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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE QUESTION OF THE IONIZATION OF OXYGEN ON PALLADIUM

(Presented by Academician A. N. Frumkin, June 11, 1962)

At present it is considered established that the kinetic regularities of electrode processes occurring with the participation of oxygen are, in a number of cases, determined by the properties of surface oxygen compounds of a chemisorption character ([1]-[8]). In the present work the activity of electrodes with respect to the ionization of oxygen was determined by the polarographic method, and the character of the surface oxygen compounds was studied by recording discharge curves. Before the experiments the electrodes were mechanically cleaned and washed with hot alkali and water.

Fig. 1. 1, 2, 3 –polarographic ionization curves at 80°; $1'$, $2'$, $3'$ –dependence of the potential on temperature at $i = i_d/2$, in $6N$ KOH on Pd, Pt, and Ag electrodes (wires with a surface area of 0.1 cm^2). The electrolyte was stirred with a magnetic stirrer at a speed of 1000 rpm.

The potential was measured relative to a mercury oxide electrode in the same solution and at the same temperature at which the experiment was carried out. For convenience in considering the results obtained, the figures give potentials relative to the hydrogen electrode. The polarographic current of oxygen ionization at different temperatures differs because of changes in solubility, in the diffusion coefficient of oxygen, and in the thickness of the Prandtl layer (at atmospheric pressure it has a maximum at 70–80°), and therefore the activity of the electrodes studied with respect to oxygen ionization at a given potential and different temperatures will be characterized by the value i/i_d (of course, only to the extent that the value i/i_d is governed by the rate of the electrochemical reaction proper, which is the case under the condition $i \ll i_d$). Fig. 1 presents $i/i_d - \varphi$ curves recorded in $6N$ KOH at 80° with continuous passage of oxygen at atmospheric pressure on Pd, Pt, and Ag (curves 1, 2, 3), and the dependence of the potential on temperature at $i = i_d/2$ (curves $1'$, $2'$, $3'$). Under the indicated conditions i_d was equal to 1.1-1.2 mA/cm^2. It is seen from examination of the curves that oxygen ionization on Pd proceeds with a smaller overvoltage

Fig. 2. Cathodic charging curves recorded on a Pd electrode in 1.8 N KOH at various temperatures after termination of anodic polarization: 1—5—immediately, 6—after 2 hours, 7—after 5 min.

Figure 2: Fig. 2. Cathodic charging curves recorded on a Pd electrode in 1.8 N KOH at various temperatures after termination of anodic polarization: 1—5—immediately, 6—after 2 hours, 7—after 5 min.

than on Pt and Ag. Thus, the process proceeds at a rate $i = i_d/2$ on Pd at a potential approximately 0.2 V more anodic than on Ag over the entire temperature interval studied (curves 1 and 3). Pt approaches Pd in activity only at high temperatures (curve 2). The magnitude of the hysteresis of the forward and reverse runs of the polarographic curves on Pd is considerably smaller (at high temperature it almost disappears) than on Pt and Ag, which also indicates a smaller degree of irreversibility of the oxygen ionization process on Pd than on Ag and Pt.

When considering the reasons for the increased or, conversely, decreased activity of an electrode material with respect to the process of oxygen ionization, it proved possible to place them in direct dependence on the properties of the oxygen bound on the surface in one form or another. The properties of the···

surface oxides; their stability can be estimated from the change in their strength with temperature, and it may be assumed that the character of the temperature dependence of the stability of surface oxides—through the reduction of which oxygen ionization occurs—and of oxides formed electrochemically, in a first approximation, does not depend on the type of oxide.

By the method of recording charging curves on Pd-, Pt-, and Ag-electrodes (1 cm^2 of visible surface) in concentrated alkali at temperatures of 20, 40, 60, 80, and 95° it was shown that the reduction potential of the surface oxides on these metals changes differently with temperature. Cathodic charging curves on Pd- and Pt-electrodes at all temperatures were recorded with a current of $1 \cdot 10^{-4}$ A/cm^2, after anodic polarization with the same current for 10 min; oxygen evolution was observed at the electrode. A certain change in the current yield of oxides with changing temperature is of no importance for our conclusions. The design of the cell provided for the fullest possible elimination of convective diffusion; before the experiment the electrolyte was purged with nitrogen so that the oxygen concentration during the experiments would be minimal. The chosen density of cathodic current made it possible to disregard the ionization of traces of oxygen diffusing to the electrode, which occurred simultaneously with the reduction of electrochemically formed oxides.

Fig. 2. Cathodic charging curves recorded on a Pd electrode in 1.8 *N* KOH at various temperatures after termination of anodic polarization: 1—5—immediately, 6—after 2 hours, 7—after 5 min.

Figure 2 presents a series of curves recorded on a Pd-electrode cleaned with glass

Fig. 3. Cathodic charging curves taken on an annealed Pd electrode in 1.8 N KOH at different temperatures after cessation of anodic polarization: 1—5, immediately; 6, after 5 min.

Figure 3: Fig. 3. Cathodic charging curves taken on an annealed Pd electrode in 1.8 N KOH at different temperatures after cessation of anodic polarization: 1—5, immediately; 6, after 5 min.

powder and degreased in a portion of electrolyte. The charging curves have two characteristic arrests, *a* and *b*, corresponding to the reduction of two different surface oxides; the amount of oxide reduced at the more cathodic potential is considerably smaller. It should be noted that, by treating the electrode appropriately—for example, by heating it for several hours in the oxidizing flame of a burner—one can obtain a surface with different properties (Fig. 3). In this case, during anodic polarization, more of the stronger oxide is formed than of the other. With increasing current density of the anodic polarization, the reduction potential of the oxides formed on both types of Pd surface shifts appreciably toward more anodic potentials. For example, when the anodic current density is increased from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ A/cm^2, the reduction potential of the surface oxides at 20° in 1.8 *N* KOH shifts by 0.1 V. Apparently, by using a sufficiently high anodic current density for oxide formation, one can obtain oxides that are reduced with a considerably smaller overvoltage (9). The overvoltage for the reduction of oxides on Pd was also noted in work (10).

