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THE OXYGEN REACTION MECHANISM IN THE RANGE OF POTENTIALS NEAR THE EQUILIBRIUM POTENTIAL

By

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Abstract

The stoichiometric number ν is particularly helpful in the case of multistep reactions to which belongs the oxygen reaction including the molecular oxygen evolution and electroreduction processes. The kinetics parameters are generalized and the mechanism of the oxygen reaction in the range of potentials near the equilibrium potential is discussed. The reaction path is considered.

As the result of studies in electrocatalysis, an ever increasing number of electrode reactions can be carried out under nearly equilibrium conditions. Here an important criterion in establishing the reaction mechanism is the stoichiometric number ν , first introduced into the theory of catalysis by Professor Horiuti.¹⁾

This criterion should be particularly helpful in the case of multistep reactions to which also belongs the oxygen reaction including the molecular oxygen evolution and electroreduction processes. Today the degree of reversibility of the oxygen reaction determines the efficiency of fuel cells and of water electrolysis and photoelectrolysis processes. In spite of considerable efforts of electrochemists of different countries, only a few studies are available in the literature²⁻⁴⁾ in which a reversible oxygen potential was attained on a platinum electrode under specific conditions.

On hydrophobic electrodes with a platinum catalyst the oxygen reaction is reversible in the potential range 1.15~1.30 V in a wide pH region. The Tafel polarization curves measured in 0.1N KOH solution are shown on Fig. 1. On the electrode in which the equilibrium is attained for the system O_2/H_2O in the range of low polarizations about 20 mV, current is linearly related to overvoltage (Fig. 2). The stoichiometric number was calculated by two methods. Using the equation below:⁵⁾

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M. R. TARASEVICH

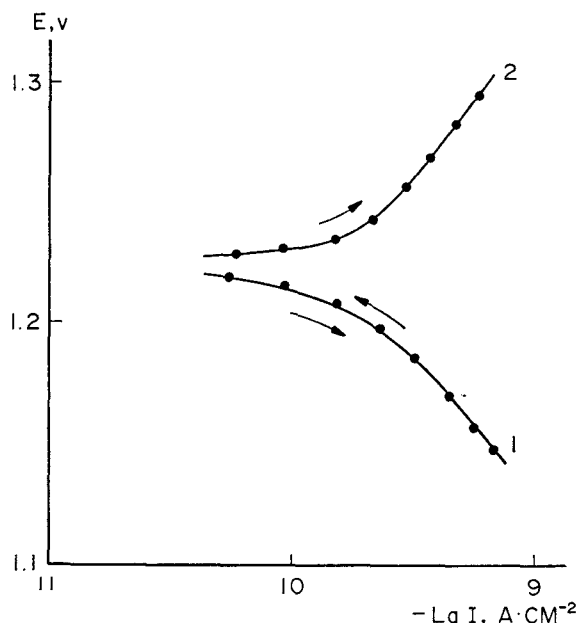


Fig. 1. The log i - E curves in 0.1 N KOH for a hydrophobic platinum electrode.

$$\nu = \frac{4F}{RT} \left[\frac{1}{b_a} - \frac{1}{b_k} \right]^{-1} \quad (1)$$

it is necessary to assume that the reaction mechanism is the same in anodic and cathodic directions. The value of ν calculated by means of Equation (1) ranges from 3.5 to 4. Though this value is close to that obtained in ref. 6), it seems to be questionable since it does not correspond to the first order in molecular oxygen of the cathodic reaction observed in experiment.

It is more correct to estimate the stoichiometric numbers for the potential range in which current is linearly related to overvoltage. In this case the assumption of an identical reaction mechanism in both directions is more justified since it corresponds to a narrower potential range. Calculation was performed with the use of the equation below:⁷⁾

$$\nu = \frac{4Fi_0}{RT} \left(\frac{d\eta}{di} \right)_{\eta \rightarrow 0} \quad (2)$$

The stoichiometric number ν thus found varies from 0.8 to 1.5. Hence the slow step occurs once. This can be the adsorption step or the addition of the first electron to the adsorbed oxygen molecule.

