THE IONIZATION OF OXYGEN ON PALLADIUM

Yu. A. Mazitov, K. I. Rozental', and V. I. Veselovskii

L. Ya. Karpov Institute of Physical Chemistry
(Presented by Academician A. N. Frumkin June 11, 1962)
Translated from Doklady Akademii Nauk SSSR, Vol. 148, No. 1,
pp. 152-155, January, 1963
Original article submitted May 10, 1962

It has been shown that the kinetics of various electrode processes involving oxygen are definitely determined by the properties of chemisorptional surface oxygen compounds [1-8]. The present work involved a polarographic determination of the activities of electrodes with respect to the ionization of oxygen in which the properties of the surface oxygen compounds were studied through charging curves. Prior to experiment, these electrodes were cleaned mechanically and rinsed with hot alkali and water.

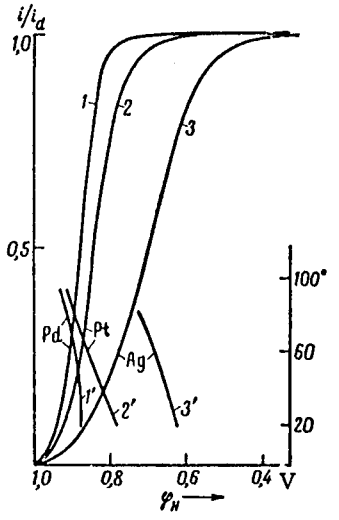

Fig. 1. 1, 2, 3) Polarographic ionization curves at 80°; 1', 2', 3') temperature dependence of the potential at $i = i_d/2$ for Pd, Pt, and Ag in 6 N KOH (wire surface, 0.1 cm^2). Electrolyte stirred magnetically at 1000 rpm.

Potentials were measured with respect to an oxidized mercury electrode held in the working solution at the working temperature. For ease of treatment, the potentials shown in the figures are values measured with respect to the hydrogen electrode. Changes in the solubility and the diffusion coefficient of oxygen, and the depth of the Prandtl layer (which, at atmospheric pressure, is a maximum at 70-80°) cause the polarographic current of oxygen ionization to vary with the temperature. Thus the activity of the working electrode with respect to the oxygen ionization at fixed potential will be characterized at each temperature by the quantity i/i_d, at least to the extent that this ratio is fixed by the rate of the electrochemical reaction itself. This condition is fulfilled when $i \ll i_d$. Figure 1 shows i/id versusφ curves for Pd, Pt, and Ag in 6 N KOH at 80° which were developed under continuous introduction of oxygen at atmospheric pressure (Curves 1, 2, 3) and other curves covering the temperature dependence of the potential at $i = i_d/2$ (Curves 1', 2', 3'). Under these conditions, the value of i_d was 1.1-1.2 ma/cm^2. A study of these curves shows the overvoltage for oxygen ionization to be less on Pd than on either Pt or Ag. Thus the potential for reaction velocity $i = i_d/2$ is at each temperature some 0.2 V more anodic for Pd than for Ag (Curves 1 and 3). Only at the higher temperatures does the activity of Pt approach that of Pd (Curve 2). The hysteresis of the forward and reverse polarographic curves is considerably less on Pd (where it disappears almost completely at high temperatures) than on either Pt or Ag. These facts indicate that the ionization of oxygen is more nearly reversible on Pd than on Ag and Pt.

Study shows that the factors responsible for increasing or diminishing the activity of the electrode material with respect to the oxygen ionization are directly related to the properties of the oxygen which is bound to the electrode surface in one form or another. The stability of the surface oxides can be estimated from their durability under variation of temperature, it being assumed, in a first approximation, that the relation involved here is the same both for surface oxides reduced in the oxygen ionization and for oxides formed electrochemically.

Charging curves developed for Pd, Pt, and Ag electrodes (1 cm^2 apparent surface area) in concentrated alkali at 20, 40, 60, 80, and 95° showed the temperature dependence of the potential required for reduction of the surface oxides to vary from metal to metal. All cathodic charging curves on Pd and Pt were developed at $1 \cdot 10^{-4}$ amp/cm^2

after a 10-minute anodic polarization at the same current density with evolution of oxygen. The fact that there was a certain change in the current yield of oxides with changing temperature was of no significance for our conclusions. The cell was constructed so as to give the most complete elimination of convectional diffusion and nitrogen was passed through the electrolyte beforehand in order to insure that the oxygen concentration would be at a minimum during the experiment. The cathodic current density was chosen so that it would be unnecessary to consider the fact that traces of oxygen might diffuse to the electrode and there ionize at the same time that the electrochemically formed oxides were undergoing reduction.

