

EFFECT OF HALOGENIDE IONS AND MONOVALENT CATIONS ON THE FORMATION OF A MULTILAYER OXIDE ON A PLATINUM ELECTRODE

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Effect of monovalent cations and halogenide anions on the rate of formation of platinum surface oxides in 1N-H₂SO₄ solutions in the potential region of 2.0–2.8 V has been studied. The surface oxide *I* has been found to be produced in a limited amount corresponding to the PtO₂ monolayer within the whole potential range presented, irrespective of the solution composition. The rate of formation of the surface oxide *II*, however, is more or less hindered by the presence of the studied ions in the 1N-H₂SO₄ solutions, while the inhibiting effect is increased in the sequence Li⁺ < Na⁺ < NH₄⁺ < K⁺ and F⁻ < Br⁻ < Cl⁻ < I⁻. The potential range of the surface oxide *II* formation (2.1–2.55 V), however, is not changed by the presence of the ions investigated, and the maximum initial rate lies again at 2.3 V as in the solutions of pure sulphuric acid. The same sequence (except for I⁻) has been also found for the increase of the inhibiting effect of these ions on the rate of oxygen evolution in the potential region $\varphi > 2$ V. On the basis of these results an assumption has been made that the surface oxide *II* is produced by a reaction of the surface intermediate products of the anodic oxygen evolution with platinum.

In the previous paper¹ conditions of the surface oxide *II* formation (denoted in some papers^{2,3} as "multilayer oxide") on a platinum anode in 1–10N-H₂SO₄ solution at a temperature of 15°C were examined. This kind of the surface oxide was found to be produced in the given solutions in a potential region of 2.1–2.55 V (RHE), while the rate of its formation at a certain potential decreases with the increasing concentration of the acid. In another paper⁴, effect of this oxide on anodic evolution of oxygen has been investigated and it turned out that its presence accelerates this electrode reaction in the potential region above approx. 1.9 V.

It is well-known that oxygen overvoltage on platinum is increased by the presence of a number of substances, among others, *e.g.*, by cations of alkali metals or ammonium, or by halogenide or rhodanide anions *etc.*, this fact being technically utilized, for example, in the electrochemical manufacture of peroxydisulphates to increase their current as well as energetic yields^{5–7}. It was therefore of interest to examine to which extent formation of the surface oxide *II* is affected by presence of these substances in the sulphuric acid solutions.

EXPERIMENTAL

Apparatus. The measurements were carried out in a three-chamber electrolytic cell, in the middle part of which the measured electrode made of a platinum wire having an active area of 0.1 or 0.3 cm² was placed. The wire was at both ends sealed into glass. In both outer cells auxiliary platinum electrodes (cathodes) connected in parallel were placed. All the three chambers of the electrolytic cell were filled with an electrolyte of the same composition. Polarization of the anode to be investigated was carried out potentiostatically using potentiostat Wenking 68 FR 0.5. In order that the electrode potential might be determined exactly even for higher current densities, the ohmic voltage drop between the electrode measured and the orifice of the Haber-Luggin capillary was evaluated from an oscilloscopic record of the course of voltage between the electrode examined and the auxiliary reference electrode after a short-term break (about 10 μs) of the polarization current. A more detailed description of the cell and further equipment have been presented in previous papers^{1,8}. When measuring the voltammetric curves, by means of which the kind and amount of the surface oxides on the platinum electrode was established, a pulse of the linearly decreasing voltage was generated by a current integrator of our own construction, where an operational amplifier AS 101 (ZPA-ČSSR) was employed. The voltammetric curves were recorded by means of X-Y recorder ENDIM 2200.

Preparation of the electrode and electrolyte. Prior to the measurements the electrode was ground with abrasive papers 5/0 and 6/0, wiped with a filter paper and rinsed with distilled water. The measurements were carried out in solutions of composition 1N-H₂SO₄ + 10⁻³N-HX, where X = F, Cl, Br, and I, or in solutions of 1N-H₂SO₄ + 1N-M₂SO₄, where M = Li, Na, K, or NH₄. All these solutions were prepared from analytical grade reagents and distilled water without any further purification.

