CATHODIC IONIZATION OF OXYGEN ON A CONTINUOUSLY RENEWED PALLADIUM SURFACE

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The studies of [1] have shown that a continual surface renewal will considerably reduce the overvoltage for cathodic separation of hydrogen on metals such as Fe, Ni, and Pd which are good hydrogen adsorbers, that is to say, on metals for which the hydrogen overvoltage is determined in comparable degree by delayed hydrogen ion discharge and slow separation of adsorbed hydrogen atoms [2-4]. Continual surface renewal has no essential effect on the hydrogen overvoltage on metals such as Pb and Sn which adsorb hydrogen weakly, that is to say, on metals for which the overvoltage is determined by delayed hydrogen ion discharge alone [2,3].

Since most instances of natural corrosion involve oxygen depolarization, theoretical and practical interest must certainly attach to an understanding of the effect of continual surface renewal of the metal on cathodic hydrogen ion discharge and cathodic reactions involving oxygen depolarization.

The effect of a mechanical surface renewal on the ionization of oxygen on palladium has been studied in the present work. Palladium was chosen here because it is a noble metal and appreciable distortion of the cathodic reactions through spontaneous dissolution is thus avoided.

The basic principle of the method is that of bringing about a continual metallic surface renewal in solution during simultaneous cathodic polarization of the metal from an external source. Renewal of the surface of the sam ple was carried out with the aid of a disk of corundum with a 53-63 μ grain diameter (No. 240 granulation). The rate of rotation of this disk could be varied from 250 to 4500 rev/min, thus altering the rate of linear movement of the atom over the electrode surface (with reference to the center of the sample) from 34.1 to 614 cm/sec. In addition to its rotatory motion, the corundum disk was also made to approach the sample surface at a fixed rate of 0.1 μ/sec. A detailed description of the apparatus has already been given in [1,6].

Disk-formed samples, 10 mm in diameter and $\approx$5 mm thick, were prepared from a 99.98% pure palladium. The experimental electrolyte was a 1 N solution of cp Na_2SO_4. 0.005 M Na_2CO_3 and 0.005 M $NaHCO_3$ were added to this solution in order to buffer it. The solution then had a pH of 9.2. The experiments were carried out at a constant temperature fo 20°C, with oxygen passing continually through the solution. The potentials indicated on each of the figures of this paper are values measured with respect to the normal hydrogen electrode.

Figure 1 shows cathodic polarization curves for palladium, without surface renewal and with surface renewal at various rates of rotation of the disk. Study of these curves indicates that continuous surface renewal reduces the oxygen ionization overvoltage on palladium as the rate of renewal is raised from zero to 1000 rev/min. Increasing the rate of renewal beyond 1000 rev/min had no effect on the overvoltage. There was no essential difference in the slopes of the linear portions of polarization curves obtained with electrodes which were being subjected to surface renewal and with electrodes which were not. This slope is represented by the coefficient b in the Tafel equation; its value proved to be about 0.06, just as in the case of platinum [6,8,9], thus approximating that of RT/nF for n = 2 and a temperature of 293°K, namely, 0.058. On this basis, the number of electrons involved in the controlling step in oxygen ionization on the electrode must be assumed equal to two. It is characteristic that continual renewal of the palladium surface considerably widened the interval of current densities over which the logarithm of the density was a linear function of the metal potential. There was, at the same time, a considerable increase in the limiting value of the diffusional oxygen current. Thus altering the rate of rotation of the corundum disk from zero to 4500 rev/min increased the limiting diffusional current for the oxygen reduction from 0.61 to 16 mA/cm^2.

It might be supposed that the increase in the limiting diffusional current in oxygen and the reduction in the oxygen ionization potential would be partially due to surface renewal and partially due to the intensive agitation

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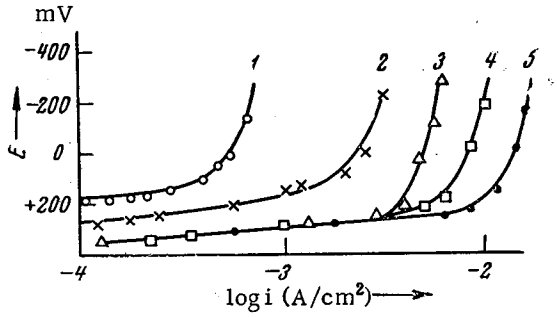

Fig. 1. Cathodic polarization curves for Pd without surface renewal (1), and with surface renewal at the following rates of rotation of the corundum disk: 500 (2), 1000 (3), 2000 (4), and 4500 (5) rev/min.

