

EFFECT OF PLATINUM SURFACE OXIDES ON THE RATE OF ANODIC EVOLUTION OF OXYGEN IN SOLUTIONS OF SULPHURIC ACID

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The rate of anodic evolution of oxygen on platinum in solutions of 1N–10N-H₂SO₄ has been studied under the conditions that the Pt surface is covered either only with surface oxide I or with oxides I and II. It has been found that at potentials higher than ≈ 1.85 V (RHE) the slope b of Tafel equation is diminished in comparison with the respective value for lower potentials. This phenomenon was explained assuming the oxygen evolution to take place *via* two parallel mechanisms in the range of higher potentials. Surface oxide II has been found to fasten oxygen evolution only according to the mechanism which is valid for potentials higher than ≈ 1.85 V.

The rate of anodic evolution of oxygen on a Pt anode depends on the way of platinum pretreatment and therefore the kinetic parameters established for different processing procedures are different. Hoare¹ gives the following values for the above-mentioned reaction (at c. 20°C): $i_0 = 8.5 \cdot 10^{-9}$ A/cm² and $b = 0.14$ (i.e. $\alpha = 0.42$). In a number of cases, however, different values were obtained from the data measured in the same potential range (1.6–2.0 V), especially for the Tafel slope b (0.065–0.16)^{2–10}. The cause is that the state of the electrode surface depends on experimental conditions which were not identical. In aqueous solutions platinum may be covered with different layers of adsorbed oxygen or of particles containing oxygen, beginning with the potential 0.7 V (RHE). According to ellipsometric measurements¹⁵ an oxidic film is formed on platinum surface starting 1.0 V. The degree of coverage of platinum surface by oxygen bound in such a way is a linear function of potential^{1,11–14} and at c. 1.5 V it attains the value $\theta = 1$. With further increase of potential this layer of PtO is transformed into PtO₂. Its amount reaches the value of a monolayer at the potential^{13,16–20} of about 2.0–2.2 V and with further increase of potential the amount of oxide (denoted as oxide I in the previous paper²⁰) does not change any more. By anodic polarization atomic oxygen penetrates, however, also the interior of the electrode²¹. According to the depth of penetration it is called either dermasorbed oxygen^{22,23} (depth 2–3 atomic layers of the platinum lattice) or absorbed oxygen^{14,24} (sometimes also called Pt–O alloy^{1,14,24,25}). In the range of potentials, when practically only oxygen is anodically evolved ($\epsilon < 2.6$ V), the electrode surface may be covered besides with oxide I also with oxide II which can form multilayer deposits^{20,26–30}. Oxide I is formed and is also stable over the whole potential region, whereas oxide II arises only by a prolonged polarization³⁰ in the range 2.1–2.55 V. Shibata and Sumino³⁰ give a much narrower potential range 2.07–2.17 V. However, according to their findings a further amount of oxide can be formed on its first layer even in the region of passivation over 2.7 V, whereas in the passivation region

over 2.55 V as found by us the originally present oxide II disappears²⁰. * Since the experimental conditions of the present work were identical with those of our study²⁰, we shall cling to the potential range of the formation of oxide II found by us. The effect of multilayer surface oxide II on the rate of anodic evolution of oxygen has not yet been investigated in detail. The only qualitative description of the results of analogous measurements is given in the paper of Shibata and Sumino³⁰.

The subject of the present communication is the study of the effect of platinum surface oxides on the kinetics and mechanism of anodic evolution of oxygen in the region of higher anodic potentials in H₂SO₄ and in particular the effect of surface oxide II.