Procedure of measuring. The electrode was after the mechanical treatment inserted into the electrolytic cell with a solution of the composition selected, and polarized for a certain period of time at a constant potential. Afterwards, the electrolyte employed was exchanged in the currentless state for a new one (of equal composition, provided the measurements were made in mixed solutions of sulphuric acid and sulphates; for the case of the measurements in sulphuric acid solutions with a halogenide addition, the electrolyte was exchanged for the 1N-H₂SO₄ solution), which did not contain dissolved oxygen or a halogen produced anodically. In this solution a pulse of a linearly decreasing potential (with a steepness of -0.05 V/s) in the region of 1.0-0.05 V was imposed upon the electrode, whereby both the surface oxides were reduced and atomic hydrogen adsorbed. From the voltammetric curve measured the charges spent in the reduction of both types of the surface oxides as well as charge spent for the hydrogen adsorption were evaluated in a way described in the previous paper¹. The temperature of all the measurements was 15 ± 0.1°C. The values of potentials presented in this paper relate to the equilibrium potential of the hydrogen electrode in the measured solution under a hydrogen pressure of 1 atm.

RESULTS

The voltammetric curves measured on the platinum electrode anodically polarized in advance in solutions containing sulphuric acid and sulphates of monovalent cations as well as in sulphuric acid solutions with a halogenide admixture have a similar course as the curves achieved by the measurements in pure sulphuric acid solutions¹. They contain two maxima of the hydrogen adsorption and according to the electrolyte composition, time, and potential of prepolarization one or two waves of the reduc-

tion of the surface oxides. The first wave having a more flat maximum at a potential 0.46 to 0.50 V corresponds to the reduction of oxide *I*, the second one with a sharp maximum at a potential of 0.12–0.13 V corresponds to the reduction of the multilayer oxide *II*. Position of the current maxima corresponding to the reduction of the surface oxide *I* is somewhat dependent on the kind of the cation and lies for the given composition of the solutions at the following potentials: 0.46 V(Li⁺), 0.47 V(Na⁺), 0.48 V(NH₄⁺), and 0.50 V(K⁺). By evaluating the charges spent for the reduction of the oxide $I(Q_0^I)$ and for the hydrogen adsorption (Q_H), ratio $Q_0^I/2Q_H$ has been found to be, within the reproducibility of the results, independent of the solution composition, potential of the electrode prepolarization (within 2.1–2.8 V) as well as of its time (within 0.5–18 h) and is equal 2.1 ± 0.25 .

Unlike oxide *I*, formation of the oxide *II* is very distinctly affected by the presence of the substances examined in the solution. From the dependence of the charge needed for the reduction of the oxide $II(Q_0^{II})$ upon the time of polarization, initial rates of formation of this oxide have been evaluated. Effect of potential of the electrode polarization upon this initial rate of formation of the oxide *II* is for the sulphuric acid and sulphates solutions of composition 1N-H₂SO₄ + 1N-M₂SO₄ graphically presented in Fig. 1. From the latter it follows that cations of alkali metals or ammonium bring down the rate of formation of the oxide *II*, whereas their inhibiting effect increases in the sequence Li < Na < NH₄ < K. The oxide *II* is in these solutions produced – similarly as in pure sulphuric acid – at potentials higher than 2.1 V, and practically independently of the kind of the cation in the solution attains a maximum at a potential about 2.3 V, *i.e.* at an equal value as in the solutions of pure sulphuric acid¹.

