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Abstract

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ON THE STATE OF OXYGEN ADSORBED ON PLATINUM

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The state of oxygen adsorbed on platinum has been studied in numerous works by the method of recording charging curves and by various pulse methods ([1-14]). Anodic charging curves have several regions (steps on the charging curves, maxima on pulse curves) indicating that, at the moment of anodic polarization up to $\varphi = 1.2$ V, i.e., even before the formation of phase oxides on the platinum surface, several forms of chemisorbed oxygen are formed, differing in bond energy. As a rule, it is possible to distinguish two or three forms of oxygen. At the same time, when such curves are recorded in the cathodic direction, i.e., during reduction of chemisorbed oxygen, the distinction between these forms disappears, and usually only one step or one maximum is observed. Such strong irreversibility is sometimes associated with aging processes of chemisorbed layers in time or with partial penetration of oxygen into the depth of platinum ([2,4,12,14]). The absence of several steps or maxima on the cathodic curves casts doubt on the stationary existence, on the surface of platinum immersed in an electrolyte solution, of several energetically distinct forms of chemisorbed oxygen.

A characteristic feature revealed in the study of chemisorbed oxygen on platinum by pulse methods is the noticeable difference between curves obtained on the first and on repeated pulses ([11]). This indicates the sensitivity of the platinum surface to the experimental conditions.

These phenomena, as well as the absence of a definite conception of the state of oxygen on the platinum surface, make it difficult to study the kinetics of anodic and cathodic processes on platinum electrodes.

In the present work, the state of chemisorbed oxygen on platinum was studied by pulse methods in the potential range 0.4–1.2 V. Using an oscillographic polarograph PO-5122, rapid i—φ curves were recorded at rates of application of sawtooth potential pulses from 0.01 to 160 V/sec, as well as potentiostatic i—t curves upon switching the potential from one value to another. Measurements were carried out on a smooth platinum electrode with a surface area of 0.0018 and 0.01 cm^2. Solutions (1 N H_2SO_4 and 1 N KOH) were prepared from distilled acid and "especially pure" alkali. The inert gas (nitrogen or argon) was

Figure 1

Figure 1: Figure 1

thoroughly purified of traces of oxygen. All potentials are given relative to the potential of the hydrogen electrode in the same solution.

We have established that, under certain conditions of electrode preparation and of carrying out the experiment, two regions of reduction of chemisorbed oxygen can also be obtained on the cathodic curves. In our experiments the platinum electrode was first strongly polarized anodically and cathodically until oxygen and hydrogen were evolved, and, before each series of experiments, already in the solution under study, it was additionally activated anodically-cathodically at potentials of 1.2 and −0.1 V. Before measurement the electrode was held for two minutes at the initial potential of 1.0 V, after which a cathodic potential pulse was applied.

It is seen from Fig. 1 that in acid, and especially clearly in alkali, two maxima of the current of removal of adsorbed oxygen are observed at 0.75 and 0.60 V, which on repeated curves are separated more distinctly and are located at 0.83 and 0.60 V. For clear manifestation of both waves in acid solutions, the correct choice of the potential interval in recording the curves is important. If measurements are begun from more positive potentials,

the maximum at 0.8 V increases sharply and may obscure the closely located maximum at 0.6 V. If, however, repeated $i-\varphi$ curves are recorded on an activated electrode starting from 0.9 V, then two maxima of comparable height can be observed, and the final potential of recording of the first $i-\varphi$ curve affects the picture obtained on the repeated curves (Fig. 1a, $3'$).

With an increase in the rate of potential application v, both current maxima increase; however, this increase is not proportional to v, but proceeds more slowly. This means that, as the rate of recording of the curve increases, the amount of reducible chemisorbed oxygen decreases (this amount can easily be found from the dependence curves $dQ/d\varphi(\simeq i/v)-\varphi$). The character of the decrease in the amount of reducible oxygen with increasing v is not the same for the two maxima in acid solutions; it is more sharply expressed for the maximum at 0.8 V. In alkaline solutions the difference is less pronounced, and therefore comparable heights of both maxima are observed at different rates.

Fig. 1. a –cathodic $i-\varphi$ curves, first $(1,2,3)$ and repeated $(1',2',3')$, recorded in 1 N H_2SO_4 at a rate $v=2.5$ V/sec (3 and $3'$) and 10 V/sec $(1,1'$; 2 and $2')$. b –the same in 1 N KOH at a rate of 10 V/sec (1 and $1'$). All curves were recorded in an inert-gas atmosphere.

The appearance of two maxima on the cathodic $i-\varphi$ curves at increased recording rates was also observed in 8 N H_2SO_4 by Will and Knorr ([9]). Beld and Breiter ([10]), who worked by the method of triangular pulses and observed only

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

one maximum, believe that the results of Will and Knorr are distorted by electrotechnical causes. Our data show that the appearance of two maxima is quite real. Depending on the experimental conditions (the interval and rate of application of potentials), either one of the maxima or both together may be observed. Moreover, under identical conditions of recording the curve, the picture may be different depending on the preliminary treatment of the electrode.

