# MOLECULAR OXYGEN REDUCTION KINETICS AT PREOXIDIZED PLATINUM ELECTRODES IN ALKALINE SOLUTIONS

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The disk−ring electrode technique was used to measure the kinetic parameters of molecular oxygen reduction at the platinum electrode in 0.1 N NaOH when adsorbed oxygen produced from water molecules at different anode potentials was present on the electrode surface.

The kinetic laws of molecular oxygen reduction at the platinum electrode had been studied in [1] as functions of the degree of surface coverage by chemisorbed oxygen ($\theta_O$). This was varied between 0 and 0.7 by varying the time for which the electrode was held at potentials of 0.6-0.85 V. The electrochemical processes of adsorption and cathodic reduction of chemisorbed oxygen on platinum are irreversible; hence by preoxidation of the electrode surface one can realize oxygen coverages significantly in excess of the coverage under equilibrium conditions.

In the present work the disk−ring electrode technique was used to study molecular oxygen reduction kinetics at platinum electrodes preoxidized by anodic polarization. To this end the electrode underwent a special, programmed treatment prior to each measurement. The treatment consisted of 20-sec periods of polarization to potentials of 1.1, 0.05, 1.1, and 0.05 V. The surface then was oxidized for 120 sec at $\varphi_{ox}=1.0$, 1.2, or 1.5 V. The measuring potential $\varphi_x$ (0.6 to 0.85 V) was established at the electrode after the oxidation. The currents at disk and ring were recorded when the electrode had been for 10 sec at $\varphi_x$. With $\varphi_{ox}=1.2$ V we also studied the influence of oxidation time on the reaction rate. The state of the chemisorbed oxygen produced at different anode potentials, as well as its amount, was checked by $i-\varphi$ and $i-\tau$ curves recorded in nitrogen atmosphere. The measurements were conducted in 0.1 N NaOH solutions. The experimental conditions and the technique of solution purification have been described before [2]. The results were theoretically analyzed by the method of [3]. The potentials refer to the hydrogen electrode in the same solution.

Potentiodynamic curves over the potential range $\Delta\varphi=0.85$ to 0.0 V which were recorded by single, triangular sweeps at a potential scan rate of 1 V/sec are reported in Fig. 1. They characterize the amounts of chemisorbed oxygen left on the platinum surface at $\varphi_x=0.85$ V after the potential had been stepped to this value from the different preoxidation potentials. Similar $i-\varphi$ curves were measured for $\varphi_x$ of 0.6, 0.65, 0.7, 0.75, and 0.8 V. The amounts of chemisorbed oxygen left over at these potentials after holding the electrode for 120 sec at $\varphi_{ox}$ are reported in Table 1.

Polarization curves for the reduction of molecular oxygen at a disk which had been oxidized at different potentials, and polarization curves for the oxidation of hydrogen peroxide at the ring are reported in Fig. 2. The polarization curves for molecular oxygen reduction at the disk have a plateau at the potentials of the diffusion region, at the given rate of rotation, just as observed with the electrode after cathodic and anodic treatment. The current at the ring goes through a maximum. A characteristic feature of the oxidized state is the decrease in current at the disk around $\varphi=0.4$ V. This decrease becomes more noticeable at higher anodic potentials of electrode pretreatment. For constant oxidation potential the current decrease is larger the longer the time for which the electrode had been held at this potential. The amount of hydrogen peroxide drawn off to the ring increases when the degree of oxidation of the platinum surface becomes higher.

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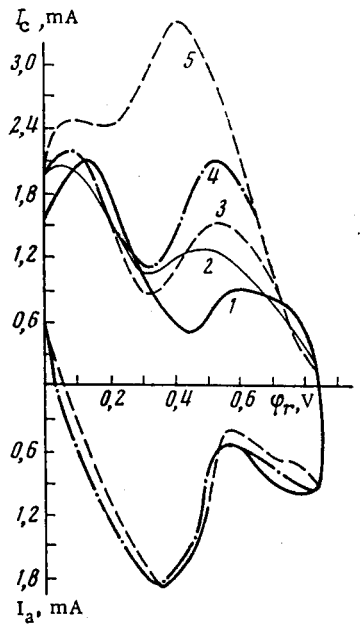