In order to compare the effect of cations on the rate of formation of the oxide *II* with their effect on the rate of oxygen evolution, the rate of this anodic reaction was measured under the conditions when currents passing through the electrode were read out 10 s after setting up the chosen value of the anodic potential in a solution of the given composition. This short time of polarization was selected for the measured rates of the oxygen evolution not to be influenced by the presence of the oxide *II* which is produced – as resulted from previous papers^{1,4} – in a determinable amount as late as after a several minutes polarization in a potential region of 2.1–2.55 V.

Total currents passing through the electrode practically correspond merely to the evolution of oxygen, since the current densities of the formation of the surface oxides are in comparison with oxygen evolution six to nine orders of magnitude lower, and likewise formation of the peroxydisulphate ions can under the given conditions still be neglected. The results of these measurements are illustrated in Fig. 2 showing that the cations examined retard the nonstationary rate of the oxygen evolution at the electrode covered merely by the surface oxide *I* in the sequence Li < Na < NH₄ < K, *i.e.* in the same sequence in which they influence the rate of formation

of the surface oxide *II*. The same sequence of the inhibiting effect of the monovalent cations studied upon the rate of the oxygen evolution, however, was established even after one-hour polarization of the electrode at a chosen potential within 2.0–2.6 V, when simultaneously also a certain quantity of the surface oxide *II* is produced on the electrodes.

Analogous results were obtained when measuring in sulphuric acid solutions with additions of the halogenide ions. It can be seen in Fig. 3, where dependences of the initial rate of formation of the oxide *II* upon the potential of polarization are plotted, that the potential region of the formation of this oxide is in these solutions evidently the same as in the solutions of pure sulphuric acid¹ as well as in the mixed solutions of the acid and sulphates of monovalent cations. It was possible to examine this finding fully for the solutions into which hydrochloric acid had been added, when the potential dependence was measured within 2.1–2.8 V. A distinct maximum of the rate of formation of the surface oxide *II* was in this case established at the potential of 2.35 V, while at the potentials above 2.6 V any formation of the oxide *II* has not been already observed. In the solutions containing additions of other halogen-

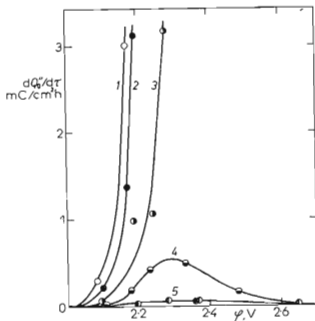


FIG. 1

Effect of Monovalent Cations on the Initial Rate of Formation of Oxide *II* in 1N-H₂SO₄ + 1N-M₂SO₄ Solutions at Various Potentials

1 H⁺; 2 Li⁺; Na⁺; 4 NH₄⁺; 5 K⁺.

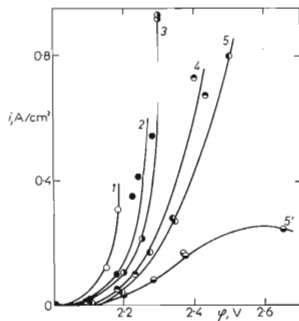


FIG. 2

Effect of Monovalent Cations on the Polarization Curve of the Oxygen Evolution in 1N-H₂SO₄ + 1N-M₂SO₄ Solutions

1 H⁺; 2 Li⁺; 3 Na⁺; 4 NH₄⁺; 5 5' K⁺.

1–5 After 10 s polarization of the electrode at the given potential; 5' after one-hour polarization at the given potential.

ide ions, only the initial increasing branch within the potential range of 2.1–2.35 was measured, for too high current densities of the oxygen evolution on the electrode examined and the considerable ohmic voltage drop between the Haber–Luggin capillary orifice and the electrode, thus produced, did not allow measurements of sufficient precision at higher potentials. It also follows from Fig. 3 that all the additions of the halogenide ions presented, cause, in spite of their low concentration, a distinct diminution of the initial rate of formation of the surface oxide *II*, and their inhibiting effect rises in the series $F^- < Br^- < Cl^- < I^-$.

