ELECTROREDUCTION OF OXYGEN ON RUTHENIUM PHTHALOCYANINE IN ALKALINE MEDIA

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Abstract

The electroreduction of oxygen on a ruthenium phthalocyanine catalyst in 1.0 M KOH is studied by rotating ring-disc electrode (RRDE) method. The polarization curves display two plateau-like regions of the limiting current, which suggests a two-step mechanism of oxygen electroreduction including the formation of an intermediate peroxide ion. The analysis of the data in the Levich and Koutecký–Levich coordinates show that already in the range of the first wave potentials the formation of a peroxide ion is accompanied by the direct four-electron reduction of oxygen to water.

Ruthenium phthalocyanine catalyst

Introduction

The idea of using organometallic complexes for four-electron reduction of oxygen stems from the biological mechanism of energy generation through the oxidation with molecular oxygen catalyzed by enzymes—macrocyclic complexes [1]. To date, the catalytic activities of a wide range of macrocyclic metal complexes, including porphyrin, phthalocyanine, and tetraazaanulene derivatives, have been explored [2–6].

To a first approximation, the mechanism of an oxygen reduction reaction (ORR) on macrocyclic complexes can be presented as follows. The preliminary interaction of molecular oxygen with a catalyst molecule leads to the weakening of the O–O bond. If the metal atom in the catalyst molecule is able to undergo a transition $M^n \rightarrow M^{n+1}$ (here M is the metal ion in the complex composition and *n* is its oxidation state in the complex), then the following stage can occur in an alkaline solution provided that the appropriate potential, steric availability, and coordination unsaturation of the central atom are established:

$$M^n + O_2 \rightarrow M^{n+1}–O_2^-$$
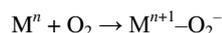
The resulting intermediate further undergoes electroreduction according to the following scheme:

$$M^{n+1}–O_2^- + \bar{e} \rightarrow M^n + \text{intermediate}$$
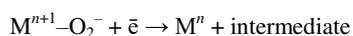
This scheme shows the primary importance of the possible transition: $M^n \rightarrow M^{n+1}$. This transition is likely to be accomplished during the catalysis on Fe and Co complexes.

Another mechanism implies the formation of an activated complex as a result of the interaction of adsorbed oxygen with a

system of conjugated π-bonds of a macrocyclic ligand. The delocalization of the electron density through conjugated double bonds promotes stabilization of {L–O₂} intermediate (L is the macrocyclic ligand) and simplifies the cleavage of the O–O bond. It should be noted that even in the case of this mechanism, a role of the central atom is crucial, since free macrocyclic ligands do not exhibit catalytic activity.

ORR on phthalocyanine complexes of the iron triad metals has been studied in detail [3]. In particular, it was shown that in solutions with the high values of pH, the reduction proceeds *via* two two-electron steps with the intermediate formation of a peroxide ion. Phthalocyanine complexes of the platinum group metals have received much less attention as ORR catalysts. Ruthenium phthalocyanines, especially in the dimeric forms, rapidly react with molecular oxygen, leading to the activation of an oxygen molecule and acceleration of ORR, *i.e.*, catalyzing the process [7]. Ebadi *et al.* [8] noted that at the high values of pH, ORR on a ruthenium phthalocyanine occurs by the two-step mechanism. Capobianchi *et al.* [9] showed that the ruthenium phthalocyanine applied to a graphene material efficiently adsorbs oxygen in 1.0 M KOH. In this case, ORR was found to involve a non-integral number of electrons, *i.e.*, the reaction may proceed by two parallel mechanisms.

From the viewpoint of kinetics, the oxygen reduction can be considered as a combination of several steps [10].

