

THE ADSORPTION OF OXYGEN ON DEGASSED SMOOTH PLATINUM IN ELECTROLYTE SOLUTIONS

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In spite of the large number of studies [1-9] concerned with the investigation by various methods of the electrochemical behavior of smooth platinum in acid solutions, the dependence of the state of a platinum surface on potential is not absolutely clear in the literature at present. The presence of hydrogen and oxygen on the surface of and within the platinum has an appreciable effect on its electrochemical properties. Therefore, the existing discrepancies in the problem of the state of the platinum surface should apparently be attributed to the differences in preparing the platinum surface before an experiment and also to the differences in methods of measuring e.g., the rate of overlap of current or potential. Thus, for example, the presence of hydrogen on a platinum surface, which is inevitable during the electrochemical treatment of its surface, complicates an investigation of the adsorption of oxygen by rapid methods [8].

In the present study an investigation was carried out under conditions in which the presence of hydrogen on the platinum surface was excluded by using a vacuum electrochemical method described previously [10]. The principal part of the apparatus, in which the platinum electrode was placed, was made of quartz and had a quartz jacket which was evacuated to a high vacuum during the vacuum treatment of the electrode to prevent the diffusion of oxygen at high temperature. In the next part of the instrument was placed an ampoule containing a solution of 1N H_2SO_4 , previously degassed under vacuum. The two remaining parts of the cell contained auxiliary electrodes, one for polarization, the other, a sulphate-mercury electrode, serving as an auxiliary reference electrode. The electrodes were soldered into the instrument, reduced three times at 400° in carefully purified hydrogen, and degassed for 2-5 hr at $850-900^\circ$ under high vacuum. After degassing and cooling the electrode, the instrument was sealed off from the high vacuum apparatus, the ampoule containing the degassed electrolyte broken by jarring the instrument and the electrochemical measurements then carried out. They were made at 25° .

Immediately after contact between the platinum electrode and the electrolyte the initial potential of platinum was measured, this being equal to 0.215 V in one case and to 0.210 V in the other. This potential is close to the zero point potential of unoxidized platinum measured by other methods [11]. A similar zero point potential for the immersion of a degassed electrode in a solution was observed for carbon by Frumkin, Ponomarenko and Burshtein [12]. After establishing a steady value for the initial potential an anode charging curve was recorded at a current density of $3.6 \cdot 10^{-8}$ A/cm² of the true surface area. The value of 2 adopted by various authors [8] was taken as the roughness factor. The experimental data obtained in two different experiments, which virtually lie on one curve are shown in Fig. 1. The charging curve in the regions of oxygen adsorption has three clearly expressed arrests in potentials: I) at 0.6-0.8 V (against N.H.E.), II) at 0.95-1.0 V, and III) at 1.4-1.5 V, which are evidence of different forms of adsorbed oxygen on platinum. In individual cases the second arrest was observed at more positive potentials: II₂ at 1.1-1.15 V.

In Fig. 1a where the charging curve is plotted on a larger scale along the abscissa axis it may be seen that in the so-called double-layer region of potentials (up to 0.6 V) the value of the capacity calculated from the slope of the charging curve is 120 mF/cm². The high value for capacity observed earlier in other studies on a cathodically-reduced platinum surface was explained by the presence of hydrogen potentials in this region [8, 9]. In our case the presence of hydrogen on the surface of platinum degassed at 900° is excluded, and the large capacity value observed apparently indicates a very early commencement of electrochemical adsorption of the first parts of oxygen during

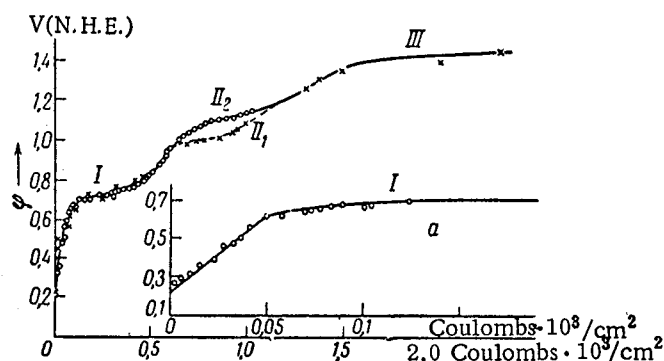


Fig. 1. Anode charging curve on a degassed Pt electrode in 1N H_2SO_4 , $t = 25^\circ$, $i = 3.6 \cdot 10^{-8} \text{ A/cm}^2$; I, II₁, II₂, III are regions of oxygen deposition at potentials of 0.6-0.8 V, 0.95-1.0 V, 1.1-1.15 V and 1.4-1.5 V respectively.

