

THE STATE OF OXYGEN ADSORBED ON PLATINUM

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The state of oxygen adsorbed on platinum has often been studied by plotting charging curves, and also by various pulse methods [1-14]. The anode charging curves have several sections (plateaux on charging curves or maxima on pulse curves), showing that at the moment of anode polarization to $\varphi = 1.2$ V (i. e., before the formation of oxide phases on the platinum surface) various types of chemisorbed oxygen are formed, differing in bond energy. As a rule two or three different types of oxygen occur. However, when the same curves are plotted on the cathode side (i. e., during reduction of chemisorbed oxygen), the difference between the types disappears and usually only one plateau or maximum is found. This marked irreversibility is sometimes due to aging of the chemisorbed layer or partial penetration by oxygen into the platinum [2, 4, 12, 14]. The absence of certain plateaux or maxima in the cathode curves casts doubt on the stable existence of energetically different types of chemisorbed oxygen on the platinum surface in contact with the electrolyte.

A peculiarity found in using pulse methods to study oxygen chemisorbed on platinum is the marked difference between the curves for the first and subsequent pulses [11]. This shows the sensitivity of the platinum surface to the experimental conditions.

These phenomena, together with the absence of a clear picture of the state of the surface oxygen, present difficulties for the study of the anode and cathode process kinetics on platinum electrodes.

The present authors have used pulse methods to study the state of chemisorbed oxygen on platinum in the potential range 0.4-1.2 V. A PO-5122 oscillographic polarograph was used to plot rapid $i-\varphi$ curves with sawtooth pulses rising at from 0.01 to 160 V/sec, and also potentiostatic $i-t$ curves with the potential switched from one value to another. The measurements were made with polished platinum electrodes of areas 0.0018 and 0.01 cm². The solutions—1 N H₂SO₄ and 1 N KOH—were prepared from redistilled acid and extra-pure alkali. The inert gas (nitrogen or argon) was carefully freed from traces of oxygen. All potentials were taken relative to a hydrogen electrode in the same solution.

We found that two stages of the reduction of chemisorbed oxygen can be detected on the cathode curves also, given certain methods of electrode preparation and certain experimental conditions. In our experiments, the platinum electrodes were preliminarily strongly polarized anodically and cathodically until oxygen and hydrogen separated, and before performing each series of experiments they were again activated at 1.2 and -0.1 V. Before each measurement the electrode was left for two minutes at the initial potential of 1.0 V, after which the cathode pulse was applied.

Figure 1 shows that two maxima are observed in the current of oxygen desorption at 0.75 and 0.60 V, both in acid and alkaline solution, but more markedly in the latter; on the repeat curves they are more clearly distinguished and occur at 0.83 and 0.60 V. To get two clear waves in acid solutions, it is important to make a correct choice of potential ranges. If the measurements are begun at more positive potentials, the 0.8 V maximum sharply increases and can obscure the nearby 0.6 V maximum. If the repeat $i-\varphi$ curve is measured from 0.9 V on an activated electrode, two maxima of comparable height can be observed; the final potential of the first $i-\varphi$ curve influences the pattern of the repeat curves (Fig. 1a, 3').

Both current maxima increase with ν , the rate of change of potential; this increase is, however, not proportional to ν , but slower. This implies that when the curves are measured at increasing rates, the quantity of

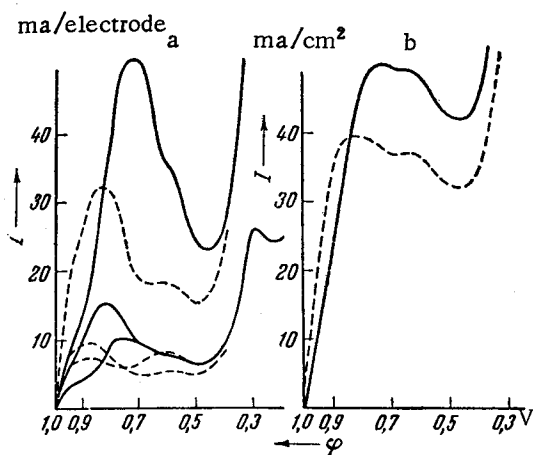


Fig. 1. (a) First (1, 2, 3) and repeat (1', 2', 3') cathodic $i-\phi$ curves in 1 N H_2SO_4 with rates $\nu = 2.5$ V/sec (3 and 3') and 10 V/sec (1 and 1', 2 and 2'). (b) The same in 1 N KOH with rate 10 V/sec (1 and 1'). All curves measured in atmosphere of inert gas.

