Reports of the Academy of Sciences of the USSR

V. I. LUKYANYCHEVA, V. S. BAGOtskii

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 155, No. 1

PHYSICAL CHEMISTRY

V. I. LUKYANYCHEVA, V. S. BAGOtskii

ADSORPTION OF OXYGEN ON DEGASSED SMOOTH PLATINUM IN ELECTROLYTE SOLUTIONS

(Presented by Academician A. N. Frumkin, November 2, 1963)

Despite the large number of works ($^{1-9}$) devoted to the study of the electrochemical behavior of smooth platinum in acid solutions by various methods, at present there is no complete clarity in the literature concerning the state of the platinum surface as a function of potential. The presence of hydrogen and oxygen on the surface and in the bulk of platinum has a substantial influence on the electrochemical properties of platinum. Therefore, the existing difference in the question of the state of the platinum surface should apparently be attributed to the different preparation of the platinum surface before the experiment, and also to the different measurement procedures, for example, the rate of applying the current or potential. Thus, for instance, the presence of hydrogen on the platinum surface, which is inevitable during electrochemical treatment of its surface, complicates the study of oxygen adsorption by rapid methods (^{8}).

In the present work the investigation was carried out under conditions excluding the presence of hydrogen on the platinum surface, using the vacuum-electrochemical method described earlier (^{10}). The main part of the apparatus, into which the platinum electrode was placed, was made of quartz with a quartz jacket which, during vacuum treatment of the electrode, in order to prevent oxygen diffusion at high temperature, was pumped down to high vacuum. Into the next part of the apparatus was placed an ampoule with a solution of $1N$ H_2SO_4 previously degassed in vacuum. The two remaining parts of the cell contained auxiliary electrodes, one for polarization, the other, sulfate-mercury, serving as an auxiliary reference electrode. The electrodes were sealed into the apparatus and were reduced three times at 400° in carefully purified hydrogen and degassed at 850—900° in high vacuum for 2 to 5 hours. After degassing and cooling of the electrode, the apparatus was sealed off from the high-vacuum installation; by shaking the apparatus the ampoule with the degassed electrolyte was broken,

Fig. 1

Figure 1: Fig. 1

and electrochemical measurements were performed. The measurements were carried out at a temperature of 25°.

Immediately after contact of the platinum electrode with the electrolyte, the initial potential of platinum was measured; it was equal in one case to 0.215 V, and in another to 0.210 V. This potential is close to the potential of the zero point of unoxidized platinum, measured by other methods ([11]). An analogous establishment of the zero-point potential upon immersion of a degassed electrode in a solution was observed for carbon by A. N. Frumkin, E. A. Ponomarenko, and R. Kh. Burshtein ([12]). After a steady value of the initial potential had been established, the anodic charging curve was recorded at a current density of $3.6 \cdot 10^{-8}$ A/cm^2 of true surface. As the roughness coefficient, the coefficient 2, adopted by various authors ([8]), was used. Figure 1 shows the experimental data obtained in two different experiments, which practically fall on one curve. The charging curve in the region of oxygen adsorption has three clearly expressed potential arrests: I, at 0.6—0.8 V versus n.h.e.; II_1, at 0.95—1.0 V; and III, at 1.4—1.5 V, indicating different forms of adsorbed oxygen on platinum. In individual cases the second arrest was observed at more positive potentials: II_2 at 1.1—1.15 V.

In Fig. 1a, where part of the charging curve is plotted on an enlarged scale,

on the abscissa axis, it is seen that in the so-called double-layer region of potentials (up to 0.6 V) the capacitance value calculated from the slope of the charging curve is equal to 120 µF/cm^2. The high capacitance value observed earlier in other studies on the cathodically reduced platinum surface was explained by the presence of hydrogen in this potential region ([8], [9]). In our case, the presence of hydrogen on the platinum surface, degassed at 900°, is excluded, and the observed large value of the capacitance indicates, apparently, a very early onset of electrochemical adsorption of the first portions of oxygen during anodic polarization of degassed platinum. The same slope of the charging curve could be explained by a high roughness coefficient (12-20 instead of 2), which, however, is very unlikely.

