G. V. Zhutaeva, N. A. Shumilova, M. R. Tarasevich

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G. V. Zhutaeva, N. A. Shumilova, M. R. Tarasevich

Study of the Ionization of Oxygen on Silver

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Recently, for the study of the kinetics of electrode processes, the method of the rotating disk electrode with a ring, and its combination with the method of triangular voltage pulses, developed by A. N. Frumkin and co-workers [1–3], has been successfully applied. The application of these methods to the study of the process of oxygen ionization on platinum made it possible to obtain a number of interesting results concerning the mechanism of this process [4], the influence on it of the state of the electrode surface, and also to investigate certain phenomena associated with the reduction of surface oxides of platinum [3]. It was of interest to use the disk electrode with a ring to study the processes of adsorption and ionization of oxygen on silver.

The electrode under investigation, in which the disk material was silver and the ring was made of platinum, had the following dimensions: $r_1 = 2.5$ mm, $r_2 = 2.7$ mm, $r_3 = 3.61$ mm, where r_1 is the radius of the disk electrode, and r_2 and r_3 are the inner and outer radii of the ring, respectively. The numerical coefficient N in the equation of Yu. B. Ivanov and V. G. Levich [1], for these geometrical parameters of the electrode, was 0.44. Before an experiment the electrode was polished with fine-grained quartz powder, degreased with hot KOH solution, and then the silver disk was cathodically polarized in the solution under study at a current of 1.5 mA/cm^2 for 2 hours. After the described treatment of the electrode, immediately before the recording of each curve, the platinum ring was activated by repeated anodic-cathodic polarization, ending with holding the electrode for one minute at a potential $\varphi = -0.2$ V. Platinization of the ring electrode was impossible for methodological reasons, but the above-described procedure for treating the ring made it possible to preserve the diffusion character of the currents of hydrogen peroxide oxidation. All experiments were carried out at a temperature of 25° in 0.1 N KOH solutions, which were purified by electrolysis and adsorption on platinized platinum meshes in an atmosphere of hydrogen and oxygen. The potential values are given relative to a hydrogen electrode in the same solution.

The study of oxygen ionization on silver was carried out at a pressure equal to 1 atm and at a rate of application to the disk of periodic triangular voltage pulses of 10 mV/sec. Potentiostatic i, ψ-curves were recorded with a two-coordinate self-recording instrument PDS-021. Figure 1 shows the polarization curve of oxygen ionization at an electrode rotation speed of 600 rpm. As can be seen,

Figure 1

Figure 1: Figure 1

even at this speed the curve lacks a well-defined limiting-current plateau, and in the potential interval $0.4 \div (-0.1)$ V an approximately linear increase of current with potential is observed. Calculation of the number of electrons participating in the reaction shows that this value in the indicated potential interval increases from 3 to 3.9–4. With an increase in the electrode rotation speed, the character of the curve does not substantially change–

is. The dependence of the current on the disk at a potential of 0.3 V on the rate of rotation of the electrode is presented in Fig. 1, curve 4. As can be seen, over the entire interval of electrode rotation rates investigated by us (600-5000 rpm), a deviation is observed of the experimentally measured current values ($I^{\mathrm{d}}_{\mathrm{expt}}$) from the diffusion-current values for the four-electron process ($I^{\mathrm{d}}_{\mathrm{theor}}$). In this case the deviations increase with increasing electrode rotation rate.

Fig. 1. 1–Polarization curve of oxygen reduction on a silver disk at an electrode rotation rate of 600 rpm; **2**–currents corrected for the amount of unreacted hydrogen peroxide; **3, 4**–dependence of the currents on the disk electrode on $\sqrt{m}$: **3**–for limiting diffusion currents; **4**–for currents at $\varphi = 0.3$ V; open circles –values of corrected currents.

In studying the ionization of oxygen on silver with the aid of a disk electrode with a ring, over the entire potential interval investigated by us, 1.0-(−0.2) V, an anodic current was recorded on the ring. This made it possible to conclude that, during the reduction of oxygen on silver, an intermediate product is formed which can be carried off into the bulk of the solution. Comparison of the polarograms of this substance on the ring and of the anodic polarization curves of H_2O_2 on platinum made it possible to identify the intermediate product with hydrogen peroxide. Using the values of the currents recorded on the ring, one can correct the experimental values of the currents on the disk at a potential of 0.3 V up to $I^{\mathrm{d}}_{\mathrm{theor}}$ over the entire interval of rotation rates (Fig. 1). This indicates that the observed deviations of $I^{\mathrm{d}}_{\mathrm{expt}}$ from $I^{\mathrm{d}}_{\mathrm{theor}}$ are associated with the sluggishness of the reduction reaction of hydrogen peroxide formed in the process of ionization of molecular oxygen on silver.