The one-step reaction involving all four electrons can be presented as follows:

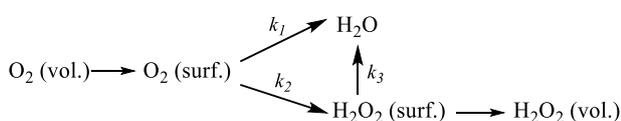$$O_2 + 2H_2O + 4\bar{e} \xrightarrow{k_1} 4OH^-$$
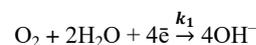
In neutral and alkaline media, this reaction often proceeds in two steps through the intermediate formation of a peroxide ion:

$$O_2 + H_2O + 2\bar{e} \xrightarrow{k_2} HO_2^- + OH^-$$

[†] Deceased.

$$HO_2^- + H_2O + 2\bar{e} \xrightarrow{k_3} 3OH^-$$
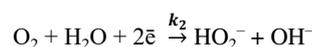
In the general case, this scheme can be presented in the following form [10]:

Scheme 1

Here O_2 (vol.) is molecular oxygen dissolved in the electrolyte volume, O_2 (surf.) is molecular oxygen adsorbed on the electrode surface, H_2O_2 (surf.) is hydrogen peroxide adsorbed on the electrode surface, and HO_2^- (vol.) is the peroxide ion which is transferred from the electrode surface to the solution.

The investigation of ORR by rotating ring-disc electrode method allows for the definition of a predominant reaction route, four- or two-electron reduction, within the accepted assumptions by measuring the currents on the disc and ring electrodes. For Scheme 1, a ratio between the reaction constants is given by the following equation [10]:

$$N \cdot \frac{I_d}{I_r} = 1 + \frac{2k_1}{k_2} + \frac{2k_3}{B}\left(1 + \frac{k_1}{k_2}\right)\omega^{-0.5} \quad (1)$$

Here N is the experimentally defined efficiency of the peroxide oxidation on the platinum ring ($N = 0.258$), I_d is the current on the disc electrode, I_r is the current on the platinum ring, k_1, k_2, and k_3 are the reaction constants for Scheme 1, $B = 0.62D^{2/3}\cdot v^{-1/6}$, where $D = 1.6\cdot10^{-5}$ cm²/s is the diffusion coefficient of molecular oxygen in 1.0 M KOH, $v = 0.952\cdot10^{-2}$ cm²/s is the kinematic viscosity of 1.0 M KOH solution at 25 °C [11]. Hence, a part of the line intercepted by the linear graph of $N\cdot I_d/I_r$ *vs.* $\omega^{-0.5}$ on the ordinate axis allows for the definition of the ratio k_1/k_2 and a slope of this graph affords the value of k_3.

Results and discussion

Figure 1 depicts the polarization curves for ORR on Ru phthalocyanine (PC) on RDDE. There are two reduction waves. The former has a plateau of the limiting current in the range of potentials of 0.4–0.5 V, and the latter—at about 0.0 V. The presence of two reduction waves is generally attributed to the two-step mechanism of oxygen reduction through the intermediate formation of a peroxide ion. The current in the range of the first wave potentials accounts only for the formation of hydrogen peroxide, whereas its further reduction to a hydroxide ion occurs at the potentials of the second wave [12]. Interestingly, in the range of potentials of the first half-wave (at about 0.7 V), the value of the ratio I_d/I_r, as will be shown below, composes about 10.

Figure 2 shows the dependences of $N\cdot I_d/I_r$ on $\omega^{-0.5}$ corresponding to equation (1), where N is the experimentally defined efficiency of oxidation of hydrogen peroxide on the platinum ring ($N = 0.258$), I_d is the current which proceeds due to reactions on the disc electrode, I_r is the current which refers to the oxidation of hydrogen peroxide on the platinum ring, and ω is the angular rotation rate.