In spite of a large number of studies carried out so far the results of

The Oxygen Reaction Mechanism

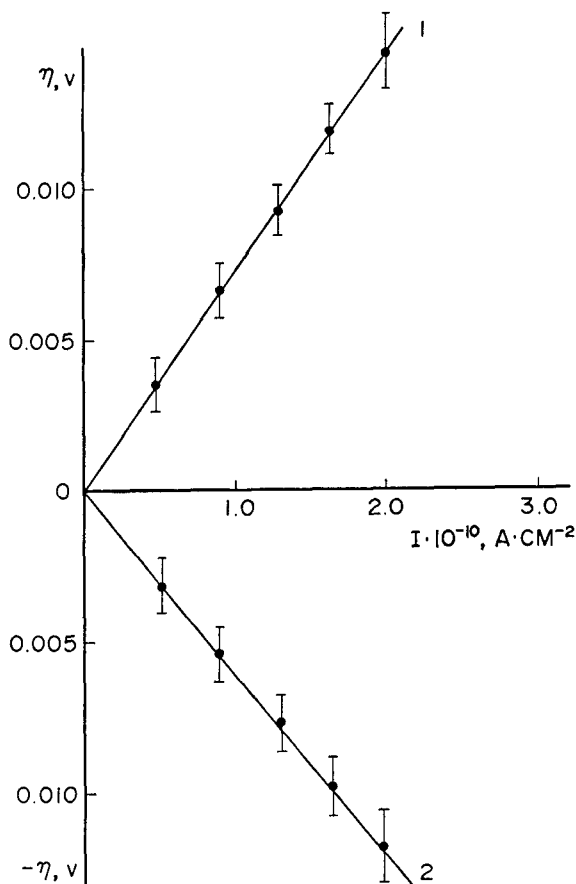


Fig. 2. The $i-\eta$ curves in 0.1 N KOH for a hydrophobic platinum electrode.

which are summarized in the literature,^{8~10)} until recently no electrocatalyst has been found which would be more active in the oxygen reaction than the platinum electrode. Only when biocatalysts and their models were included among the system under investigation, solution of this problem became tangible.

In the presence of the enzyme laccase immobilized by adsorption on carbon black, the reversible potential of the system O_2/H_2O is attained and electroreduction of molecular oxygen proceeds at a high rate.¹¹⁾ The exchange current per molecule of adsorbed laccase exceeds by an order and a half that per surface platinum atom. In the potential range 1.20~1.18 V current depends linearly on overvoltage (Fig. 3). In the potential range

M. R. TARASEVICH

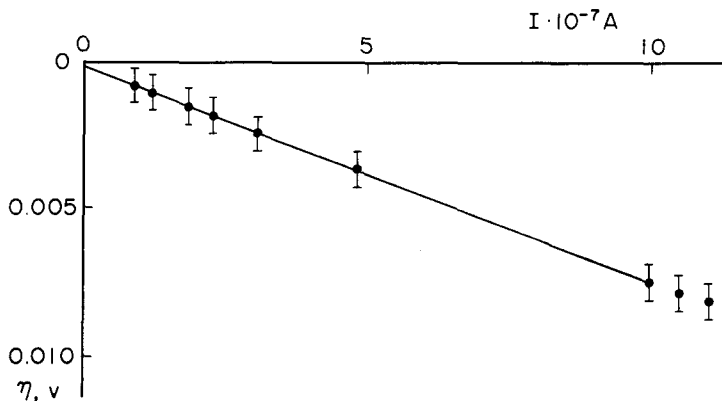
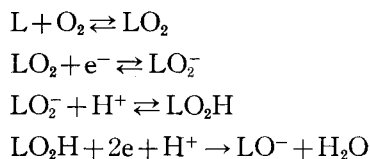


Fig. 3. The i - η curves of oxygen reduction at an electrode with immobilized laccase at pH=5.

1.18–1.15 V the slope $\partial E/\partial \log i$ is 0.03 V and in the range 1.15~1.10 V it rises up to 0.06 V. In that case Equation (1) is inapplicable because at a potential higher than 1.23 V laccase undergoes reversible inhibition.

In calculations by means of Equation (2) use was made of the exchange current value found by extrapolation to the steady-state potential of the curve section with the slope 0.03 V. For 15 independent experiments the value of ν varied from 0.75 to 1.8 with the mean value 1.15. Hence the slow step occurs only once. If, as usual, it is assumed that $\alpha=0.5$, it is possible to suggest the following oxygen reduction mechanism in the presence of laccase (L):



This scheme agrees with the experimentally observed kinetic parameters: $\partial E/\partial \log i$, $\partial E/\partial \log P_{O_2}$ and $\partial E/\partial \text{pH}$. The slow two-electron step can be explained by the presence of a two-electron acceptor in the active site of laccase from which two electrons are transferred to the oxygen molecule. It should be noted that the observed kinetic parameters can also be described by a slow one-electron step if the possibility of a barrierless ($\alpha=1$) mechanism is taken into account.

Considering the complexity of investigation and use of enzymes in electrochemical systems, electrocatalysis of the oxygen reaction by organic complexes of transition metals — oxides models appears to be more realistic.