EXPERIMENTAL

Apparatus: Arrangement of the electrolytic vessel was similar to that described in paper²⁰. The container for collecting the anodic gas was placed over the measured Pt wire electrode. This device was ended by a thermostated gas burette. Gasometric measurements served to determine the current yields of oxygen evolution from which the partial currents of both main possible anodic reactions were calculated, *i.e.*, of oxygen evolution and of the formation of peroxydisulphate ion. Anodic evolution of ozone and of peroxymonosulphuric acid (Caro's acid) was not followed. Potentiostat Wenking 61 RS or a potentiostat of our own construction were used to measure the polarization curves under potentiostatic conditions. Current was measured with an amperemeter or milliamperemeter (Metra Dli, ČSSR) or it was registered with an compensation millivoltmeter KBT (Messgerätewerk Magdeburg, GDR) which was used to scan the voltage on a precise resistance connected to the polarization circuit between the output of the potentiostat and the auxiliary electrode. Potential of the studied electrode was measured by means of a voltmeter MV 84 (Clamman & Grahnert, GDR) against a reference hydrogen electrode, immersed into the solution of the same composition as that in the anodic compartment. In order to determine the potential even at high current densities, the ohmic voltage drop IR between the measured electrode and the end of the Haber-Luggin capillary was measured from the chronopotentiometric curves after switching out the circuit^{20,31}. The nature of oxidic layers on the surface of Pt electrode was determined voltammetrically at linearly decreasing potential as described earlier²⁰.

Measuring procedure: Prior to measurement the platinum electrode was polished with emery paper 5/0 and 6/0 and rinsed with distilled water. Further procedure of pretreating depended on the kind of subsequent measurement. Measuring of anodic polarization was carried out with the electrode previously polarized at 1.9 V for 30 min. (All values of electrode potentials in this paper are referred to the equilibrium potential of hydrogen electrode in the same solution (RHE). Then the potential was lowered to 1.65 V and afterwards increased stepwise after each current stabilization. The current was taken as stabilized, if its change did not exceed 2% rel. during 10 min.

When studying the effect of different surface oxides the electrode was polarized for a certain time at the potential at which the respective oxide is formed²⁰. Then the polarization curve was measured passing from the highest potentials to the lowest ones. The currents were read off already 5 s after each adjusting of potential. This procedure had the purpose to prevent any possible changes in the composition of the surface layer during measurement. Afterwards the electrode

* According to the newest observations⁴⁹ using ellipsometric method our earlier results about the formation of oxide II in the potential range 2.1–2.55 V with the maximum formation rate at 2.3 V were fully confirmed.

was charged with a pulse of linearly decreasing potential ranging from 1.0 to 0.05 V, the rate of potential decrease being 0.005 V/s. The amount and the kind of platinum surface oxide was determined from the voltammetric curve²⁰. In some cases the electrode was pretreated by means of a specific procedure, as it is described in the Results. All measurements were carried out at 15°C.

Chemicals: Solutions of H₂SO₄ were prepared by diluting 96% acid of the reagent grade purity with distilled water. Further purification of solutions proved unnecessary.

RESULTS

Stationary polarization curves, shown in Fig. 1, can be divided into several parts. In the first one (A) the dependences $\epsilon - \log i$ are linear, their slope increasing moderately with increasing acid concentration (Table I). In part B the shape of the curves is slightly concave with the slopes also increasing with increasing acid concentration. In both parts the stabilization of current to a stationary value lasted 30–100 min. By polarization at 2.1 V (in 1N-H₂SO₄) to 2.2 V (in 10N-H₂SO₄) the current density after initial decrease began to increase which lasted several hours before stabilization was reached. This phenomenon is manifested on the stationary polariza-

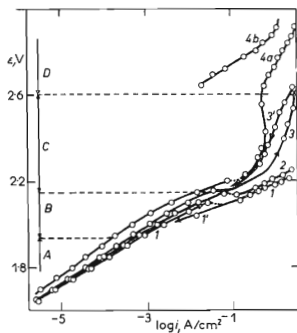


FIG. 1

Stationary Polarization Curves of Oxygen Evolution and of Peroxydisulphate Formation on Pt Anode in H₂SO₄ Solutions

H₂SO₄ concentration: 1, 1' 1N; 2 2.5N; 3, 3' 5N; 4a, 4b 10N. Measured 1, 2, 3, 4a, 4b from lower potentials towards higher, 1', 3' from higher potentials towards lower; partial polarization curve 4a: of oxygen evolution, 4b: of peroxydisulphuric acid formation.