Fig. 1

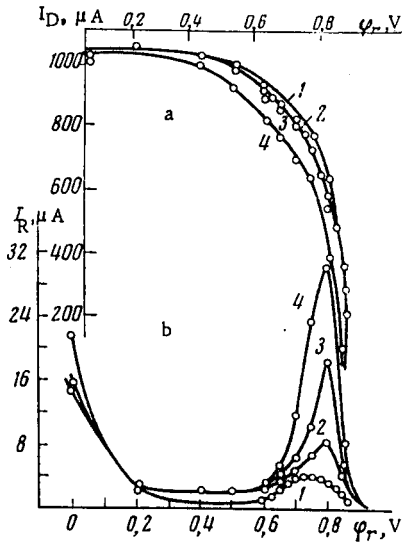


Fig. 2

Fig. 1. The i–$\varphi$ curves for reduction of chemisorbed oxygen over the potential range from 0.85 to 0.0 V recorded after stepping the potential to this range from $\varphi_{ox}$ = 0.85 (1), 0.9 (2), 1.0 (3), 1.2 (4), and 1.5 V (5); v = 1 V/sec, $\tau_{hold}$ at $\varphi_{ox}$ was 5 sec.

Fig. 2. Polarization curves for molecular oxygen reduction at the disk (a) and for hydrogen peroxide oxidation at the ring (b) as functions of the potential of surface pretreatment: 1) the electrode after cathodic and anodic treatment, 2) $\varphi_{ox}$ = 1.0 V, 3) $\varphi_{ox}$ = 1.2 V, and 4) $\varphi_{ox}$ = 1.5 V.

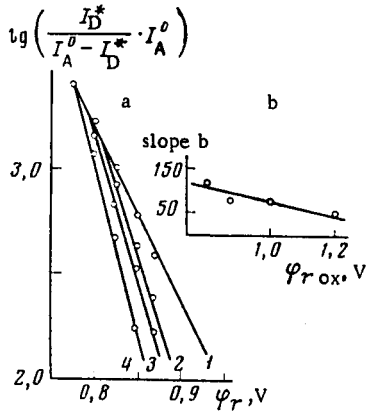


Fig. 3. Polarization curves for the reduction of molecular oxygen plotted as log $[I_D^* I_A^0/(I_A^0 - I_D^*)]$ vs $\varphi$, functions of the potential of pretreatment (a), and the slope, b, of the polarization curves as a function of the potential, $\varphi_{ox}$, of pretreatment (b). 1) to 4) in part a: same as in Fig. 2.

Polarization curves for the kinetic current of oxygen reduction, $I_p$, are reported in Fig. 3. This quantity was determined by extrapolating plots of $1/I_D^*$ vs $1/\omega^{1/2}$ to $\omega^{-1/2} = 0$, or by using the relationship $I_p = I_D^* I_A^0/(I_A^0 - I_D^*)$ ($I_D^*$ is the current of the disk electrode corrected for the current at the ring electrode, $I_A^0$ is the (corrected) limiting diffusion current at the disk, and $\omega$ is the angular rate of rotation of the electrodes). It can be seen from the drawings that the slope of the polarization curves decreases smoothly from 120 to 60 mV as the potential of surface oxidation becomes higher.

The partial currents of molecular oxygen reduction to water ($I_1$) and to hydrogen peroxide ($I_2$), as well as values for the ratio $I_2/(I_1 + I_2)$, are reported in Fig. 4. A significant decrease of the rate of molecular oxygen reduction via the first reaction pathway and an increase in the reduction rate of the process involving intermediate hydrogen peroxide formation are observed on the oxidized electrode as the potential of electrode

TABLE 1. Amounts of Chemisorbed Oxygen at the Potentials of Molecular Oxygen Reduction

| $\varphi_r$, V | $\varphi_{ox}$ | | | $\varphi_r$, V | $\varphi_{ox}$ | | |
|---|---|---|---|---|---|---|---|
| | 1,0 | 1,2 | 1,5 | | 1,0 | 1,2 | 1,5 |
| 0,6 | 0,11 | 0,11 | 0,12 | 0,75 | 0,28 | 0,339 | 0,53 |
| 0,65 | 0,16 | 0,175 | 0,32 | 0,8 | 0,37 | 0,415 | 0,66 |
| 0,7 | 0,24 | 0,3 | 0,5 | 0,85 | 0,6 | 0,678 | 1,05 |

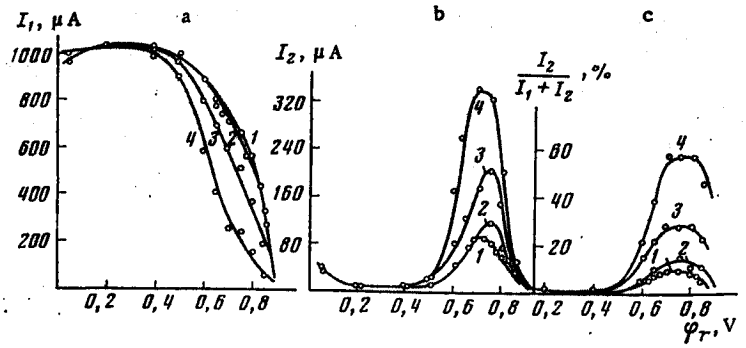


Fig. 4. Partial currents of molecular oxygen reduction $I_1$ (a), $I_2$ (b), and $I_2/(I_1+I_2)$ (c), as functions of disk potential, which were obtained with different disk pretreatments; 1) to 4) as in Fig. 2.