Potential dependences of currents passing through the electrode after 10 seconds polarization at a chosen potential in the solutions of the composition presented, are given in Fig. 4. This Fig. shows that additions of the halogenide ions retard the rate of the oxygen evolution in the sequence $F^- < I^- < Br^- < Cl^-$.

DISCUSSION

The measurements made have shown that cations of the alkali metals and ammonium as well as the halogenide anions have a diverse effect on the rate of formation of the surface oxides *I* and *II*. The total amount of the surface oxide *I* produced on a plati-

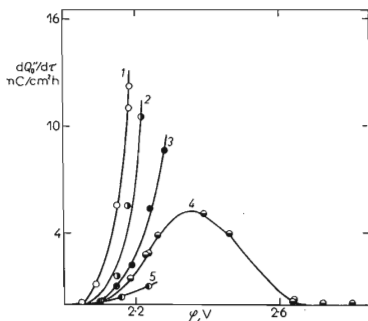


FIG. 3

Effect of Halogenide Anions on the Initial Rate of Formation of Oxide *II* in $1N-H_2SO_4 + 10^{-3}N-HX$ Solutions

1 Without halogenides; 2 F^- ; 3 Br^- ; 4 Cl^- ; 5 I^- .

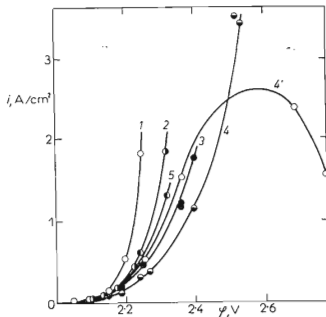


FIG. 4

Effect of Halogenide Ions on the Polarization Curve of the Oxygen Evolution in $1N-H_2SO_4 + 10^{-3}N-HX$ Solutions

1 Without admixtures; 2 F^- ; 3 Br^- ; 4, 4' Cl^- ; 5 I^- . 1–5 after 10 s polarization at the given potential 4' after one-hour polarization at the given potential.

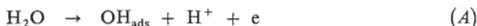
num electrode in mixed solutions of $1N-H_2SO_4 + 1N-M_2SO_4$ ($M = Li, Na, K, NH_4$) or $1N-H_2SO_4 + 10^{-3}N-HX$ ($X = F, Cl, Br, I$) in a potential region of 2.0–2.8 V (RHE) corresponds roughly to two monolayers of oxygen. This means that the limiting coverage of platinum with this kind of the surface oxide is in the mixed solutions of the given composition equal and is in no way affected by presence of the ions mentioned.*

The oxide *I* layers produced on the platinum electrode at potentials above 2.1 V differ thus very much from those produced at lower potentials from 0.9 to 1.5 V, whose formation is considerably suppressed in presence of the substances being adsorbed^{10–16}.

Our finding is in good accordance also with the results achieved by Kokoulina, Krasovickaja, and Krištálik¹⁶, who found that in the potential region of 1.5–2.1 V the inhibiting effect of the Cl^- ions on the formation of oxide *I* attenuates, so that at a potential of 2.1 V its amount is independent of concentration of Cl^- within 0–0.1M. The established independence of the covering of platinum with oxygen (in the form of the oxide *I*) on the presence of the surface active substances at potentials above 2.1 V gives evidence of a relatively firm bond of oxygen with platinum. At yet higher concentrations of chlorides ($1M-Cl^-$) added to the solution of $1N-H_2SO_4$, however, the quantity of oxide *I* decreases¹⁶. Similarly, it was found by Tjurin and Volodin¹⁷ that amount of oxide *I* decreases distinctly at a high concentration of CH_3CN in the H_2SO_4 solution.

Formation of the oxide *II* on the surface platinum anode is very markedly influenced by the presence of the studied monovalent cations or anions in the sulphuric acid solutions. Except for iodides, the substances presented diminish the rate of the oxide *II* formation in the same sequence in which they diminish the rate of the oxygen evolution. This agreement and the potential region of oxide *II* formation lead us to the assumption that the oxide *II* is formed by the reaction of intermediates of oxygen evolution with platinum.