Figure 2 gives the dependence of the currents on the ring electrode, as well as the percentage ratio of the amount of hydrogen peroxide not reacted on the disk to $I^{\mathrm{d}}_{\mathrm{expt}}$, on the disk potential. As can be seen from curve 2, at a potential of 0.85 V the amount of H_2O_2 leaving the disk is equal to $I^{\mathrm{d}}_{\mathrm{expt}}$. Consequently, under these conditions the ionization of molecular oxygen proceeds only as far as hydrogen peroxide, which corresponds to the number of electrons participating in the reaction being equal to two. When the potential is shifted in the cathodic direction, first a sharp and then a gradual decrease is observed in the amount of hydrogen peroxide being carried away. The data obtained confirm the change

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

in the number of electrons participating in the reaction, which was shown by us earlier by calculation.

Fig. 2. Dependence of the current on the ring electrode (**1**) and of the ratio of H_2O_2 unreacted on the disk to $I^{\mathrm{d}}_{\mathrm{expt}}$ (**2**) on the disk potential at $m = 600$ rpm.

When measuring the polarization curves of oxygen ionization, hysteresis is observed between the cathodic and anodic scans, namely, the reverse anodic scan of the curves is shifted into the region of higher current densities (Fig. 3). Investigation of this phenomenon with the aid of the ring electrode showed that the increase in the current on the disk during anodic recording of the curve corresponds to a decrease in the amount of hydrogen peroxide recorded on the ring. It could be assumed that the observed acceleration

ionization of oxygen is associated with the reduction of the electrode surface during the cathodic branch of the curve. Indeed, when the amplitude of the voltage pulses from the anodic side is decreased, which corresponds to a decrease in the degree of oxidation of the electrode (Fig. 4), an increase in the current at the disk electrode and a decrease in the amount of hydrogen peroxide recorded at the ring are observed. The phenomenon described may be connected either with acceleration of the hydrogen peroxide reduction process, or with a change in the mechanism of oxygen ionization, for example with an increase in the fraction of the four-electron process proceeding without the intermediate formation of H_2O_2.

Fig. 3. 1, 1′—Polarization curve for the reduction of oxygen on silver at an electrode rotation rate of 2400 rpm; 2, 2′—dependence of the current at the ring electrode on the disk potential (1, 2—cathodic branch; 1′, 2′—anodic branch)

In the present work, using a combination of the triangular-voltage-pulse method and a disk electrode with a ring, we continued the study of the reduction process of oxygen adsorbed on silver during its anodic polarization up to 1.0 V, occurring in a nitrogen atmosphere [6]. It was of interest to determine by what path the surface oxides of silver are reduced: directly to OH′, or through the formation of intermediate products. In the latter case, intermediate reaction products, for example hydrogen peroxide, can be detected at the ring. In these experiments periodic triangular pulses with an amplitude of 1.0–(−0.2) V and a potential sweep rate from 0.01 to 10 V/sec were applied to the disk. Simultaneously, a potential of 1.2 V was maintained at the ring, corresponding to the limiting current of hydrogen peroxide oxidation. It was established that over the entire

Figure 4

Figure 4: Figure 4

range of rates of potential application, hydrogen peroxide is not detected at the ring. This fact makes it possible to conclude that oxygen adsorbed on silver during its anodic polarization is reduced directly to OH′, bypassing the intermediate formation of hydrogen peroxide.

Fig. 4. Polarization curves of oxygen reduction I and curves of the current I at the ring electrode as functions of the disk potential at $m = 2400$ rpm for amplitudes of the triangular pulse: 1–$\Delta\varphi$ 1.0–(−0.2) V; 2–$\Delta\varphi$ 0.9–(−0.2) V; 3–$\Delta\varphi$ 0.8–(−0.2) V; 4–$\Delta\varphi$ 0.6–(−0.2) V; 5–$\Delta\varphi$ 0.4–(−0.2) V; 6–$\Delta\varphi$ 0.2–(−0.2) V; 7–$\Delta\varphi$ 0–(−0.2) V

Institute of Electrochemistry
Academy of Sciences of the USSR

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