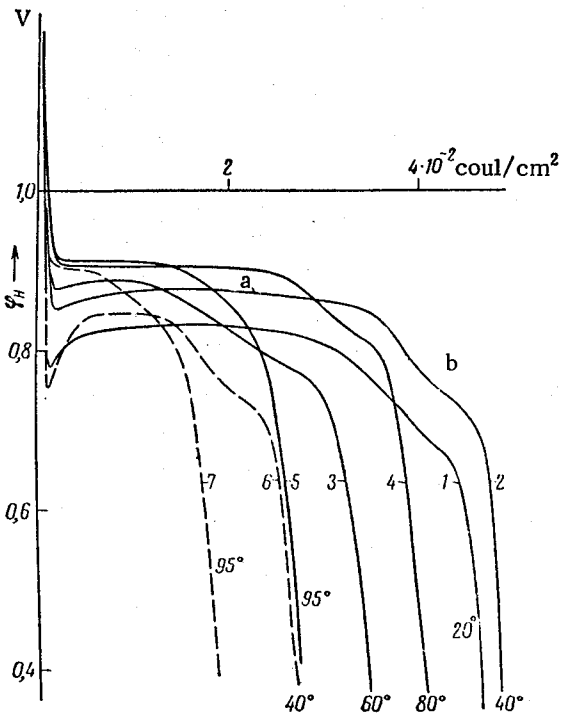

Fig. 2. Cathodic charging curves for a Pd electrode at various temperatures, developed after completion of anodic polarization: 1-5) Developed immediately; 6) after 2 hours; 7) after 5 minutes.

Figure 2 presents a series of curves developed on a Pd electrode which had been cleaned with powdered glass and degreased in a portion of the electrolyte. These curves show two characteristic plateaus, a and b, which correspond to the reduction of two different surface oxides, the oxide reduced at the higher cathodic potential being present in considerably smaller amount. It should be noted that the properties of the surface can be altered by suitable treatment, for example by heating for several hours in the oxidizing flame of a burner (Fig. 3). In this last case, it is the compound of higher stability which is formed in a larger amount by anodic polarization. Increase in the current density for anodic polarization causes the potential for reduction of the oxides formed on either type of Pd surface to undergo a considerable displacement toward more highly anodic values. Thus an increase in the anodic current density from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ amp/cm^2 displaces the potential for reduction of the surface oxides in 1.8 N KOH at 20° by 0.1 V. It is clear that oxides which will be reduced with diminished overvoltage can be obtained by using a sufficiently high anodic current for oxide formation. The existence of an overvoltage for the reduction of the oxides on Pd has also been noted in [10].

An increase in the alkali concentration displaces the reduction potential in the direction of more highly anodic values. Here it can prove to be that the displacement of the two plateau potentials will be different because of differences in the effect of the alkali concentration on formation of the two oxides.

It is noteworthy that there is a marked displacement of the potential for the reduction of the Pd surface oxides with rising temperature; this clearly accounts for the high temperature coefficient of the activity of the electrode with respect to the oxygen ionization. The temperature coefficient of the potential for reduction of the oxides electrochemically formed on Ag and Pt is lower and the temperature coefficient for the activity with respect to the oxygen ionization is therefore less on these metals than on Pd. (In the case of Pt, one need only take account of the marked effect of temperature on the conditions of oxide formation; increase in temperature has the same effect as a diminution of the current density and the oxide produced is therefore the one which undergoes reduction at the more cathodic potential.)

Estimates of the durability of the oxide and its temperature dependence can be obtained from the rate of oxide breakup as measured by the decrease in the plateau length on cathodic charging curves developed at various times after completion of anodic polarization. The dotted curves of Figs. 2 and 3 were obtained a certain time after stopping polarization. A study of these curves shows a displacement of the reduction potential to more cathodic values and an increase in oxide stability with the passage of time with an accompanying rapid breakup of the oxide. At 40°, for example, the amount of surface oxides fell to one-half of the initial value two hours after breaking off anodic polarization (Curve 6, Fig. 2). This same reduction in the amount of oxides occurred in 5 minutes at 95° (Curve 7, Fig. 2), the more stable compound breaking up at lower rate (Curve 6, Fig. 3). Our results, a part of which are shown in Figs. 2 and 3, indicate that the displacement of the oxide reduction potential toward more highly cathodic values per unit time (a quantity characterizing the rate of increase of oxide stability) increases insignificantly with rising temperature, both for Pd and for Pt, while the rate of oxide breakup on Pd is approximately twice as high as on Pt.

At 95°, only one-quarter of the oxide on Pt breaks up in 5 minutes as compared with one-half on Pd. The fact that the charging curves reflect the character of the adsorbed oxygen films and the increase in the stability of these films with the passage of time was first pointed out by A. N. Frumkin [11]. The results obtained with platinum have recently been explained in terms of changes in the state of oxide films [12, 13].