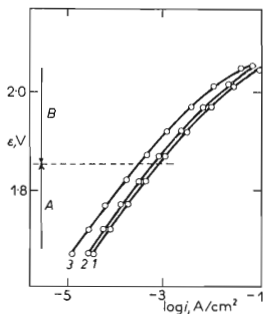


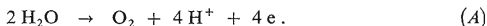
FIG. 2

Polarization Curves of Oxygen Evolution from 1N-H₂SO₄ on Platinum Anode, Pre-polarized at 1.9 V

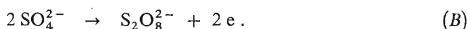
Pre-polarization time, in min: 1 1; 2 5; 3 60.

zation curves by a decrease of the potential on the boundary of regions B and C. The decrease of overvoltage, the so-called activation of electrode, is irreversible. If the potential is decreased after activation of the electrode, greater currents appear in the whole region B than prior to activation (Fig. 1, curve 1'). In region C the steepness of the curves increases continuously and in 10N-H₂SO₄ the slope acquires negative values. The increase of overvoltage in this region is not completely reversible which is indicated by hysteresis (Fig. 1, curves 3 and 3'). In section D which was studied in the described arrangement only in 10N-H₂SO₄ a decrease in the slope of the polarization curve occurs again.

It was established from gasometric measurements that in regions A, B and C the current is entirely consumed by the reaction of oxygen evolution



Partial currents of further reactions are too small to be registered, the mean deviation of gasometric measurements being $\pm 1.2\%$ rel. Only in the region D the current yields of oxygen begin to decrease distinctly due to concurrent anodic oxidation of sulphate ions to peroxydisulphate



Polarization curves of both given anodic reactions (A) and (B) in region D are illustrated in Fig. 1 by curves 4a and 4b. It can be seen that a strictly linear course, following Tafels relation, can be found only in region A. Corresponding kinetic parameters of reaction (A) for different concentrations are listed in Table I.

TABLE I

Kinetic Parameters of Oxygen Evolution on Platinum Electrode as Determined in Region A of Stationary Polarization Curves (Fig. 1) at 15°C

N-H ₂ SO ₄	<i>a</i> V	<i>b</i> V	<i>i</i> ₀ · 10 ⁹ A/cm ²	<i>α</i>
1	1.092	0.123	1.33	0.465
2.5	1.126	0.129	1.86	0.443
5	1.145	0.131	1.81	0.436
10	1.244	0.142	1.75	0.403

Fig. 2 shows non-stationary polarization curves of oxygen evolution from 1N-H₂SO₄ on a platinum electrode, previously polarized at 1.9 V for various times. Under these conditions only oxide I is formed on the electrode surface. From the shape of the curves it is evident that while oxygen overvoltage increases with prepolarization time in both regions A and B, the slope of the polarization curves is independent of it.

This means that only Tafel constant a increases with increasing time of prepolarization, whereas constant b remains unchanged. In region A the Tafel constant $b = 0.135$ which is in good agreement with the value given by Hoare¹. The value of Tafel constant a increases approximately linearly with the logarithm of prepolarization time in the range of $\tau = 60 - 3600$ s, the value of $(da/d \log \tau)$ being approximately 30 mV. Voltammetric curves of the reduction of surface oxides, registered after measuring the non-stationary polarization curves of oxygen deposition, indicate that the charge consumed by the reduction of oxide I is independent of the prepolarization time for $\tau > 5$ min. However, the potential range of oxide I reduction is shifted towards negative values with prepolarization time and the originally single reduction wave splits into a wave with two maxima. Simultaneously the amount of oxygen dissolved inside the platinum electrode is increased, too.

In the case that oxide II is formed in addition to oxide I, polarization curves show a different course. From Fig. 3 it is evident that the potential of oxygen evolution in region A changes with the time of prepolarization as it is with an electrode free of surface oxide II, *i.e.*, only constant a changes, whose relative increase with time

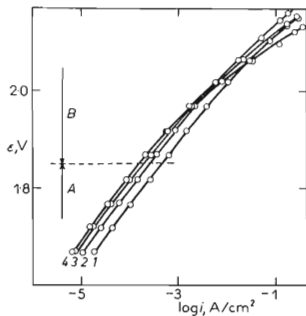


FIG. 3

Polarization Curves of Oxygen Evolution from 1N-H₂SO₄ on Platinum Anode, Pre-polarized at 2.15 V

Prepolarization time, in min: 1 0.5; 2 5; 3 20; 4 60.