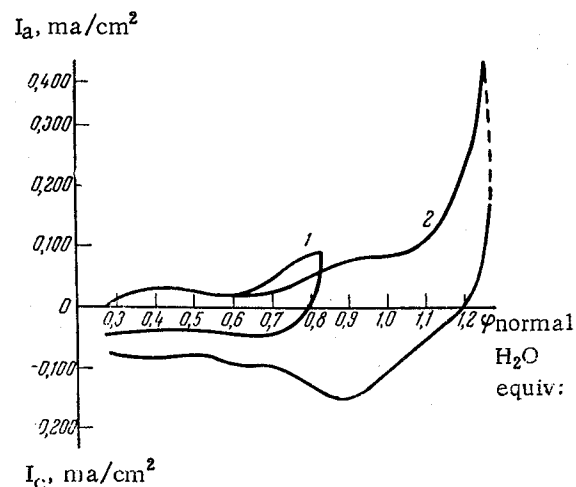


Fig. 2. Anode-cathode cycles of $i-\phi$ curves in 1 N H_2SO_4 , measured at $\nu = 0.2$ V/sec on platinum degassed in vacuum.

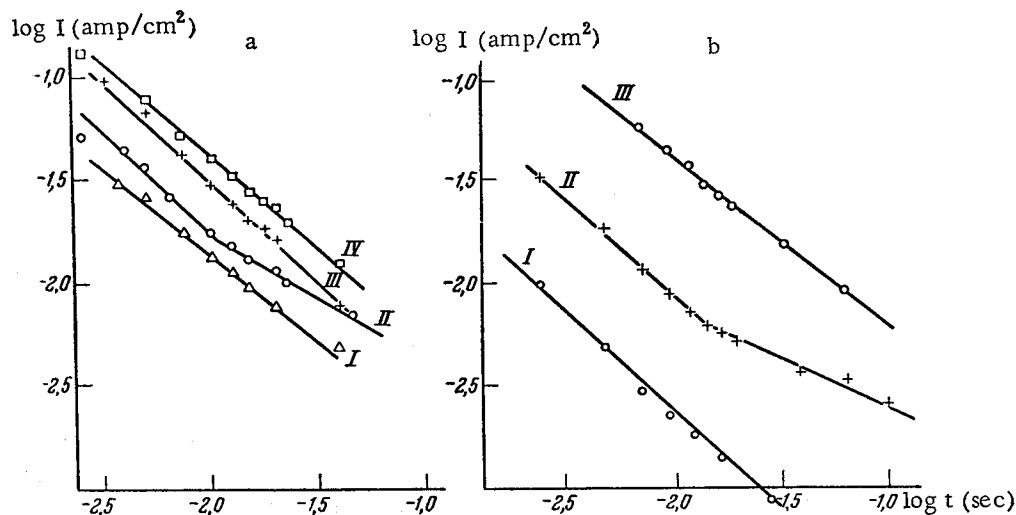


Fig. 3. Current decay curves for instantaneous potential change from ϕ_B (retention) to ϕ_k (measurement) in 1 N H_2SO_4 (a) and 1 N KOH (b). Switching time 0.001 sec., scanning rate 20 V/sec. (a) $\Delta\phi \approx 1.0-0.8$ V (I); $1.0-0.7$ V (II); $\Delta\phi = 1.0-0.6$ V (III); $1.0-0.5$ V (IV). (b) $\Delta\phi = 1.0-0.9$ V (I); $1.0-0.8$ V (II); $1.0-0.55$ V (III).

reduced chemisorbed oxygen decreases: this quantity can easily be found from the curves of $dQ/d\phi$ ($\approx i/\nu$) versus ϕ . In acid solution, the amount of reduced oxygen does not decrease with increasing ν in the same way for both the maxima; it does so more sharply for the 0.8 V maximum. The difference is less marked in alkaline solutions, so that the heights of the maxima remain similar at various ν values.

WillandKnorr[9] observed two maxima on the cathodic $i-\phi$ curves for 8 N H_2SO_4 when the sweep rate was increased. Bold and Breiter [10], working with triangular pulses, observed only one maximum and suggested that Will and Knorr's results were distorted by electrical effects. Our data show that the two maxima are quite real. According to the experimental conditions (range and rate of change of potential), it is possible to observe either one or both of the maxima. Moreover, even with the same potential conditions, the pattern can vary according to the mode of preparation of the electrodes.

