2.4 V for many hours.

The electric resistance of the surface layer was estimated from the ohmic potential drop,  $IR$ , between the tip of the Haber-Luggin capillary and the measured electrode. The value of  $IR$  consists in our case of the potential drops  $U_1$  in the oxide layer and  $U_2$  in the electrolyte between the tip of the capillary and the electrode surface. The  $U_2$  value can be considered as independent of time at constant current, so that changes of  $IR$  with time are attributed to changes of  $U_1$ . At the beginning of measurement, when the electrode is free from surface oxides, the value of  $U_1$  can be set equal to zero; its value at a time of polarization  $\tau$  will be  $U_1 = IR_\tau - IR_0$ , where  $IR_0$  and  $IR_\tau$  are the values of  $IR$  corresponding to the beginning ( $\tau = 0$ ) of polarization and to time  $\tau$ .

During measurement in 1N-H<sub>2</sub>SO<sub>4</sub> with constant current density  $i = 0.5$  A/cm<sup>2</sup>, the  $IR$  value did not increase even after five hours and was equal to  $108 \pm 3$  mV. Hence, the resistance of the oxide layer was within the range of experimental error in determining  $IR$ . *i.e.*  $U_1 \leq 6$  mV. From this we can estimate the maximum possible intensity of the electric field in the oxide layer. The total charge for reduction of the oxides was found as  $Q_0^I + Q_0^{II} = 30$  mC/cm<sup>2</sup>. Assuming that the layer consists of platinum dioxide, the density of which is 10.2 g/cm<sup>3</sup> (ref.<sup>32</sup>), and the roughness factor of the surface  $\sigma = 5$ , we obtain the total thickness of the layer of oxides I and II as 33 Å. From this and the upper limit of  $U_1$  we conclude that the intensity of the electric field in the oxide layer cannot be higher than  $1.8 \cdot 10^4$  V/cm and that the specific resistance of the oxide layer is not larger than  $3.6 \cdot 10^4$  Ωcm. In a similar way it can be concluded that the resistance of the oxide layer deposited on platinum in 10N-H<sub>2</sub>SO<sub>4</sub> during formation of peroxydisulphate did not exceed 12 mΩ cm<sup>2</sup> even after 27 hours polarization with a constant current density of 1 A/cm<sup>2</sup>.

## DISCUSSION

According to our measurements, two kinds of surface oxides can be formed anodically on platinum at potentials higher than 2.1 V. The oxide I is deposited in the whole studied potential range (0.9–3.0 V); its amount attains both on the ground and preheated electrodes a limiting value, *e.g.* in 1N-H<sub>2</sub>SO<sub>4</sub>  $2.04 \pm 0.13$  expressed as  $Q_0^I/2Q_H$ . A higher value was measured by Biegler and Woods<sup>6</sup> on a preheated electrode, namely 2.66. Recently also Tjurin and Volodin<sup>2</sup> reported a higher value,

$Q_0^I/2Q_H = 2.5$ , for an electrode activated by multiple anodic and cathodic pulses at 1.2 and 0 V, and with the same solution. The higher values may be due to different modes of evaluating  $Q_H$ .\*

In contrast to the oxide I, the oxide II is formed only in the potential range of 2.1–2.55 V and only on electrodes ground before use. This is in accord with the concept of James<sup>17</sup> who considers a mechanical stress of the electrode caused by mechanical treatment as a necessary condition for the formation of this oxide. Intense heating in an oxidation flame apparently removes surface defects which can play a role of active centers for the formation of the oxide II.

The dependence of the amount of the oxide II on time is approximately linear during the first hour (Figs 6–8); the rate of its formation then diminishes. Of various functional relationships between  $Q_0^{II}$  (which is proportional to the thickness of the oxide layer) and duration of polarization  $\tau$ , the following one suits best our experimental data (Fig. 10):

$$(Q_0^{II})^2 + k_1 Q_0^{II} = k_2 \tau. \quad (1)$$

This parabolic relationship was derived for the case where the rate-controlling steps are both diffusion of ions through the oxide layer and chemical formation of the oxide<sup>34</sup>. It was verified in the case of oxidation of copper at 1000°C at low oxygen pressures<sup>35</sup> and in oxidation of iron at 1000°C by oxygen<sup>36</sup> or water vapour<sup>37</sup>. The fact that this model suits our system where the platinum is covered by both forms of surface oxides means that the layer of oxide I does not substantially hinder the passage of mobile particles (ions), the movement of which in the layer of oxide II is more influenced by the gradient of chemical potential than by the gradient of electric potential.