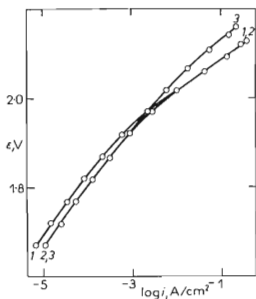


FIG. 4

Polarization Curves of Oxygen Evolution from 1N-H₂SO₄ on Platinum Anodes, Pretreated in Different Ways

1 Polarization for 90 min at 2.15 V; 2 after reduction of oxide I at 0.28 V followed by its repeated deposition by polarization at 2.15 V for 5 min; 3 after reduction of both oxides and repeated deposition of only oxide I by polarization at 2.15 V for 5 min.

is the same as it is in the case of prepolarization at 1.9 V. Constant b has the same value as if the electrode is covered only with oxide I. The slope of polarization curves in region B diminishes with prepolarization time, which means that with increasing amount of surface oxide II the electrode is gradually activated. Voltammetric curves of reduction of electrodes measured after investigation of polarization curves showed that total charge necessary for the reduction of surface oxide I does not change in this case beginning with $\tau = 0.5$ min. The reduction proceeds always in two waves which are shifted towards more negative potentials with increasing time of prepolarization. The charge for reduction of surface oxide II increases gradually and the position of the peak is practically independent of prepolarization time. The amount of atomic oxygen dissolved inside the electrode increases with prepolarization time.

Evidence of the assumption that the change in the character of polarization curves in the region B is brought about by the presence of surface oxide II was given by the following experiment, making use of the differing rates of formation of the two kinds of platinum surface oxides²⁰. First, the electrode was polarized for one and half hour in 1N-H₂SO₄ at 2.15 V so that both surface oxides were formed; then the polarization curve of oxygen evolution was measured in the range 1.67–2.15 V (Fig. 4, curve 1). The slope of the curve in region B is small as it is typical in the case when activation of the electrode takes place. By subsequent linear decrease of potential to 0.28 V oxide I was removed from the surface, whereas oxide II remained unchanged. Then the electrode was polarized again at 2.15 V for 5 min to restore the layer of oxide I. The respective polarization curve was denoted 2 in Fig. 4. Its slope in regions A and B is the same as with curve 1 only constant a in region A is by about 30 mV smaller which corresponds to smaller prepolarization time. The surface of the electrode was then freed from both kinds of oxides by a linearly decreasing potential pulse 1.0–0.1 V and the electrode was again polarized at 2.15 V for 5 min to make possible the deposition of oxide I, but not of oxide II having a much slower rate of formation. This was confirmed by the voltammetric curve of reduction of surface oxides after measuring the non-stationary polarization curve of oxygen evolution (Fig. 4, curve 3). Its slope in region B corresponds to inactive electrodes, i.e., those covered only by oxide I (Fig. 2).

If the electrode, activated by deposition of oxide II, is polarized for a longer time in the region of peroxydisulphate formation ($\varepsilon > 2.6$ V) it becomes inactive and the polarization curves of oxygen evolution have the same slope in both regions A and B (Fig. 5, curve 3). Only after reduction and prolonged polarization in the region of oxide II formation, the slope in region B is somewhat less steep than in region A (Fig. 5, curve 5).

DISCUSSION

The results of measurement of stationary polarization curves of oxygen evolution on platinum electrodes confirmed the fact^{5,8,32–34} that the dependences ε –log i do not show a uniform linear course over the whole potential range where the mentioned reaction proceeds as the only one ($\varepsilon < 2.5$ V). Kinetic parameters calculated for region A are in agreement with the data given by Hoare¹ and prove that in the range of current densities $i > 10^{-5}$ A/cm² impurities in the chemicals used had no

appreciable effect (contrary to the measurement for $i < 10^{-7}$ A/cm² (ref.³⁵)). The earlier finding that both overvoltage and the slope of polarization curve increase with increasing concentration of sulphuric acid^{1-8,32-37} are also supported by the measured data. From the kinetic parameters it followed that the exchange current density i_0 is in the measured concentration range independent of the activity of water in sulphuric acid solutions (see³⁸) within the limits of experimental error. A similar conclusion resulted from the data of Izgaryšev and Jefimov³². The results of Erdey-Grúz and coworkers³⁹ cannot be compared with the our ones, as they may be affected by the specific influence of added caprolactam, too.