The Oxygen Reaction Mechanism

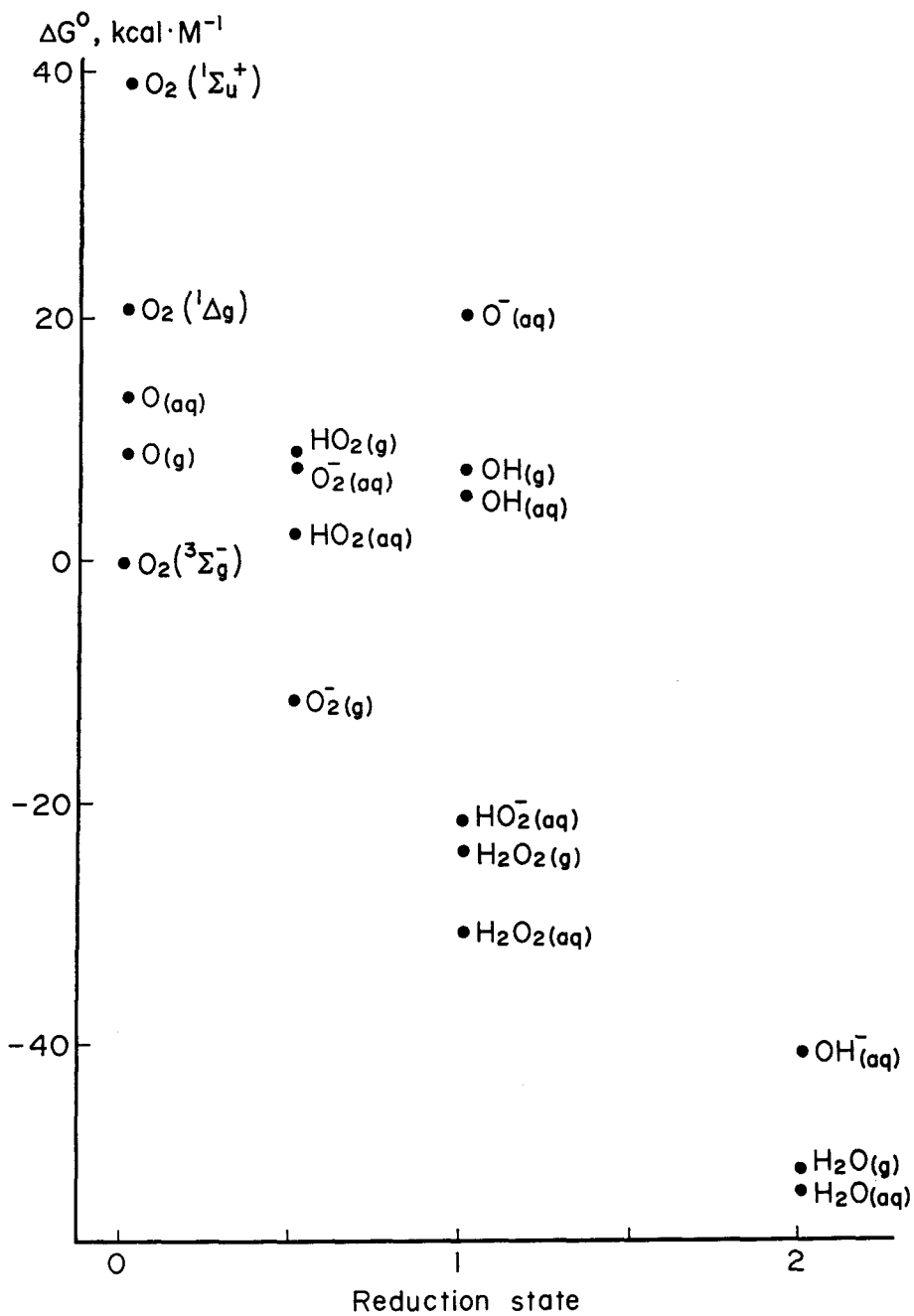


Fig. 4. Energy diagram for oxygen-containing particles in the system $\text{O}_2/\text{H}_2\text{O}$.

M. R. TARASEVICH

In this connection a question arises as to possible means of increasing the oxygen reaction rate.

Available data suggest the following main reasons of the low rate of this reaction :

1. The necessity of breaking (formation) of the bond in the oxygen molecule. Only the reaction pairs : $O_2 \rightleftharpoons H_2O$, $H_2O_2 \rightleftharpoons H_2O$ involving breaking of the O-O bond are irreversible.

2. The occurrence of the reaction *via* intermediate hydrogen peroxide formation. A higher kinetic stability of H_2O_2 as compared to O_2 in the cathodic reaction is due to the fact that protonation involved in the second electron transfer strengthens the O-O bond in the water molecule.

Oxygen in the ground state has two unpaired electrons with parallel spins, which results in a high stability of the molecule. Two ways of activating the oxygen molecule are possible. The first is transfer of the oxygen molecule from the ground state to the singlet state 1A_g or ${}^1\Sigma_u^+$, requiring expenditure of 22.5 and 38.5 kcal/mole (Fig. 4), respectively. The second way consists in activation of the oxygen molecule in the course of its adsorption (coordination). It is clear that in the case of electrocatalysis the second way is realized. Taking into account the spin forbiddenness, the first step should involve transfer of one electron.

Increasing the rate of the oxygen reaction in both directions and making it reversible require first of all levelling of the energy profile of the reaction (Fig. 4) and elimination of intermediate hydrogen peroxide formation. Activation of O_2 and H_2O (OH^-) particles and increase of their energy to the necessary level are achieved by their adsorption binding (coordination). Therefore the reaction site must effectively bind and readily lose both the particles, or there should be two reaction sites with fast electron exchange.

It may be suggested that the optimum reaction path should include transfer of the first electron (most likely, a slow one), followed by simultaneous transfer of two electrons inside the reaction complex. Breaking (formation) of the O-O bond and addition (loss) of protons also occurs inside the reaction complex during simultaneous transfer of electrons or immediately after it. This eliminates intermediate formation of kinetically stable hydrogen peroxide.

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