Fig. 2. Anodic-cathodic cycles of $i - \varphi$ curves in 1 N H_2SO_4, recorded at a rate $v = 0.2$ V/sec on platinum degassed in vacuum.

In Fig. 2 are presented anodic and cathodic $i - \varphi$ curves in 1 N H_2SO_4, recorded immediately after anodic ones with a delay at the anodic potential of no more than 1 sec on platinum reduced with hydrogen at high temperature and then degassed in vacuum according to the procedure used in (^{14}).

From Fig. 2 it is evident that, as oxygen is deposited on the surface, it is chemisorbed up to potentials of 1.2 V in the form of two forms and is then removed successively likewise in the form of two forms at potentials of 0.85 and 0.65 V.

Upon a stepwise switching of the potential from some potential φ_{B}, at which the electrode was held for about two minutes, to a new value φ_k, a current appears (anodic or cathodic, depending on the direction of the jump), which, however, falls comparatively rapidly to zero. As is seen from Fig. 3, the decay curves in the coordinates $\lg i$–$\lg t$ in the time interval from 0.002 to 0.05 sec have a linear form with a slope close to 1, which corresponds to a dependence of the type $i = k/t$ (at small t, $i = k/(a + t)$ is also possible). At times greater than 0.05 sec, the current decay slows down.

Fig. 3. Current-decay curves upon a stepwise change of the potential from φ_{B}, the holding potential, to φ_k, the recording potential, in 1 N $\mathrm{H_2SO_4}$ (a) and in 1 N KOH (b). Jump time $t = 0.001$ sec, sweep rate 20 V/sec. For a: I–$\Delta\varphi = 1.0$-0.8 V; II–1.0-0.7; III–1.0-0.6, IV–1.0-0.5 V. For b: I–1.0-0.9 V, II–1.0-0.8, III–1.0-0.55 V.

It is seen from Fig. 3 that some of the straight lines have a break. In acid this break is clearly visible upon switching from 1.0 to 0.7 V, and in alkali from 1.0 to 0.8 V. The break is observed for jumps precisely in that range of potentials in which two closely spaced maxima appear on the i–φ curves, i.e., it may be associated with the simultaneous occurrence of two processes with rates that do not differ very greatly.

Fig. 4. Charging curves constructed by integrating anodic and cathodic i–t curves, recorded at various φ_{v} holding potentials in 1 N H_2SO_4 (a) and in 1 N KOH (b).

Figure 4: Fig. 4. Charging curves constructed by integrating anodic and cathodic i–t curves, recorded at various φ_{v} holding potentials in 1 N H_2SO_4 (a) and in 1 N KOH (b).

By integrating the i–t curves, one can determine the change in the amount of chemisorbed oxygen upon changing the potential from φ_{B} to φ_k. Having carried out such calculations successively for different potential values, one can construct charging curves; such curves are shown in Fig. 4 for acidic and alkaline solutions. As can be seen, on the cathodic charging curves two arrests are observed in the oxygen region, in contrast to the charging curves measured by the usual method. In acidic solutions the arrests are located in the potential region 0.83 and 0.65 V; the length of these arrests is approximately 0.4 and 0.5 μC/cm^2 (on the curve recorded from 1.0 V). In alkaline solutions the arrests are located at 0.75 and 0.65 V, with amounts of electricity of about 0.7 and 0.5 μC/cm^2. Taking roughness into account, these amounts correspond to surface coverages somewhat less than a monolayer.

The presence of two maxima on the cathodic i–φ curves, or of two plateaus on the cathodic charging curves, indicates the possibility of the simultaneous presence of at least two forms of oxygen on the platinum surface.

The experimental data presented also clearly illustrate the phenomenon of strengthening of the bond energy of chemisorbed oxygen with time. The potential of the first maximum on repeated curves, which differ by a considerably shorter holding time (1.0 sec instead of 2 min), is located ⋯

is shifted by 80 mV in the negative direction relative to the first curves. That is, holding at positive potentials leads to aging of the adsorbed oxygen.

The observed character of the current-decay curves at short times can be explained by surface inhomogeneity. Indeed, from the equation for the current decay $i = k/t$, in combination with the equation $i = -\gamma \, d\theta/dt$, expressing the stoichiometric relation of the current to the change in coverage, it is easy to find that the reduction current is

$$i = f_k e^{h\theta}$$

(where f_k depends on the potential φ_k). An equation of this form was derived by Temkin [16] for the reaction rate on a uniformly inhomogeneous surface.

Fig. 4. Charging curves constructed by integrating anodic and cathodic i–t curves, recorded at various φ_{v} holding potentials in 1 N H_2SO_4 (a) and in 1 N KOH (b)

On the basis of the experimental data one can draw the qualitative conclusion that the behavior of oxygen chemisorbed on the surface of platinum differs in acid and in alkali. Comparison of the amounts of electricity under the curve of the first and repeated pulses shows that the rate of formation of chemisorbed oxygen under otherwise identical conditions is greater in alkali than in acid. This is also evident from the current curves obtained when the potential is switched in the anodic direction: in alkaline solutions the currents are larger, i.e., the chemisorption process is completed more rapidly, which is probably connected with the retarded process of displacement of oxygen by anions in acidic solutions.

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