Under the conditions that only oxide I is present on the electrode surface, the oxygen overvoltage increases with the time of prepolarization while the slope of polarization curves in region A remains constant. This finding is in agreement with the data found earlier^{4,5,40-42}.

Busing and Kauzmann⁴⁰ explain their results, measured in solutions which had not been previously electrolyzed, by adsorption of impurities on platinum surface. Bockris and Huq⁴, however, found a similar dependence when using pre-electrolyzed solutions which they explain

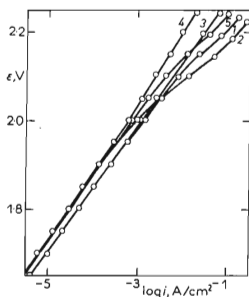


FIG. 5

Polarization Curves of Oxygen Evolution from 5N-H₂SO₄ on a Prepolarized Pt Electrode

Prepolarization: 1 3 min at 2.24 V; 2 100 min at 2.24 V; 4 after measuring curve 2 the electrode was polarized for 19 h at 2.68 V; 3 after measuring curve 4 the electrode was polarized at 0.1 V for 60 min and at 2.24 V for 3 min; 5 after measuring curve 4 the electrode was polarized for another 100 min at 2.24 V.

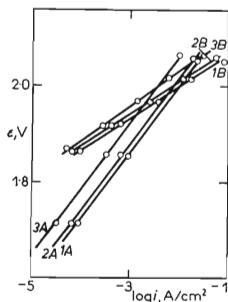


FIG. 6

Partial Polarization Curves of Oxygen Evolution according to the First and Second Mechanism, Evaluated from Total Polarization Curves in Fig. 2

by deactivation of the platinum surface by the growing amount of platinum oxides. Šolc⁴ assumes the activation energy of oxygen evolution to be a linear function of surface coverage by oxygen which reaches the stationary state only slowly. However, according to the hitherto findings, only a few tens of seconds up to some minutes^{13,20} are necessary to attain equilibrium amount of oxide I at 1.9 V, so that the time increase of oxygen overvoltage at a constant current, when the prepolarization time is longer than 5 min cannot be accounted for by the increasing amount of this oxide. A more probable explanation that the qualities of this oxide change with time is also supported by the shift of maxima of the reduction current on the voltammetric curves to more negative potentials and also by the reduction of surface oxide I in two waves (ascribed^{43,44} to two forms of oxide I) when the prepolarization time is increased. Tjuriin and coworkers^{43,44} found a direct correlation of the rate of oxygen evolution to the amount of both forms of oxide I on the surface of platinum anode. Besides, atomic oxygen dissolved inside platinum can also play a role. Its amount increases with the time of polarization at constant potential²⁰. Therefore, it cannot be excluded that it is just this form of oxygen which modifies the energetic properties of the surface oxide I on which the oxygen evolution takes place. Experimental proofs of this hypothesis are, however, still lacking, as the explanation of Schultze⁴² of the time dependence of oxygen overpotential affected by the total oxygen content in platinum does not differentiate individual kinds of oxygen species on and in platinum. Recent papers of Hoare^{14,24} do not bring evidence of such a hypothesis, either. The up to now available experimental data seem thus not to be conclusive, even in the case when platinum is covered only by oxide I, for a quantitative expression of the effect of surface states of platinum in the kinetics and mechanism of oxygen evolution. The time dependence of oxygen overpotential may also be caused by the adsorption of sulphate ions^{45,46}.

The measured decrease of the polarization curve of oxygen evolution when passing from region A to B (Figs 1–3) might be caused by several factors: 1) By the change of surface properties of the electrode, 2) by arising of such conditions at the electrode surface under which only the slope of the polarization curve changes whereas the reaction route remains the same, 3) by changing the reaction route.