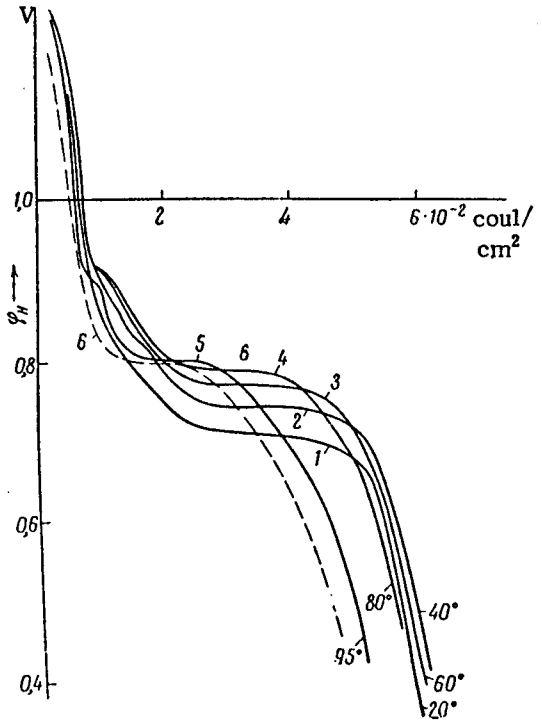

Fig. 3. Cathodic charging curves at various temperatures for a previously heated Pd electrode in 1.8 N KOH, developed after completion of anodic polarization: 1-5) Developed immediately; 6) after 5 minutes.

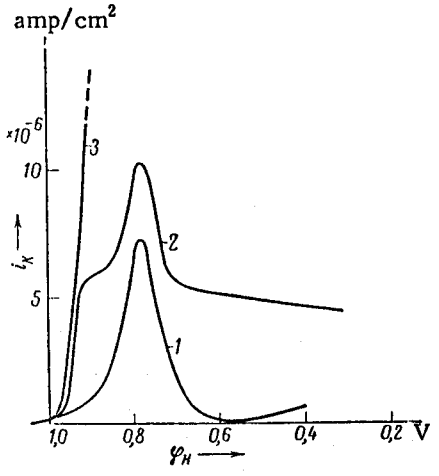

Fig. 4. Polarographic curves developed on a Pd electrode after anodic polarization in a 6N KOH solution which was: 1) Free of oxygen; 2) saturated with oxygen, but not agitated; 3) saturated with oxygen and agitated.

Figure 4 shows polarographic curves obtained after brief anodic polarization in solutions free of oxygen (differential cathodic charging curves) (1) and curves obtained in a solution saturated with oxygen (2). The maximum on Curve 1 clearly corresponds to the potential for reduction of the adsorbed atomic oxygen resulting from anodic polarization. The potential of this maximum is displaced toward more highly anodic values with increasing temperature while the height of the maximum diminishes because of an increase in the rate of oxide breakup. Curve 2 was developed in an atmosphere of oxygen and shows a plateau at a potential which is more anodic than the potential of the maximum on Curve 1; this potential characterizes reduction of oxygen which is weakly adsorbed on the surface, possibly in molecular form.

It should be considered that the Pd oxides have quite high electrical conductivity, possibly of the electron type, and that charge transfer through the film can occur without alteration of the film depth, ionization of oxygen proceeding readily on a surface which has been previously covered with an electrolytic oxide film.

We have, in the present work, attempted to show that there is a close relation between the ionization of oxygen and the properties of the surface oxides.

LITERATURE CITED

1. V. I. Veselovskii, Proceedings, Fourth Conference on Electrochemistry [in Russian], p. 24 (1959).
2. A. A. Rakov, V. I. Veselovskii et al., ZhFKh, 32, 12, 2702 (1958); ibid, 33, 549 (1959); ibid, 35, 2296 (1961).
3. A. N. Frumkin, Intern. Committee Electrochem. Thermodyn. and Kinetics (Proc. 9th Meeting, Paris, 1957) London, 1959, p. 396.
4. L. M. Volchkova, L. G. Antonova, and A. I. Krasil'shchikov, ZhFKh, 23, 441. 714 (1949); ibid, 27, 512 (1953).
5. M. A. Gerovich, R. I. Kaganovich et al., DAN, 137, 634 (1961).
6. K. I. Rozental' and V. I. Veselovskii, ZhFKh, 35, 2670 (1961)
7. A. N. Frumkin and V. V. Sobol', DAN, 141, 917 (1961).
8. V. A. Lunenok-Burmakina, A. P. Potenskaya, and A. I. Brodskii, DAN, 137, 1402 (1961).
9. A. Hickling and G. G. Vrjosek, Trans. Farad. Soc., 57, 123 (1961).
10. F. G. Will and C. A. Knorr, Zs. Electrochem., 64, 270 (1960).
11. A. N. Frumkin, ZhFKh, 14, 1200 (1940).
12. Ts. Zalkind and B. N. Ershler, ZhFKh, 25, 555 (1951); V. I. Nesterova and A. N. Frumkin, ZhFKh, 26, 1178 (1952); A.D. Obrucheva, ZhFKh, 26, 1448 (1952).
13. H.A. Laitinen and C.G. Enker, J. Electrochem. Soc., 107, 773 (1960).