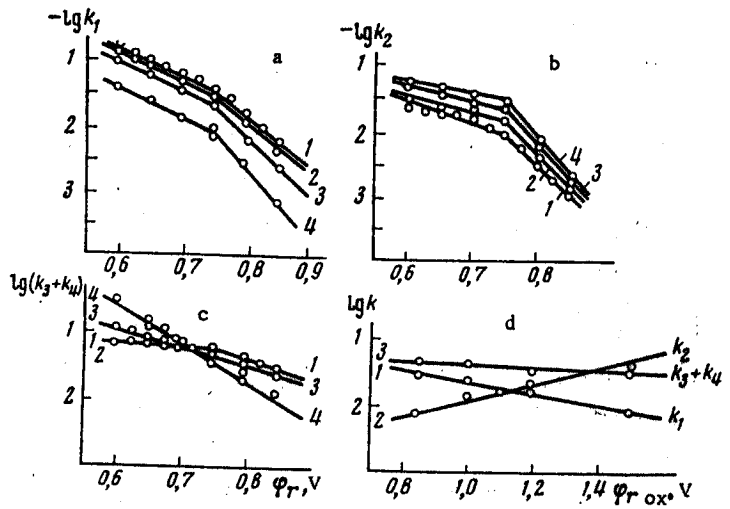


Fig. 5. The rate constants of molecular oxygen reduction, $k_1$, $k_2$, and $(k_3+k_4)$, as functions of the disk potential (a-c), and the logarithms of the rate constants as functions of the potential of pretreatment, $\varphi_{ox}$, at the constant potential of molecular oxygen reduction of $\varphi_r = 0.75$ V (d). 1) to 4) in a) to c): as in Fig. 2.

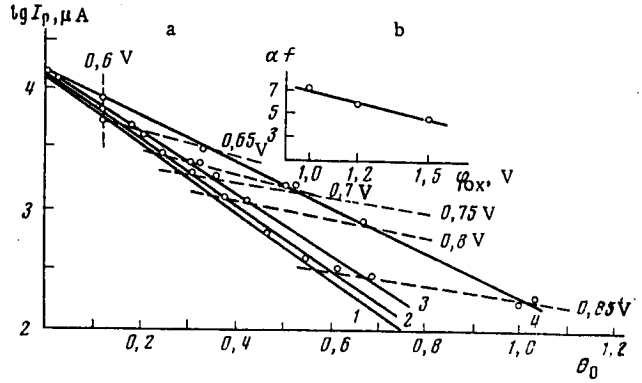


Fig. 6. The logarithm of the total rate of molecular oxygen reduction as a function of surface coverage by oxygen and of the oxidation potential (a), and αf as a function of the potential of pretreatment, $\varphi_{ox}$ (b). 1) to 4) in part a: as in Fig. 2.

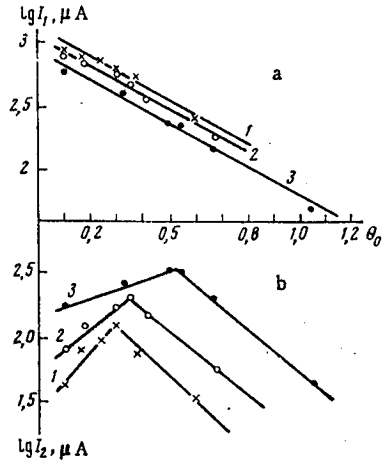


Fig. 7. Partial currents of molecular oxygen reduction $I_1$ (a) and $I_2$ (b) as functions of surface coverage by chemisorbed oxygen, $\theta_O$. 1) to 3) $\varphi_{ox}$ as in Fig. 2.