Since the change of the slope was observed at potentials at which no characteristic change in the composition of surface layers could be detected voltammetrically (*e.g.* for 1N-H₂SO₄ at 1.85–1.94 V) explanation 1) can be excluded. From the experimental results it also follows that the change in the slope of polarization curves when passing from region A to B is not conditioned by the existence of oxide II on the electrode. This conclusion is also supported by the finding that the existence of surface oxide II does not affect the kinetics and the mechanism of oxygen evolution in region A. In the second case we assume that in both regions the rate determining process is the reaction



where S denotes a free active center on the electrode surface. This reaction is described by the kinetic equation

$$i = F \cdot k \cdot a_{H_2O}(1 - \Theta) \exp(\alpha F \eta / RT). \quad (I)$$

Assuming the validity of this equation, a decrease of the slope of the polarization curve, *i.e.*, the increase of the reaction rate of oxygen evolution at the same overvoltage must have necessarily been caused either by an increase of activity of water, a_{H_2O} , or by an increase of the amount of free active centers $(1 - \Theta)$ with increasing potential in region B, both of these assumptions being very improbable. Another alternative for the same reaction route would mean that one of the

processes consecutive to reaction (C) must have become the rate determining process. However, this would lead to a further decrease of the resulting rate of oxygen evolution, *i.e.*, the slope of the polarization curve would increase.

The only remaining cause of the decrease of the slope b with increasing potential is that the evolution of oxygen proceeds simultaneously by another mechanism after a certain value of potential has been attained. This explanation which was not plausible in the case discussed by Damjanovič, Dey and Bockris¹⁵, can be accepted in our case. We use the assumption that the relation for partial current densities, for the case that oxygen is produced by two independent mechanisms, can be written in the usual simple form (for $\eta > RT/nF$)

$$i_1 = i_{01} \cdot \exp(\alpha_1 n_1 F \eta / RT) \quad \text{and} \quad i_2 = i_{02} \cdot \exp(\alpha_2 n_2 F \eta / RT). \quad (2), (3)$$

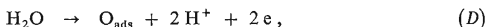
The resulting current density is given by the sum of both partial current densities. If $i_{01} > i_{02}$ and $\alpha_1 n_1 < \alpha_2 n_2$, then it is possible to find two sections on the polarization curve η - $\log i$ of which the section corresponding to the region of lower overvoltages has a higher slope than that for higher overvoltages ($b_1 > b_2$). There is a transition region between the two regions in which currents i_1 and i_2 are comparable and where the simple Tafel equation is not valid.

On the basis of this general concept the measured dependences of η - $\log i$ were calculated assuming that in region A oxygen is formed only by one single mechanism which, in region B, is accompanied by another mechanism. The intermediates of the second mechanism are supposed not to affect in region B the reaction rate of the first mechanism, *i.e.* the dependence η - $\log i_1$ is in both regions expressed by one straight

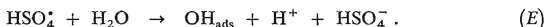
TABLE II
Kinetic Parameters of Partial Reactions of Oxygen Evolution on Platinum Electrode from 1N-H₂SO₄ after Various Prepolarization Times

Prepolarization		First mechanism		Second mechanism	
V	time min	a_1 , V	b_1 , V	a_1 , V	b_1 , V
1.9	1	1.043	0.135	0.900	0.066
	5	1.059	0.135	0.910	0.066
	60	1.102	0.135	0.916	0.068
2.15	0.5	1.077	0.135	0.979	0.074
	5	1.107	0.135	0.989	0.070
	20	1.129	0.135	0.958	0.065
	60	1.137	0.135	0.921	0.060

line. The current density i_2 was calculated from the relation $i_2 = i - i_1$. The results of the treatment of polarization curves as measured on platinum covered only with surface oxide I are in Fig. 6. As can be seen, partial polarization curves of oxygen evolution by both concurrent mechanisms are linear, which supports the above-mentioned assumptions. From Table II it follows that the values of Tafel constants a_1 and a_2 increase with prepolarization time, as in region A, discussed earlier. The evolution of oxygen according to the second mechanism cannot obviously proceed *via* reaction (C) and oxidation of water must take another course. One of the possible rate determining reactions could be *e.g.* the two-electron oxidation of water



or a reaction of the primarily discharged radical HSO_4^* with a water molecule



In both cases the slope of the polarization curve, calculated from the relation⁴⁷

$$b = v_i RT / [(n_a + n_i \alpha_i) F], \quad (4)$$

(v_i is the stoichiometric number of the rate determining reaction, n_a is the number of electrons transferred in the preceding steps, n_i is the total number of electrons exchanged in the rate determining reaction, recalculated to a unit transfer of the overall reaction) attains the value $b = 2.3RT/F$ under the assumption that in both cases $\alpha_i = 0.5$). The agreement of these values with the measured value of constant $b_2 \approx 68$ mV does not exclude any of the suggested mechanism. However, measurements using the isotope ^{18}O in similar solutions of perchloric acid showed⁴⁸ that reaction (E) proceeds under the exchange of oxygen between radical HSO_4^* and a water molecule only in the potential range over 2.3 V. Therefore the depolarization of water molecules through two-electron reaction (D) seems to be more probable. The increase of Tafel constant a_2 with time can be explained by the decrease of the adsorption heat of the product of the rate determining reaction on the electrode surface. Total content of the bound oxygen (surface-bonded and dissolved inside the electrode) increases with time which affects the surface properties of the surface layer.