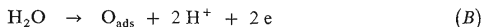
The oxygen evolution proceeds in the potential region below 1.85 V by a mechanism in which the rate determining process is the one-electron oxidation of water¹⁸



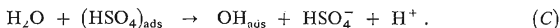
At the potentials above 1.85 V oxygen is according to our previous results⁴ produced by another parallel mechanism whose rate determining process may be either

* In view of the fact that the voltammetric curves of the reduction of the surface oxides produced were recorded as late as about 15 seconds after the end of the anodic polarization and electrolyte exchange, it was not possible to record the unstable recently discovered form of the surface oxygen on the platinum electrode, which disappears already about 0.2 ms after the end of the anodic polarization and which, together with the total amount of the surface oxygen being in the form of oxide *I*, exceeds at potentials $\phi \geq 2.0$ V two monolayers of oxygen⁹.

the two-electron oxidation of water



or reaction of water with sulphate radicals (produced by the preceding electrode oxidation of sulphates)



At the potentials of 2.1–2.2 V the oxygen evolution reaction begins to be markedly retarded, which becomes evident by a striking enhancement of the oxygen overvoltage on the polarization curves^{4,19–29}. This effect is in the literature explained in several ways. The inhibition of the oxygen evolution is according to Beck and Moulton²³ due to the adsorption of electrolyte anions which block the free surface of the electrode for the discharge of water molecules. According to some Soviet authors^{19,30,31} the surface reactions of chemisorbed oxygen particles become the rate determining process of oxygen evolution in the potential region above 2.1 V. This explanation is supported by the results of the impedance measurements^{27,29} in the region of a potential jump. It was suggested that the surface layers (platinum surface oxides and chemisorbed partially discharged anion-radicals of an electrolyte of the dipole nature) concentrate in themselves also a certain part of the total voltage difference between the inside of the electrode and the bulk of the electrolyte, whereby this part of total voltage has no effect on the rate of the electrode reactions²⁷. Likewise the theoretical analysis of the effect of chemisorbed particles of the anion-radical type on the kinetics of the electrode process, considering the potential dependence of adsorption and reactivity of the particles, made it possible to elucidate the experimentally observed course of the polarization curves with a potential jump³².

If we then assume that in the potential region above 2.1–2.2 V some of the chemical reactions of oxygen containing radicals become the rate determining process of the oxygen evolution, it means that in this region the concentration of appropriate oxygen containing substances on the electrode surface rises distinctly. It follows from the results of the present as well as previous papers^{1,4} that the oxide *II* begins to be produced just at the potential of 2.1 V, *i.e.* at the initial point of the “potential jump” mentioned. An explanation thus offers according to which the oxide *II* is produced by a reaction of platinum with atomic oxygen or oxygen containing radicals which are intermediate products of the oxygen evolution reaction. According to this hypothesis both reactions – the oxygen evolution and formation of the oxide *II* – have the first step identical, which, to some extent, accounts for a similar effect of halogenide anions and monovalent cations, present in the solution, on both reactions considered. Quantitatively, however, the effect of the same ions on both reactions is appreciably different. Thus, for example, the rate of the oxide *II* formation

is in the solutions containing lithium ions by more than two orders of magnitude greater than in the solution of potassium ions, while the rates of the oxygen evolution differ in both cases by one order of magnitude only (Figs 1 and 2). It must be recognized, however, that both reactions have different rate determining processes: while the evolution of oxygen is in the considered region controlled by a chemical reaction of oxygen containing radicals, the formation of the oxide *II* is controlled by the reaction of oxygen containing radicals with platinum.