Formally the same expression is obtained if diffusion of mobile particles through layers of oxides I and II is rate-controlling in the formation of surface oxide II. The flux of mobile particles through the oxide I layer of thickness  $L_I$  is expressed by the equation

$$N_I = D_I(a_2 - a_1)/L_I, \quad (2)$$

which is the integrated form of the Fick's first law for constant activity gradient of the mobile particles. Their flux through the oxide II layer of thickness  $L_{II}$  is given analogously:

$$N_{II} = D_{II}(a_3 - a_2)/L_{II}. \quad (3)$$

In Eqs (2) and (3),  $D_I$  and  $D_{II}$  denote diffusion coefficients of the mobile particles in the layers of oxides I and II,  $a_1$ ,  $a_2$  and  $a_3$  activities of the mobile particles in the metal-oxide I, oxide I-oxide

\* In the last paper of Biegler, Rand and Woods<sup>33</sup>, published after our paper was submitted for publication, it has been shown that the value of  $Q_0^I/2Q_H$  given in their previous paper<sup>6</sup> was based on an erroneous assumption. The new corrected value<sup>33</sup>,  $Q_0^I/2Q_H = 2.05$ , is in full agreement with that found by us. The same applies for the results of Tjurin and Volodin<sup>2,7</sup> who used the same procedure as Biegler and Woods<sup>6</sup> in evaluating the ratio  $Q_0^I/2Q_H$ .

II, and oxide II–solution interfaces, respectively (provided that the oxide I lies between the metal and the oxide II). Our results show that the oxide I practically ceases to be formed after an anodic polarization longer than 1 min and that the whole flux of mobile particles is consumed mostly in formation of the oxide II, hence

$$N_I \approx N_{II} = k \, dL_{II}/d\tau. \quad (4)$$

On eliminating  $a_2$  and rearranging Eqs (2)–(4) we obtain

$$k(L_I/D_I + L_{II}/D_{II}) \, dL_{II} = (a_3 - a_1) \, d\tau. \quad (5)$$

At constant electrode potential, the difference  $a_3 - a_1$  can be considered as constant; on integrating Eq. (5) and introducing the relation between the thickness of the layer  $L_{II}$  (cm) and the charge for its reduction  $Q_0^{II}$  (C/cm<sup>2</sup>)

$$L_{II} = Q_0^{II} M / n F \rho \sigma, \quad (6)$$

where  $M$ ,  $\rho$  and  $\sigma$  denote molar mass, density of the oxide II and roughness factor, respectively, we obtain Eq. (1) in which the constants  $k_1$  and  $k_2$  are given as

$$k_1 = 2D_{II} n F L_1 \sigma \rho / D_I M, \quad (7)$$

$$k_2 = 2(a_3 - a_1) D_{II} n^2 F^2 \rho^2 \sigma^2 / k M^2. \quad (8)$$

As mobile particles, either atomic oxygen or Pt<sup>4+</sup> and O<sup>2-</sup> ions were considered. In the first case, Fick's law holds regardless of the intensity of the electric field, in the second we have to deal with movement of charged particles and assume that the approximate equation for the flux of ions in an electric field of small intensity<sup>3,8</sup>,

$$N = -D(da/dx) + D(aEz_i e v / kT), \quad (9)$$

applies, where  $v$  denotes frequency factor and other symbols have their usual meaning. The condition for the validity of Eq. (9) is

$$eErz_i \ll kT, \quad (10)$$

where  $r$  means distance between two stable positions of an ion in the crystal lattice of the oxide. We found that the intensity  $E$  of the electric field in the oxide layer on platinum does not exceed the value of  $1.8 \cdot 10^4$  V/cm. Assuming  $r = 10^{-8}$  cm and  $z_i = 2$ , we obtain from the inequality (10)  $eErz_i / kT \leq 1.46 \cdot 10^{-2} \ll 1$ , i.e. the condition of small intensity of the electric field in the oxide layer is fulfilled.