The results of measurements on a platinum electrode pretreated for different times at 2.15 V, where also oxide II is formed were treated in a similar way. The course of polarization curves of both reactions is illustrated in Fig. 7 and the respective values of Tafel constants are presented in Table II, too. The rate of oxygen evolution by the first mechanism is not affected by oxide II, as the time dependence of constant a_1 is in this case analogous to the case when the electrode is covered only by oxide I, whereas constant b_1 remains in both cases unchanged. With increasing amount

of oxide II on the electrode surface the slope b_2 decreases, being somewhat higher at shorter prepolarization times and *vice versa*, than it is in the case when the electrode is covered only with oxide I. The effect of the amount of oxide II on the slope b_2 of the polarization curve in region B is shown in Fig. 8. As can be seen, the Tafel slope approaches a certain limiting value which (considering the effect of the roughness of the surface) is attained when the amount of surface oxide II corresponds approximately to a monolayer of oxygen. This limiting value is $b_{2\text{lim}} = 59 \text{ mV}$, which corresponds to the value $2.3RT/F$. The decrease of b_2 with increasing amount of oxide II can most probably be ascribed to a change in the structure of electrode surface layer and thereby also of the interphase boundary electrode-electrolyte which is reflected in the increase of transfer coefficient α .

All these findings can also serve to explain the observed activation effect of polarization at potentials, when the surface oxide II is formed, on the rate of oxygen evolution on electrodes which were not prepolarized at this potential. Considering that the initial rate of oxide II formation is by far less than that of oxide I at the same potential, the effect of oxide II is manifested only after c. 10 min. Therefore the current density of oxygen evolution under potentiostatic conditions on a non-prepolarized electrode in the region above 2.1 V first decreases, due to the prevailing time effect of oxide I transformation, then passes through a minimum and finally increases to a certain stationary value, as it was also stated in paper³⁰.

The increase of the slope of polarization curves of oxygen evolution in region B at electrodes, previously prepolarized at potentials of peroxydisulphate formation

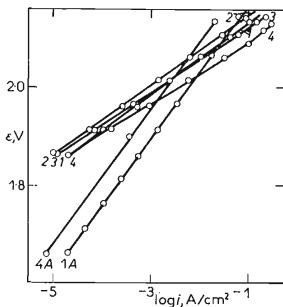


FIG. 7

Partial Polarization Curves of Oxygen Evolution according to the First and Second Mechanism, Evaluated from Total Polarization Curves in Fig. 3

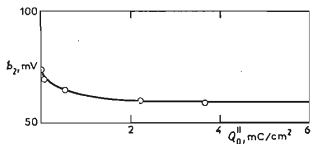


FIG. 8

Dependence of Slope b_2 of the Polarization Curve of Oxygen Evolution according to the Second Mechanism on the Amount of Surface Oxide II on Platinum Anode

($\varepsilon > 2.6$ V, Fig. 5) can be explained so that compact oxidic layers formed during prepolarization inhibit the alternative mechanism of oxygen evolution. This compact structure is so stable that even after long-termed reduction its effect is not eliminated (Fig. 5, curves 4, 5). The fact that the slope of polarization curves measured after reduction and long-termed polarization of the electrode at potentials of oxide II formation does not attain the value characteristic of an active electrode is in agreement with the former observation²⁰ that prepolarization in the persulphate region inhibits the formation of oxide II.

We can conclude that the results found extend our knowledge on the behaviour of platinum anode in the evolution of oxygen from solutions of sulphuric acid in the region of higher anodic potentials as well as on the causes of different slopes of Tafel polarization curves found by various authors in the potential range 1.8–2.1 V.

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