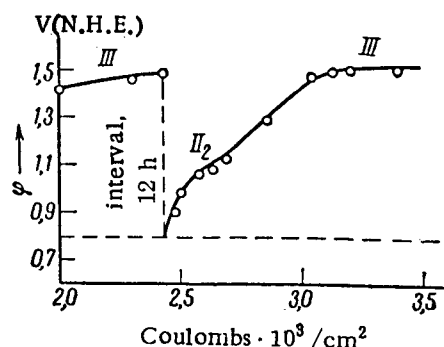


Fig. 2. Drop in potential after switching off the anode current. Resumption of the anodic charging curve after an approximate interval of 12 hours in 1N H_2SO_4 , $t = 25^\circ$; $i = 3.6 \cdot 10^{-8} \text{ A/cm}^2$.

the anodic polarization of degassed platinum. Such a slope for the charging curve could be explained by a high value for the roughness factor (12-20 instead of 2) but this is not very likely.

The length of the first arrest (up to 0.8 V) is approximately $0.5 \text{ mCoulomb/cm}^2$ which corresponds to $1.3 \cdot 10^{15}$ oxygen atoms per square centimeter of the true surface. This value is about equal to the number of platinum atoms on the surface calculated from the lattice parameters of 3.2 Å, about 10% of the oxygen being sorbed at potentials more negative than 0.6 V. However, it is possible that part of this oxygen penetrates into the platinum lattice, as was shown for oxygen which is sorbed at more positive potentials. This problem requires an additional investigation.

The second arrest is approximately equal to the first. The third arrest is more suppressed than the first two. The potential of the second arrest depends on the experimental conditions. A less positive value is obtained on a freshly-prepared surface (part II₁ in Fig. 1). A more positive value of the potential is obtained after switching off the current (see also Fig. 2) or after increasing the temperature (part II₂ in Fig. 1).

The results indicate that it is possible for oxygen to be adsorbed on a carefully degassed platinum surface in at least three forms, differing from each other in bond energy. Within the limits of the adsorption region of each of these forms the variation of the potential with the amount of electricity is almost linear, which is indicative of the logarithmic Frumkin-Temkin adsorption isotherm, characteristic for a uniformly heterogeneous surface [13]. These forms of adsorbed oxygen also differ from each other in their relative stability, as will be seen later.

The first parts of oxygen which are adsorbed on platinum at the potentials of the second and third arrests determine the electrode potential only in the presence of the anode current. After switching off the current the potential is slowly displaced towards potentials of 0.8 V which correspond to the first stage (Fig. 2). In order to reach the potential of the second and third arrests again after switching off the current the same amount of electricity must again be supplied as in the first recording of the charging curve in the same region of potentials (Fig. 2).

A large hysteresis is observed between the anode and cathode charging curves on degassed platinum, even at very low current densities (Fig. 3). If, with cathode operation, the platinum potential is reduced to the initial value of 0.2 V from the potentials of the second anode process by the same current density as with forward operation, then only 20% of the adsorbed oxygen is removed from the platinum (Fig. 3, curve 1'). After switching off the cathode current the potential is again displaced in the positive direction and with a repeated reduction as much oxygen is again removed (Fig. 3, curve 1''). Such irreversibility indicates a gradual penetration of the oxygen below the upper layer of metal after being adsorbed. For cathodic polarization the rate of reduction of oxygen is limited by its diffusion on the surface. The first cathodic reduction curve has barely noticeable arrests at 0.9 and 0.6 V which correspond to the amount of oxygen remaining on the surface. At the time of recording the cathodic curve the residual oxygen on the degassed platinum succeeds in penetrating into the platinum. The following data provide confirmation that oxygen penetrates below the upper layer of the metal: after removal of only 40% of the previously adsorbed oxygen from the platinum the anodic charging curve can again be obtained (Fig. 3, 2), the same as for pure platinum. The rate of penetration of oxygen into degassed platinum depends on the anode potential of the