The effect of the halogenide ions may be explained by the fact that they diminish by their adsorption the surface effective for the discharge of water, or that they reduce concentration of active centres upon which oxidation of water occurs to produce oxygen containing radicals which are intermediate products of both the evolution of gaseous oxygen and formation of the surface oxide *II*. The sequence of the inhibiting effect of ions in the series $\text{Cl}^- > \text{Br}^- > \text{I}^-$ on the evolution of oxygen corresponds to the same sequence of the strength of their bond with the platinum surface³³. An exception are fluorides which are adsorbed, according to Kazarinov³³, on the oxidized platinum most firmly of all the halogenides, but by our measurements they inhibit the oxygen evolution and the oxide *II* formation only very little. It is possible, however, that the sequence of the bond strength of individual halogenide ions with platinum, as it was examined by Kazarinov in the potential region of 1.5–2.0 V, is changed at higher potentials (above 2.1 V) in such way as it resulted from their effect, found by us, on the rate of the oxygen evolution and oxide *II* formation. It must be likewise mentioned that the little effect of fluoride ions, established by us, on the enhancement of the oxygen overvoltage does not agree with previous findings^{34–36}, according to which the fluoride ions belong to the most efficient substances which increase the oxygen overvoltage just in the region of high anodic potentials, so that they were suggested as substances used to increase the current yields of the formation of peroxydisulphate ions^{5–7}. A more detailed explanation of this disagreement will obviously require further investigation.

A further anomaly exists with the effect of iodide ions which inhibit the oxygen evolution relatively very little, whereas their inhibiting effect on the formation of the oxide *II* is greater than the effect of bromide ions. This anomaly could not be up to now satisfactorily explained either by a further study of the dissolution of the oxide *II* layer in the solutions containing iodides.

The effect of cations of alkali metals and ammonium on the rate of the oxygen evolution is explained in the literature by their adsorption on the layer of primarily adsorbed anions, whereby the access of water molecules to the electrode and hence their discharge to oxygen²⁵ is hindered. According to another opinion, the present cations increase the bond strength of the adsorbed anions, thus the decomposition of oxygen containing surface compounds, which are intermediate products of the reaction of the oxygen evolution²¹, being retarded. On the basis of the assumptions made formerly on the common initial stage of the mechanism of the oxide *II* forma-

tion and oxygen evolution in the appropriate potential region, the inhibiting effect of the studied cations on the rate of the oxide *II* formation can be derived from both interpretations.

By comparing potential courses of the formation of the oxide *II* and the oxygen evolution (Figs 1 and 2, or 3 and 4), we find a difference in that the rate of the oxide *II* formation is reduced at potentials higher than 2.3 V, whereas the potential dependence of the oxygen evolution have a steadily increasing course. This difference is due to the fact that the polarization curves of the oxygen evolution were measured after a short time of the polarization at a chosen potential (Figs 2 and 4), during which the inhibiting effect due to the adsorption of sulphate ions did not become evident yet. In contrast to this, on the polarization curve of the oxygen evolution, measured as late as one hour after the polarization at a chosen potential (Fig. 2, curve 5' and Fig. 4, curve 4'), a distinct decrease of the currents at potentials higher than about 2.4 V can be seen. This decrease may be accounted for the probable inhibiting effect of the adsorbing sulphate ions, whose surface concentration markedly rises at potentials higher than 2.3 V (ref.³⁷). The higher rate of the oxygen evolution in the potential region of 2.1–2.5 V after the one-hour polarization is, in comparison with the rate of this reaction after the ten seconds polarization (compare curves 4 and 4' in Fig. 4), evidently due to the activation effect of the oxide *II* produced directly in the potential region given⁴. Although the results presented give a distinct evidence of the inhibiting effect of the sulphate ions adsorption on the rate of the oxygen evolution in the potential region above 2.3 to 2.5 V, a complete suppression of the oxygen evolution does not take place, since, according to Kasatkin²⁶, oxygen begins in this potential region to be evolved by another reaction, in which the water molecules discharge directly on the adsorbed anions of the electrolyte.

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