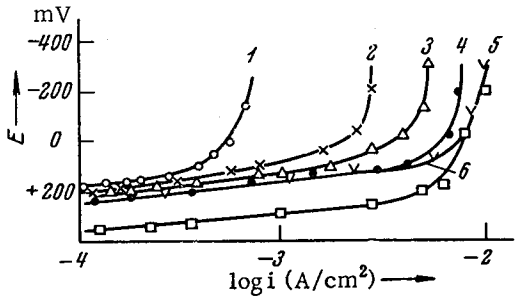

Fig. 2. Cathodic polarization curves for Pd without surface renewal or electrolyte agitation (1), with electrolyte agitation through rotation of the corrundum disk at a fixed rate of 2000 rev/min, and at the following distances from the electrode surface: 10 (2), 1 (3), 0.2 (4), and 0.07 (6) mm, (5) the same, but with surface renewal.

which always accompanies renewal. This supposition was checked in experiments on the effect of electrolyte agitation without surface renewal, allowing the corundum disk to merely rotate at a certain distance from the surface of the electrode. The results of these experiments are shown in Fig. 2. The curves of this figure indicate that the limiting diffusional current continually increased as one passed from bulk electrolyte agitation through disk rotation at 10 mm from the electrode to agitation through rotation in the immediate neighborhood of the electrode surface. On the other hand, the limiting diffusional current under surface renewal (curve 6 of Fig. 2) was only slightly different from the current observed under electrolyte agitation from rotation of the corundum disk at closest approach of approximately 70 μ to the electrode surface (curve 5 of Fig. 2). Thus the data would indicate that surface renewal, in itself, has no appreciable effect on the limiting current in oxygen, the marked increase in the current being solely due to the intensive agitation of the electrolyte which accompanies renewal.

The overvoltage for oxygen ionization is only slightly dependent on the agitation of the electrolyte, but is reduced markedly by mechanical renewal of the surface. Reasoning in analogy with the hydrogen overvoltage [1], one would assume that continual renewal of the palladium surface would reduce the impedance in those stages of the oxygen ionization overvoltage which depend on adsorption processes on the electrode surface. Thus it has been postulated in [6,7] that the oxygen overvoltage on Pd is closely dependent on the presence of surface oxides and sulfate anions adsorbed from solution, the anion adsorption effect actually being greater than that of surface oxidation in the interval of potentials from 0.3 to 0.5 V. Our experiments over this interval indicate that surface renewal has no appreciable effect on either the stationary potential on Pd or on the limiting diffusional current in oxygen. This suggests that the palladium surface is free of oxide films under these conditions, the principal effect coming from anions (principally SO_4^{2-}) which are adsorbed on the electrode surface from the solution thereby retarding the cathodic ionization of oxygen [6-8]. The surface adsorbed anions would be immediately removed by the renewal process under our experimental conditions, thereby eliminating, either in whole or in part, the retarding effect of these ions on the cathodic ionization of the oxygen. It can be supposed that the removal of the adsorbed ions from the palladium surface was more or less complete when the rate of rotation of the corundum disk was greater than 1000 rev/min, since increasing this rate to 4500 rev/min did not displace the linear section of the cathodic curve for the oxygen reduction in the positive direction (Fig. 1).

On the basis of the data of [1] one could conclude that mechanical renewal of the surface would have no appreciable effect on the rate of the electrochemical reaction of electron transfer. It could then be assumed that the oxygen ionization overvoltage on palladium would be determined by electron transfer alone at rates of surface renewal in excess of 1000 rev/min, while the reduction of the overvoltage (the difference between the linear segments of the curve developed with and without surface renewal at disk rates in excess of 1000 rev/sec) would, to a certain degree, be determined by the elimination of the retarding effect from anion adsorption from solution. Thus at a current density of 0.2 mA/cm^2, the oxygen ionization overvoltage for renewed and unrenewed electrodes was 0.34 and 0.52 V, respectively (the potential of the reversible oxygen electrode in the solution of pH 9.2 being taken as 0.7 V). The 0.18 V reduction in the overvoltage resulting from surface renewal is approximately 35% of the total value; in conformity with the above remarks this is to be assigned to the adsorptional retardation of the cathodic ionization of the oxygen. On this basis, retarded oxygen ionization resulting directly from delayed charge transfer the accounts for 65% of the total oxygen overvoltage.

Thus continual renewal of the metal surface in solution considerably facilitates the cathodic ionization of oxygen, both in itself (reduction in the oxygen ionization overvoltage) and by the intensive agitation of the electrolyte (marked increase in the limiting diffusional current for the oxygen reduction).

It can be assumed that facilitation of the cathodic ionization resulting from surface renewal can be one of the factors responsible for the enhanced corrosion of metals under oxygen depolarization.

LITERATURE CITED

1. N. D. Tomashov, N. M. Strukov, and L. P. Vershinina, DAN, 171, No. 5, 1134 (1966).
2. P. D. Lukovtsev and S. D. Levina, ZhFKh, 29, No. 6, 1508 (1955).
3. P. D. Lukovtsev, ZhFKh, 27, No. 8, 1243 (1953).
4. A. N. Frumkin and N. A. Aladzhalova, ZhFKh, 18, No. 12, 493 (1944).
5. N. D. Tomashov, G. P. Chernova, et al., Zav. lab., 24, No. 3, 299 (1958).
6. V. S. Bagotskii, L. N. Nekrasov, and N. A. Shumilova, UKh, 34, No. 10, 1607 (1965).
7. V. V. Sobol', E. I. Khrushcheva, and V. A. Dagaeva, Élektrokhimiya, 1, No. 11, 1332 (1965).
8. L. Myuller and L. N. Nekrasov, DAN, 154, No. 2, 437 (1964).
9. A. I. Krasil'shchikov and V. A. Andreeva, ZhFKh, 27, No. 3, 389 (1953).