It follows from Eq. (9) that the first Fick law can be used for the movement of charged particles if  $E \ll -(kT/e z_i v) \, dx/dlna$ . However, our experimental data do not enable us to decide whether this inequality is fulfilled since the distribution of activity of the mobile particles along the gradient of the electric field cannot be determined.

The mentioned facts bring nevertheless an evidence for the probability of the proposed mechanism and kinetics of growth of oxide layers on platinum during simultaneous formation of both kinds of oxides.

*The rate of formation of the oxide II layer as function of potential* (Fig. 9) has a distinct maximum at 2.3 V at all concentrations of sulphuric acid used, suggesting

that this rate is controlled by at least two mutually counteracting effects: one stimulating the formation of the oxide with increasing potential prevailing in the range 2.1 to 2.3 V and the other (or others) hindering it or accelerating the decomposition of the oxide prevailing in the range 2.3–2.55 V.

The initial increase of the rate of formation of the oxide II at constant concentration of the acid in the potential range 2.1–2.3 V can be attributed to an increase of the difference  $a_3 - a_1$  (Eq. (5)) or to increasing intensity of the electric field in the oxide layer resulting in a more rapid motion of mobile particles (ions).

The drop in the rate of formation of the oxide II in the potential range 2.3–2.55 V can have several reasons: a) Adsorption of  $\text{SO}_4^{2-}$  ions or  $\text{HSO}_4$  radicals, which, according to recent measurements<sup>39</sup>, is manifested distinctly at potentials 2.3 V and above. b) Formation of another type of oxide, not reducible in the potential region of hydrogen adsorption and capable of diminishing strongly the activity of oxygen ions on the electrode surface. A similar type of surface oxide was found<sup>40</sup> on rhodium at potentials above 3.6 V. This explanation is in accord with the finding that the oxide II cannot be formed on platinum prepolarized at more than 2.6 V (the potential region where peroxydisulphates are formed) even after the electrode was reduced for one hour at 0.1 V. If the formation of the oxide II were inhibited only by adsorption of  $\text{HSO}_4$  radicals, then the polarization at 0.1 V would result in their desorption<sup>39</sup> and the formation of the oxide II during subsequent polarization at 2.2–2.4 V would not be hindered. c) The net rate of formation of the oxide II layer is influenced also by its dissolution which also apparently depends on potential. This concept is supported by the fact that the oxide II formed on platinum at 2.1 to 2.5 V is removed by maintaining the electrode at more positive potentials for several hours. A further support is obtained from the comparison of the net rate of formation of the oxide II with the overall corrosion rate of platinum anode. It follows from Fig. 9 that the current corresponding to formation of the oxide II in 10N- $\text{H}_2\text{SO}_4$  in the potential range 2.3–2.55 V is 0 to  $1.4 \cdot 10^{-7}$  A/cm<sup>2</sup>, which compares well with the overall corrosion rate of platinum,  $10^{-8} - 10^{-7}$  A/cm<sup>2</sup> in 15N- $\text{H}_2\text{SO}_4$  at 25°C in the same potential range<sup>41,42</sup>.

*The dependence of the rate of formation of the oxide II on concentration of sulphuric acid* can also have several reasons. It is well known that oxygen evolution on platinum anode is slowed down by increasing concentration of sulphuric acid practically in the whole potential region<sup>28–30</sup>. Since the initial steps in the mechanisms of oxygen evolution and formation of surface oxides on platinum are probably identical<sup>31</sup>, the overall decrease in the rate of formation of the oxide II with rising concentration of sulphuric acid can be well understood both in the increasing (2.1 to 2.3 V) and decreasing (2.3–2.55 V) branches. This retarding effect can be attributed to a decrease in water activity at higher acid concentrations<sup>43</sup> as well as to increasing surface coverage of platinum with  $\text{HSO}_4$  radicals in the potential range of forma-

tion of the oxide II, especially beginning from 2.3 V. Also, more rapid dissolution of the primarily formed oxide layer in the more concentrated acid cannot be excluded. Direct experimental evidence about the influence of sulphuric acid in concentrations 1–10N on the overall corrosion rate of platinum is lacking (the rate of corrosion was reported<sup>42</sup> to be larger in 15N than in 20N-H<sub>2</sub>SO<sub>4</sub>).