pretreatment becomes higher. The fraction of the process which goes via intermediate hydrogen peroxide formation, $I_2/(I_1+I_2)$, increases from 10 to 70% as the oxidation potential becomes higher. The logarithms of the rate constants $k_1$, $k_2$, and $k_3+k_4$ are presented as functions of disk potential for different degrees of oxidation of the platinum surface in Fig. 5. At the constant oxygen reduction potential of $\varphi_r=0.75$ V (Fig. 5d), the relative size of $k_1$ and $k_2$ depends on the oxidation potential; at $\varphi_{ox}<1.2$ V one has $k_1>k_2$, and the values are close to the $k_1$ on an active electrode which did not undergo special oxidation. At more positive oxidation potentials $\varphi_{ox}>1.2$ V one has $k_1<k_2$. It must be mentioned that the oxidized electrode exhibits an insignificant decrease in the total rate, $k_3+k_4$, with which the hydrogen peroxide reacts further by reduction and decomposition, as the oxidation potential of platinum becomes higher.

Thus, the data reported above indicate that the cathodic reduction of molecular oxygen at strongly oxidized platinum surfaces in alkaline solutions goes chiefly via the intermediate formation of hydrogen peroxide. Increasing degrees of surface coverage by chemisorbed oxygen serve to suppress the process which goes directly to water.

The data of Table 1 enable us to plot the rates of molecular oxygen reduction at the platinum electrode as functions of surface coverage by chemisorbed oxygen, and to compare the kinetic reaction parameters at constant coverage. Curves 1-4 in Fig. 6 represent the logarithm of the kinetic current of molecular oxygen reduction as a function of surface coverage. As in the case of lower $\theta_O$ [1], the total rate of the process decreases exponentially with increasing degree of coverage of the platinum surface by chemisorbed oxygen:

$$I_p=k_0\exp(-\alpha f\theta_O). \quad (1)$$

The slope αf decreases with increasing oxidation potential from 7 to 4, i.e., one finds an acceleration of molecular oxygen reduction at $\theta_O$=const when the potential of preoxidation of the platinum surface becomes higher.

The variation of $\alpha f$ with preoxidation potential of the surface correlates with the variation of the slope of the polarization curves.

The value of constant $k_0$ in Eq. (1) (which corresponds to the adsorption rate of molecular oxygen on a pure platinum surface, $\theta_O = 0$) as determined in the present work practically coincides with the $k_0$ value found in [1].

The logarithms of the partial currents $I_1$ and $I_2$ are presented in Fig. 7 as functions of $\theta_O$ for different oxidation potentials. It can be seen from the figure that there is significant inhibition of molecular oxygen reduction via the first pathway at all surface preoxidation potentials, over the full range of surface coverages from $\theta_O = 0$ to $\theta_O = 1$. Yet the reaction following the second pathway is only inhibited at large $\theta_O$ values; at $\theta_O < 0.5$ one finds some increase in the reaction rate with increasing $\theta_O$. The $\log I_2 - \theta_O$ curves are displaced toward higher reaction rates as $\varphi_{ox}$ increases.

The experimental data concerning the effect of chemisorbed oxygen on the kinetic laws of molecular oxygen reduction at the platinum electrode which were obtained in [1] and in the present work are in harmony with the assumption that the adsorption of molecular oxygen on the electrode surface is slow:

$$O_2 + M \rightarrow MO_2. \tag{2}$$

Allowing for the effect of the different forms of chemisorbed oxygen species on molecular oxygen adsorption we can write the equation for the cathodic current in the following form:

$$i = nFkP_{O_2}\left(1 - \sum_i \theta_i\right)\exp\left(-\sum_i \alpha_i f_i \theta_i\right). \tag{3}$$

Consider the potential region of low coverages by oxygen which became chemisorbed upon discharge of water molecules, when $\theta_{OH} > \theta_O$. We shall assume that the reaction

$$H_2O + M \rightleftharpoons MOH + H^+ + e \tag{4}$$

is taking place reversibly in this potential range. For this case, the following equations hold under stationary conditions:

$$k((1-\theta_{OH})\exp[(1-\alpha)F\varphi/RT - (1-\alpha)f\theta_{OH}] = c_{H^+}\theta_{OH}e^{-\alpha F\varphi/RT}e^{\alpha f\theta_{OH}}, \tag{5}$$

$$e^{-\alpha f\theta_{OH}} = k\left(\frac{\theta_{OH}}{1-\theta_{OH}}\right)^{\alpha}(c_{H^+})^{\alpha}e^{-F\varphi/RT}. \tag{6}$$