Fig. 1. Anodic charging curve on a degassed Pt electrode in 1 N H_2SO_4, $t = 25°$, $i = 3.6 \cdot 10^{-8}$ A/cm^2; I, II_1, II_2, III are regions of oxygen deposition, respectively, at potentials 0.6-0.8 V; 0.95-1.0 V; 1.1-1.15 V; 1.4-1.5 V

The length of the first plateau (up to 0.8 V) is approximately equal to 0.5 µC/cm^2, which corresponds to $1.3 \cdot 10^{15}$ oxygen atoms per square centimeter of true surface. This value is approximately equal to the number of platinum atoms on the surface, calculated from the lattice parameter 3.2 Å, with 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 sorbed at more positive potentials. This question requires further investigation.

The second plateau is approximately equal in magnitude to the first. The third plateau has a more diffuse character than the first two. The potential of the second plateau depends on the experimental conditions. On a freshly treated surface, a less positive value is obtained (region II_1 in Fig. 1). A more positive value of the potential is obtained after an interruption of the current (see also Fig. 2) or after increasing the temperature (region II_2 in Fig. 1).

The data obtained indicate that, on a thoroughly degassed platinum surface, adsorption of oxygen is possible in at least three forms, differing from one another in bond energy. Within the adsorption regions of each of these forms, the dependence of the potential on the amount of electricity is close to linear, which indicates the logarithmic Frumkin–Temkin adsorption isotherm characteristic of a uniformly heterogeneous surface ([13]). At the same time, as will be seen below, these forms of adsorbed oxygen differ from one another in relative stability.

The first portions of oxygen adsorbed on platinum at the potentials of the second and third plateaus determine the electrode potential only in the presence of an anodic current. After the current is switched off, the potential slowly shifts to potential values of 0.8 V, corresponding to the first plateau (Fig. 2). In order, after an interruption of the current, to again reach the potential of the second and third plateaus, it is necessary once more to expend the same amount of electricity as during the first recording of the charging curve in the same potential region (Fig. 2).

A large hysteresis is observed between the anodic and cathodic charging curves on degassed platinum even at very low current densities.

current densities (Fig. 3). If, during the cathodic sweep, the platinum potential is brought, at the same current density as in the forward sweep, from the potentials of the second anodic process to the initial value of 0.2 V, then only 20% of the adsorbed oxygen is removed from the platinum (Fig. 3, curve 1′). After the cathodic current is switched off, the potential again shifts in the positive direction, and upon repeated reduction the same amount of oxygen is again removed (Fig. 3, curve 1″). This character of irreversibility indicates the gradual penetration of oxygen, after its adsorption, beneath the upper layers of the metal. Under cathodic polarization, the rate of oxygen reduction is limited by its diffusion to the surface. The first cathodic reduction curve has slightly noticeable plateaus at 0.9 and 0.6 V, which correspond to the amount of oxygen that remained on the surface. The remaining part of the oxygen, by the time the cathodic curve is taken on degassed platinum, has time to penetrate into the depth of the platinum. Confirmation that oxygen penetrates beneath the upper layers of the metal is provided by the following data: after the removal from platinum of only 40% of the previously adsorbed oxygen, it is again possible to obtain an anodic charging curve (Fig. 3, 2) identical to that on clean platinum. The rate of oxygen penetration into the depth of degassed platinum depends on

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

the anodic potential of the platinum electrode and on the temperature.

Fig. 2. Potential drop after switching off the anodic current. Continuation of the anodic charging curve after a currentless interruption of 12 h in $1N$ H_2SO_4, $t = 25°$; $i = 3.6 \cdot 10^{-8}$ A/cm^2

By the method of potentiostatic recording of the dependence i—φ, it was established that, at the potentials of the first anodic hold at 25°, oxygen penetration into the depth of platinum occurs at a rate negligible in comparison with the rate at which the charging curve is recorded. However, when the temperature was increased to 85°, the penetration rate increased 10–15 times; at the same time, the amount of deposited oxygen at the potentials of the first anodic process increased substantially and, at low current densities, was equal to 50 monolayers.