The composition of the surface oxide II has not been determined as yet except for the unpublished work of Shibata cited by James<sup>17</sup>. Kozawa<sup>16</sup> attempted to analyze it by X-ray diffraction but obtained only a diffraction peak due to platinum metal. Nagel and Dietz<sup>14</sup> judged the composition of the oxide layer on the basis of an analogous colour change produced by reaction of potassium iodide solution with platinum dioxide prepared by anodic oxidation of platinum by direct current with superimposed alternating current<sup>44</sup>. We therefore prepared a layer of PtO<sub>2</sub> on platinum by the same method<sup>44</sup> and recorded its voltammetric curve; however, no wave characteristic for the oxide II appeared on the curve so that the identity of both kinds of surface oxides was not proved.

Our results support the final remark of James<sup>17</sup> to certain objections of Conway and bring further information about the conditions of formation and existence of the oxide II, namely dependence on anodic polarization, concentration of sulphuric acid and pretreatment of the electrode.

The dependence of the rate of formation of the surface oxide II on potential and concentration of sulphuric acid described in the present work enables to explain certain findings reported by other authors. For example, James<sup>17</sup> failed to prepare the oxide II by polarizing a platinum electrode in 1 or 2N-H<sub>2</sub>SO<sub>4</sub> at 25°C for a longer time by a current density of 10 A/cm<sup>2</sup>, since the electrode potential was in the range 2.59–3.35 V, where this oxide according to our results cannot be formed. Only after diminishing the current density to 1 A/cm<sup>2</sup>, when the electrode potential did not exceed 2.29 V, an optimum value for the formation of the oxide II, this oxide was formed. Obručeva's finding<sup>13</sup>, that even after four hours polarization of a platinum anode in 8N-H<sub>2</sub>SO<sub>4</sub> by 0.1 A/cm<sup>2</sup> the oxide II was not formed, can be explained as follows: The mentioned current density corresponds to a potential of 2.2 V (according to some published data<sup>28–31</sup>, since the potential value was not given in the cited work<sup>13</sup>) at which the deposited amount of the oxide II on a ground electrode after 4 hours would correspond to  $Q_0^{II} = 1 \text{ mC/cm}^2$  (Fig. 9); this would not give a distinct delay on the cathodic discharge curve used by Obručeva<sup>13</sup> for identification of surface oxides. Finally, certain "irreproducible" effects in the measurement of limiting coverage of smooth platinum<sup>6</sup> by the oxide I can be probably attributed to the oxide II formed simultaneously, since the reported potential of 2.98 V against normal mercurous sulphate electrode corresponds to 2.3 V on our scale, an optimum value for the formation of this surface oxide.

#### REFERENCES

1. Gilroy D., Conway B. E.: *Can. J. Chem.* **46**, 875 (1968).
2. Tjurin Ju. M., Volodin G. F.: *Elektrochimija* **6**, 1186 (1970).
3. Mayell J. S., Langer S. N.: *J. Electrochem. Soc.* **111**, 438 (1964).
4. Fleischmann M., Mansfield I. R., Wynne-Jones W. F. K.: *J. Electroanal. Chem.* **10**, 511 (1965).
5. Vijh A. K., Conway B. E.: *Z. Anal. Chem.* **224**, 160 (1967).