Putting (6) into (3) we obtain

$$i = nFkP_{O_2}\theta_{OH}^{\alpha}(1-\theta_{OH})^{1-\alpha}(c_{H^+})^{\alpha}e^{-\alpha F\varphi/RT}, \tag{7}$$

or, solving for $\varphi$:

$$\varphi = \frac{2.3RT}{\alpha F}\lg nFk\theta_0^{\alpha}(1-\theta_0)^{1-\alpha} + \frac{2.3RT}{F}\lg c_{H^+} + \frac{2.3RT}{\alpha F}\lg P_{O_2} - \frac{2.3RT}{\alpha F}\lg i. \tag{8}$$

With $\alpha \simeq 0.5$, Eq. (7) describes the experimental data in the region of large polarizations and low surface coverages by chemisorbed oxygen, where the oxygen is retained predominantly in the form of OH. In the region of sufficiently high positive potentials one can assume that on electrodes which had been exposed for a sufficiently long period of time or which had been specially subjected to preoxidation, species of the type of M–O are chiefly adsorbed:

$$H_2O + M \rightleftarrows MO + 2H^+ + 2e. \tag{9}$$

Under stationary conditions the following equations will hold:

$$k(1-\theta_0)e^{2(1-\alpha)F\varphi/RT}e^{-(1-\alpha)f\theta_0} = (c_{H^+})^2\theta_0 e^{-2\alpha F\varphi/RT}e^{\alpha f\theta_0}, \tag{10}$$

$$e^{-\alpha f\theta_0} = k\left(\frac{\theta_0}{1-\theta_0}\right)^{\alpha}(c_{H^+})^{2\alpha}e^{-2F\varphi/RT}. \tag{11}$$

Putting (11) into (3) we obtain

$$i = nFkP_{O_2}\theta_0^{\alpha}(1-\theta_0)^{1-\alpha}(c_{H^+})^{2\alpha}e^{-2\alpha F\varphi/RT}, \tag{12}$$

or, solving for $\varphi$:

$$\varphi = \frac{2{,}3RT}{2\alpha F}\lg nFk\theta_0^{\alpha}(1-\theta_0)^{1-\alpha} + \frac{2{,}3RT}{F}\lg c_{H^+} + \frac{2{,}3RT}{2\alpha F}\lg P_{O_2} - \frac{2.3RT}{2\alpha F}\lg i. \quad (13)$$

With the simplest assumption that $\alpha \simeq 0.5$, Eq. (13) describes the data in the region of low polarizations with long times of exposure of the platinum electrode, even when it was oxidized at different anode potentials. The smooth change of the slope $\partial\varphi/\partial \log i$ from 120 to 60 mV which is found for oxidized electrodes can be explained by the gradual transition of OH species into O species.

The equations reported above describe the experimental data which refer to a definite state of adsorbed oxygen. In order to allow for the time variations described in the work one must make additional assumptions concerning the aging of adsorbed oxygen which leads to the change in the $\alpha_i f_i$ values in Eq. (3) and, possibly, in the constants in Eqs. (6) and (11).

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# EFFECT OF pH ON $CO_2$ ADSORPTION ON THE SMOOTH PLATINUM ELECTRODE


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The adsorption of $CO_2$ on smooth platinum was studied by the potentiodynamic-sweep technique in phosphate buffer solutions over the pH range from 0.4 to 13.5. The potential dependence of stationary coverage and adsorption rate was found in solutions of different pH. The results obtained allow new suggestions to be put forward concerning the adsorption and reduction mechanism of $CO_2$ on platinum.


The adsorption of $CO_2$ on platinum electrodes had first been studied by Giner [1], who showed that it occurs upon interaction between the $CO_2$ and hydrogen adsorbed on the electrode. It was shown by different methods [2, 3] that the product of $CO_2$ chemisorption in many respects is similar to the intermediate species produced during the adsorption of organic materials such as methanol, formaldehyde, formic acid, and CO. The adsorption of $CO_2$ on hydrogen-covered platinum electrodes was found to be irreversible, and there is no further reduction of the chemisorbed species at room temperature.

There is no unified opinion concerning the mechanism of cathodic $CO_2$ reduction or concerning the composition of the adsorbed species on platinum, even though many papers have dealt with this problem [2-9]. Certain necessary studies are lacking, in particular, there are practically no data on the effect of pH on this process, since the measurements were done in acidic solutions. Only in [6] have adsorption measurements been made at two pH values (1 N $H_2SO_4$ and 0.1 N $H_2SO_4$). The effect of solution composition on $CO_2$ chemisorption on platinized platinum and on the electrooxidation of the chemisorbed species has been studied in [10] in order to find out in which form the $CO_2$ is interacting with the hydrogen adsorbed on the sur-


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