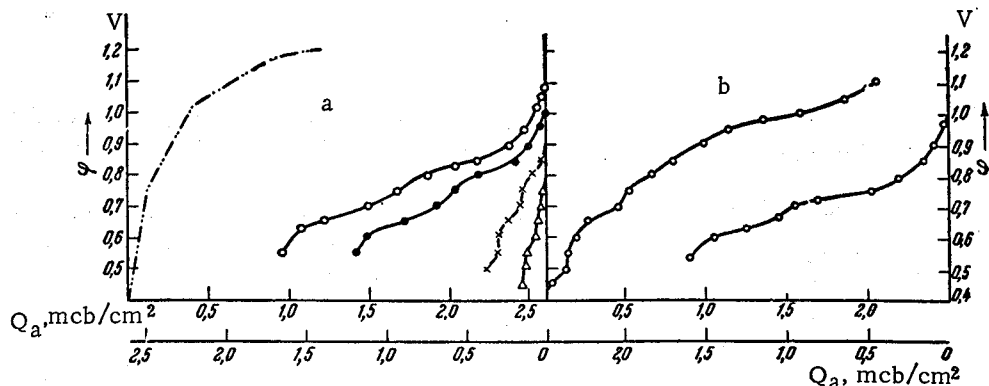


Fig. 4. Charge curves constructed by integrating the anodic and cathodic $i-t$ curves for various retention potentials φ_B in 1 N H_2SO_4 (a) and 1 N KOH (b).

Figure 2 shows anodic and cathodic $i-\varphi$ curves for 1 N H_2SO_4 : they were measured directly after anode curves (with ≤ 1 sec retention at the anode potential) on platinum which had been reduced by high-temperature hydrogen and then degassed in a vacuum by the method of [14].

From Fig. 2 it is seen that, on meeting the surface, oxygen is chemisorbed up to potentials of 1.2 V in two forms, and is also subsequently removed in two forms, at 0.85 and 0.65 V.

On instantaneous switching from one potential φ_B , at which the electrode has been left for about two minutes, to another potential φ_K , a current appears: it is anodic or cathodic according to the direction of the transition, but falls comparatively rapidly to zero. As seen from Fig. 3, the decay curves of $\log i$ versus $\log t$ between 0.002 and 0.05 sec. are linear and have slopes close to -1, indicating a law of the form $i = k/t$ (or, for small t , possibly $i = k/[a + t]$). At times above 0.05 sec. the current decay rate decreases.

Some of the lines have a bend (Fig. 3). In acids this bend appears on switching from 1.0 to 0.7 V, in alkali from 1.0 to 0.8 V. It is observed in transitions in exactly the potential regions for which the $i-\varphi$ curves have two maxima close together, i. e., it may be associated with the simultaneous occurrence of two processes with similar rates.

By integrating the $i-t$ curves we can determine the change in the amount of chemisorbed oxygen for a potential change from φ_B to φ_K . By making this calculation for various potentials we can construct the charging curves; these are shown for acid and alkali solutions in Fig. 4. As seen, the cathode charging curves have two plateaux in the oxygen region—thus differing from those measured by conventional methods. In acid solutions the plateaux occur at 0.83 and 0.65 V; their lengths are ≈ 0.4 and 0.5 mcb/cm² (on the curves measured at 1.0 V). In alkaline solutions they occur at 0.75 and 0.65 V with charges of about 0.7 and 0.5 mcb/cm². Allowing for roughness, these charges correspond to surface coverage rather less than a monolayer.

The existence of two maxima on the $i-\varphi$ curves, or of two plateaux on the cathode charging curves, shows that at least two types of oxygen may be simultaneously present on the platinum surface.

The above experimental data also clearly illustrate the increase with time of the chemisorption bond energy of oxygen. The potentials of the first maxima on the repeat curves, which have appreciably smaller retention times than the first curves (1 sec instead of 2 min), are 80 mV more negative. Thus retention at a positive potential leads to aging of adsorbed oxygen.

The shapes of the current decay curves at small times may be due to surface irregularity. In fact, from the current decay equation $i = k/t$ and the equation $i = -\gamma d\theta/dt$, which expresses the stoichiometric relation between current and change of surface coverage, it is easily seen that the reduction current is given by $i = f_K e^{h\theta}$, where f_K is a function of φ_K . An equation of this type is given by Temkin [16] for the reaction rate on a uniformly irregular surface.

The above experimental data show qualitatively that oxygen, chemisorbed on platinum surfaces in acids and alkalis, behaves in varying ways. Comparison of the quantities of electricity under the first and repeat pulses shows that, under identical conditions, chemisorbed oxygen is formed more rapidly in alkali than in acid. This is also to be seen from the current curves obtained by switching the potential to the anode side; in alkaline solutions the current is greater, i. e., chemisorption is completed more quickly—probably owing to the slower displacement of anions by oxygen in acid solutions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