During the second and subsequent recordings of the charging curve, after holding the electrode at more positive potentials (within the second hold), at room temperature it was possible to observe additional deposition of oxygen at the potentials of the first anodic process and deposition of oxygen in amounts corresponding to clean platinum at the potentials of the second anodic process (Fig. 3, 1, 2, 3). Apparently, the rate of penetration of subsequent portions of oxygen at room temperature is hindered and is determined by the diffusion coefficient of oxygen in platinum. From anodic charging curve 3, obtained immediately after curve 2,

Fig. 3. Anodic and cathodic charging curves on a degassed electrode in $1N$ H_2SO_4, $t = 25°$, $i = 3.56 \cdot 10^{-8}$ A/cm^2, respectively: $1, 1', 1''$—on clean platinum; 2—on anodically oxidized platinum after removal of 40% of the oxygen; 3—on a completely anodically oxidized platinum surface

It is seen that without preliminary reduction, according to the amount of electricity, the area II_2 is the same as on the preceding curves 1 and 2, whereas the first area, owing to the oxygen remaining on the platinum surface, is considerably smaller; the fact that oxygen is present on the platinum surface on curve 2 and has not had time to penetrate into the depth of the platinum is also indicated by cathodic curve 1 (Fig. 4). This oxygen is removed at more positive potentials, 0.9 and 0.6–0.5 V, corresponding to the two forms of adsorbed oxygen. Repeated cathodic curves (Fig. 4, 2, 3, 4) do not have these areas and characterize the reduction of oxygen arriving at the surface from the depth of the platinum; the rate of reduction in this case is limited by the rate

Figure 4

Figure 4: Figure 4

of diffusion of oxygen to the surface. By repeated cathodic polarization over a very long time it is possible, with difficulty, to remove all electrochemically adsorbed oxygen.

Fig. 4. Cathodic charging curves on a degassed Pt electrode in $1N$ H_2SO_4, $t = 25°$, $i = 3.56 \cdot 10^{-8}$ A/cm^2; 1 –on the completely anodically oxidized platinum surface after anodic charging curve 3; 2, 3, 4 –repeated cathodic curves obtained after shifting the platinum potential in the anodic direction to 0.5-0.6 V

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

We express our deep gratitude to Academician A. N. Frumkin for valuable comments in the performance and discussion of this work.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
30 X 1963

REFERENCES

1. A. N. Frumkin, V. S. Bagotskii et al., *Kinetics of Electrode Processes*, Moscow, 1952.
2. Ts. I. Zalkind, B. V. Ershler, ZhFKh, **25**, 565 (1951).
3. A. D. Obrucheva, ZhFKh, **26**, 1448 (1952).
4. S. E. Wakkad, S. H. Emara, *J. Chem. Soc.*, 1952, No. 2, 461.
5. J. Giner, *Zs. Electrochem.*, **63**, 386 (1959).

6. H. A. Laitinen, C. E. Enk, *J. Electrochem. Soc.*, **107**, 773 (1960).
7. L. Young, *Anodic Oxide Films*, London, 1961, p. 278.
8. S. Schuldiner, R. Roe, *J. Electrochem. Soc.*, **111**, 332 (1963).
9. B. V. Ershler, G. Deborin, A. N. Frumkin, *Izv. AN SSSR, OKhN*, 1937, No. 5, 1069; V. Erschler, *Acta physicochim. U.R.S.S.*, **7**, 327 (1937).
10. R. Kh. Burshtein, N. A. Shumilova, K. Gol' berg, ZhFKh, **20**, 789 (1946); N. A. Shumilova, R. Kh. Burshtein, DAN, **61**, 475 (1948); R. Kh. Burshtein, V. I. Luk' yanycheva, ZhFKh, **28**, 824, 919 (1954).
11. N. A. Balashova, A. N. Frumkin, DAN, **20**, 443 (1938); N. A. Balashova, DAN, **103**, 639 (1955); A. V. Gorodetskaya, B. N. Kabanov, ZhFKh, **7**, 529 (1933); T. N. Voropaeva, B. V. Deryagin, B. N. Kabanov, DAN, **128**, 981 (1959); T. P. Birintseva, B. N. Kabanov, ZhFKh, **37**, No. 11 (1963).
12. A. N. Frumkin, E. A. Ponomarenko, R. Kh. Burshtein, DAN, **149**, 1123 (1963).
13. M. I. Temkin, ZhFKh, **14**, 1153 (1940).
14. T. V. Kalish, R. Kh. Burshtein, DAN, **88**, 863 (1953).
15. A. N. Frumkin, A. I. Shlygin, DAN, **2**, 173 (1934); A. Frumkin, A. Slygin, *Acta phys. Chem. U.R.S.S.*, **3**, 791 (1936); **5**, 819 (1936); V. Ershler, A. Frumkin, *Trans. Farad. Soc.*, **35**, 464 (1939); V. I. Nesterova, A. N. Frumkin, ZhFKh, **26**, 1178 (1952); V. E. Kazarinov, N. A. Balashova, DAN, **139**, 641 (1961).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.