6. Biegler T., Woods R.: *J. Electroanal. Chem.* **20**, 73 (1969).
7. Tjurin J. M., Volodin G. F.: *Elektrochimija* **5**, 1203 (1969).
8. Gilman S. in the book: *Electroanalytical Chemistry* (A. J. Bard, Ed.), Vol. 2, p. 111. Arnold, London 1967.
9. Hoare J. P. in the book: *Advances of Electrochemistry and Electrochemical Engineering* (P. Delahay, C. Tobias, Eds). Vol. 6, p. 201. Interscience, New York 1967.
10. Hoare J. P.: *The Electrochemistry of Oxygen*. Interscience, New York 1968.
11. Genshaw M. A. in the book: *Electrosorption* (E. Gileadi, Ed.), p. 73. Plenum Press, New York 1967.
12. Damjanovic A. in the book: *Modern Aspects of Electrochemistry*, Vol. 5 (J. O'M. Bockris, B. E. Conway, Eds), p. 369. Butterworths, London 1969.
13. Obručeva A. D.: *Ž. Fiz. Chim.* **26**, 1448 (1952).
14. Nagel K., Dietz H.: *Electrochim. Acta* **4**, 1 (1961).
15. Shibata S.: *Bull. Chem. Soc. Japan* **36**, 526 (1963); **40**, 696 (1967).
16. Kozawa A.: *J. Electroanal. Chem.* **8**, 20 (1964).
17. James S. D.: *J. Electrochem. Soc.* **116**, 1681 (1969).
18. Kališ T. V., Burštejn R. Ch.: *Dokl. Akad. Nauk SSSR* **81**, 1093 (1951).
19. Schuldiner S., Warner T. B.: *J. Electrochem. Soc.* **112**, 212 (1965).
20. Hoare J. P., Meibuhr S. G., Thacker R.: *J. Electrochem. Soc.* **113**, 1978 (1966).
21. Balej J.: *This Journal* **30**, 2663 (1965).
22. Balej J.: *This Journal* **35**, 1954 (1970).
23. Bewick A., Bewick A., Fleischmann M., Liler M.: *Electrochim. Acta* **1**, 83 (1959).
24. Vondrák J., Špalek O.: *Chem. listy* **64**, 609 (1970).
25. Visscher W., Devanathan M. A. V.: *J. Electroanal. Chem.* **8**, 127 (1964).
26. Breiter M., Hoffmann K.: *Z. Elektrochem.* **64**, 462 (1960).
27. Honz J., Němec L.: *This Journal* **34**, 2030 (1969).
28. Čejfec V. L., Rivlin I. J.: *Ž. Prikl. Chim.* **28**, 1291 (1955).
29. Kaganovič R. N., Gerovič M. A., Jenikeev E. Ch.: *Dokl. Akad. Nauk SSSR* **108**, 107 (1956).
30. Izgaryšev N. A., Jefimov E. A.: *Ž. Fiz. Chim.* **30**, 1807 (1956).
31. Chu Yung-chao, Shu Tsen-yen, King Chi-hsung, Wang Tsen-woo: *Sci. Rec., New Ser. II*, **1958**, 384.
32. Lafitte P., Gandadam P.: *Compt. Rend.* **198**, 1925 (1934).
33. Biegler T., Rand D. A. J., Woods R.: *J. Electroanal. Chem.* **29**, 269 (1971).
34. Evans U. R.: *Trans. Electrochem. Soc.* **46**, 247 (1924).
35. Wagner C., Grunewald K.: *Z. Physik. Chem.* **40B**, 455 (1938).
36. Bénard J.: *Bull. Soc. Chim. France* **1949**, D 89.
37. Fischbeck K.: *Z. Elektrochem.* **39**, 316 (1933).
38. Young L.: *Anodic Oxide Films*, p. 13. Academic Press, New York 1961.
39. Pospelova N. V., Rakov A. A., Veselovskij V. I.: *Elektrochimija* **5**, 1318 (1969).
40. Pospelova N. V., Rakov A. A., Veselovskij V. I.: *Elektrochimija* **6**, 722 (1970).
41. Čemodanov A. N., Kolotyркиn J. M., Dembrovskij M. A., Kudrjavina T. V.: *Dokl. Akad. Nauk SSSR* **171**, 1384 (1966).
42. Čemodanov A. N., Kolotyркиn J. M., Dembrovskij M. A.: *Elektrochimija* **6**, 460 (1970).
43. Erdey-Grúz T., Golopencza-Bajor O., Gallyas M.: *Acta Chim. Acad. Sci. Hung.* **50**, 179 (1966).
44. Altmann S., Busch R. N.: *Trans. Faraday Soc.* **45**, 720 (1949).

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