Increasing the alkali concentration shifts the reduction potential toward more anodic potentials, and the magnitudes of the shifts of the two delays may differ, which can be explained by the different effect of changes in alkali concentration on the formation of one or the other type of oxide.

Attention is drawn to the large magnitude of the shift in the reduction potential of surface oxides on Pd with change in temperature; the consequence of this, apparently, is the large value of the temperature coefficient of the electrode activity with respect to oxygen ionization.

Fig. 3. Cathodic charging curves taken on an annealed Pd electrode in 1.8 N KOH at different temperatures after cessation of anodic polarization: **1—5** —immediately, **6** —after 5 min.

On Ag and Pt the temperature dependence of the reduction potential of electrochemically formed oxides is smaller; correspondingly, the temperature coefficient of the increase in activity with respect to oxygen ionization on these metals is lower than on Pd (for Pt it is only necessary to take into account the strongly manifested, in this case, influence of the temperature change in the conditions of oxide formation; an increase in the temperature of oxide formation acts analogously to a decrease in the anodic-current density, i.e., an oxide is then formed which is reduced at a more cathodic potential).

The strength of the oxides and its temperature dependence may conveniently be judged from the rate of oxide decomposition, to which there corresponds a decrease in the length of the delays on cathodic charging curves taken some time after the cessation of anodic polarization. The dashed curves in Figs. 2 and 3 were obtained after an interruption. From their consideration it is evident that, along with some strengthening of the oxides with time, to which a more cathodic reduction potential corresponds, rapid decomposition of the oxides takes place. For example, at 40° the amount of oxides on the surface two hours after the anodic polarization is switched off decreases by half (curve 6 in Fig. 2). At 95° the same decrease in the amount of oxides occurs in 5 min (curve 7 in Fig. 2); the rate of decomposition of the more stable oxide is lower (curve 6 in Fig. 3). From the results obtained by us and partly presented in Figs. 2 and 3 it may be concluded that the magnitude of the shift of the oxide-reduction potential toward more cathodic potentials, referred to unit time (characterizing the rate of strengthening of the oxides), on Pd, as also on Pt, changes only slightly with increasing temperature (in the temperature range investigated), whereas the rate of oxide decomposition on Pd is approximately twice as great as on Pt. At 95° on Pt, over 5 min, only one quarter of the oxides present is destroyed, instead of one half on Pd. Such an interpretation of the charging curves, reflecting the character of the adsorbed oxygen layers and their strengthening with time, was first given by A. N. Frumkin ([11]). In subsequent works ([12], [13]), the results obtained on platinum were explained by a change in the state of the oxide layers.

Figure 4 presents polarographic curves recorded in a solution not containing oxygen, after brief anodic polarization (dif-

differential cathodic charging curve (1) and in a solution saturated with oxygen (2). The maximum on curve 1 apparently corresponds to the potential of reduction of atomically adsorbed oxygen, which appears under anodic polarization. As the temperature is raised, the potential of the maximum shifts toward more anodic potentials; the height of the maximum decreases with increasing temperature because of an increase in the rate of decomposition of the oxides. The retardation on curve 2, observed in an oxygen atmosphere at a potential more anodic than the potential of the maximum on curve 1, apparently characterizes the reduction of oxygen weakly adsorbed on the surface (possibly in molecular form).

With respect to the oxides on Pd, it should evidently be considered that their electrical conductivity is very high (probably of the electronic type), and that charge transfer through the oxide layer can occur without a change in the thickness of the oxide film. This follows from the fact that ionization of oxygen proceeds readily on a surface previously covered electrochemically with an oxide film.

Fig. 4. Polarographic curves recorded on a Pd electrode after anodic polarization in a 6N KOH solution: 1 —containing no oxygen, 2 —saturated with oxygen (without stirring), 3 —the same with stirring.

Thus, in the present work we have attempted to show the close connection between the regularities of oxygen ionization and the properties of surface oxides.

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CITED LITERATURE

1. V. I. Veselovskii, *Proceedings of the 4th Conference on Electrochemistry*, 1959, p. 24.
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. Vochkova, L. G. Antonova, 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' , V. I. Veselovskii, ZhFKh, **35**, 2670 (1961).
7. A. N. Frumkin, V. V. Sobol' , DAN, **141**, 917 (1961).
8. V. A. Lunenok-Burmakina, A. P. Potemskaya, A. I. Brodskii, DAN, **137**, 1402 (1961).
9. A. Hickling, G. Q. Vrjosek, *Trans. Farad. Soc.*, **57**, 123 (1961).
10. F. G. Will, C. A. Knorr, *Zs. Electrochem.*, **64**, 270 (1960).
11. A. N. Frumkin, ZhFKh, **14**, 1200 (1940).
12. Ts. Zalkind, N. E. Ershler, ZhFKh, **25**, 555 (1951); V. I. Nesterova, A. N. Frumkin, ZhFKh, **26**, 1178 (1952); A. D. Obrucheva, ZhFKh, **26**, 1448 (1952).
13. H. A. Laitinen, C. G. Enke, *J. Electrochem. Soc.*, **107**, 773 (1960).

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