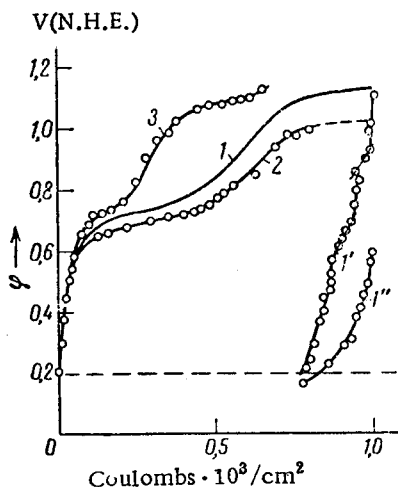


Fig. 3. Anode and cathode charging curves on the degassed electrode in 1N H_2SO_4 , $t = 25^\circ$, $i = 3.56 \cdot 10^{-8} \text{ A/cm}^2$: 1, 1', 1'') on pure platinum; 2) on anodically oxidized platinum after removing 40% of the oxygen; 3) on a completely anodically oxidized platinum surface.

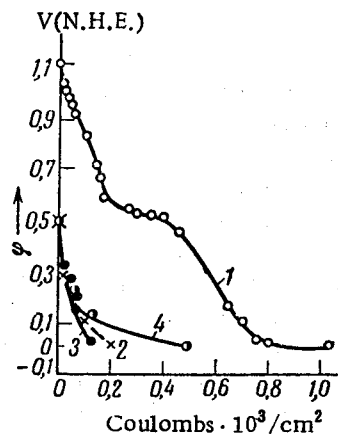


Fig. 4. Cathode charging curves on degassed Pt electrodes in 1N H_2SO_4 , $t = 25^\circ$, $i = 3.56 \cdot 10^{-8} \text{ A/cm}^2$: 1) on completely anodically oxidized surface of platinum after anode charging curve 3; 2), 3), 4) repeated cathode curves after restoring the potential of platinum in the anode direction to 0.5-0.6 V.

platinum electrode and on temperature. By recording the $i - \varphi$ relationship potentiostatically it was found that at the potentials of the first anodic arrest at 25° the penetration of oxygen into platinum takes place at an insignificant rate compared with the recording of the charging curves. However, with an increase in temperature to 85° the rate of penetration increased by a factor of 10-15, the amount of oxygen deposited at the potentials of the first anodic process increasing considerably and being equal to 50 monolayers at low current densities.

With the second and subsequent recordings of the charging curves, after subjecting the electrode to more positive potentials (within the limits of the second arrest) at room temperature, additional deposition of oxygen at potentials of the first anodic process, and the deposition of oxygen in amounts corresponding to pure platinum at potentials of the second anode process (Fig. 1, 1, 2, 3), could be observed. The rate of penetration of the subsequent parts of oxygen at room temperature is apparently delayed and is determined by the diffusion coefficient of oxygen in platinum. From the anode charging curve 3, obtained immediately after curve 2, it is seen that without preliminary reduction according to the amount of electricity the II_2 stage is obtained just as on the preceding curves 1 and 2, while the first stage due to the oxygen remaining on the platinum surface is considerably smaller; the cathode curve 1 (Fig. 4) also provides evidence that the oxygen present on the platinum of curve 2 does not succeed in penetrating into the platinum. This oxygen is displaced at more positive potentials, 0.9 V and 0.6-0.5 V, which correspond to two forms of adsorbed oxygen. The repeated cathode curves (Fig. 4, 2, 3, 4) do not have these stages and characterize the reduction of oxygen arriving at the surface from within the platinum, the rate of reduction being limited in this case by the rate of diffusion of oxygen on the surface. It is possible to remove all the electrochemically adsorbed oxygen with difficulty, after a very long time, by repeated cathodic polarization.

The results obtained on the penetration of anodically adsorbed oxygen into platinum at room temperature confirm the data obtained earlier for smooth platinum under other conditions [3, 9, 14]. However, in these studies the penetration of oxygen was observed at higher temperatures or stronger anodic polarizations. The effect of the penetration of oxygen into degassed platinum is shown much more strongly than on cathodically reduced smooth platinum in which the deep layers of atoms are apparently filled by sorbed gases. It should also be noted that the behavior of smooth and platinized platinum in this respect is substantially different. On platinized platinum the penetration of oxygen deep into the lattice has not been observed at room temperature [1, 15].

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