As can be seen from Fig. 2, these dependences are linear in a rather broad range of potentials. The value of an Y-axis intercept
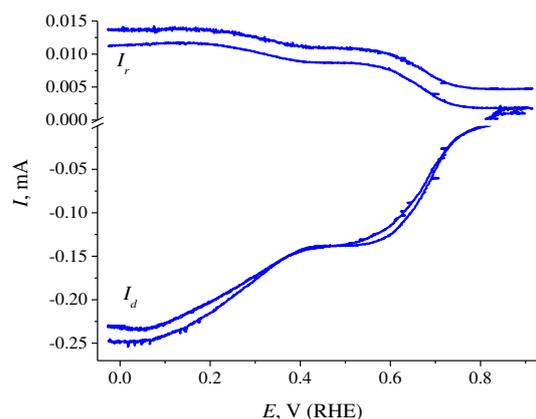

Figure 1. Polarization curves for the reduction of oxygen and the oxidation of hydrogen peroxide on Ru PC. I_d is the current on the disc, I_r is the current on the ring.
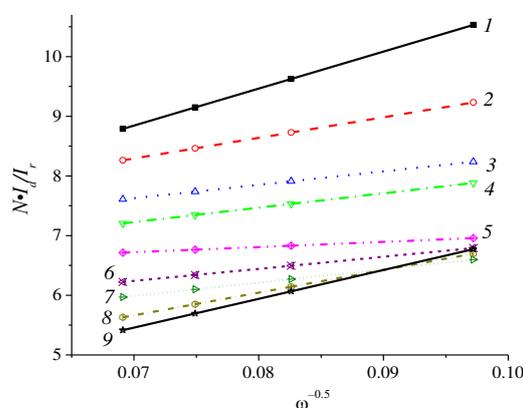

Figure 2. Dependence of $N\cdot I_d/I_r$ on the angular rotation rate (ω, s⁻¹) at the following potentials: 0.76 (*1*), 0.74 (*2*), 0.72 (*3*), 0.70 (*4*), 0.68 (*5*), 0.66 (*6*), 0.64 (*7*), 0.62 (*8*), 0.60 (*9*) V (RHE).

resulting from the extrapolation to zero depends nonlinearly on the potential and goes through a minimum at about 0.68 V. The values of slope coefficients in all cases differ from 0 and also ambiguously change depending on the potential. According to the previously published analysis [10], the observed pattern corresponds to the situation when three reactions proceed on the electrode surface simultaneously (Scheme 1): direct four-electron reduction of oxygen to water and sequential two-step reduction with the intermediate formation of a peroxide ion and its further reduction to water. According to this scheme, we calculated the ratios of the constants k_1/k_2, which account for the oxygen reduction to water and to hydrogen peroxide, respectively, and the constant k_3, which refers to the reduction of hydrogen peroxide to water (Figs. 3 and 4).

As can be seen from the figures presented, in the range of potentials from 0.74 to 0.60 V, the value of the ratio k_1/k_2 with the corresponding confidence interval ranges from 1 to 2. This result indicates that the reactions of oxygen reduction by the two- and four-electron mechanisms proceed in this range of potentials with close rates and their ratio changes only slightly at the potentials varying from 0.62 to 0.74 V. The dependence of the constant k_3 on the potential has a minimum at $E \approx 0.64$ V.

The higher values of k_3 at $E > 0.64$ V can be caused by the chemical or electrochemical decomposition of HO_2^-, which is not taken into account in Scheme 1. This effect can account for
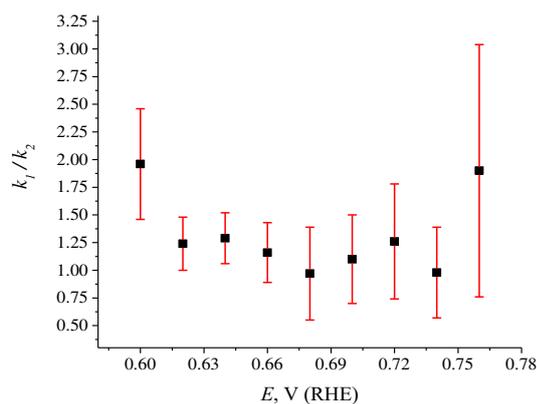
Figure 3. Dependence of the ratio k_1/k_2 on the potential of oxygen reduction on Ru PC in 1.0 M KOH.
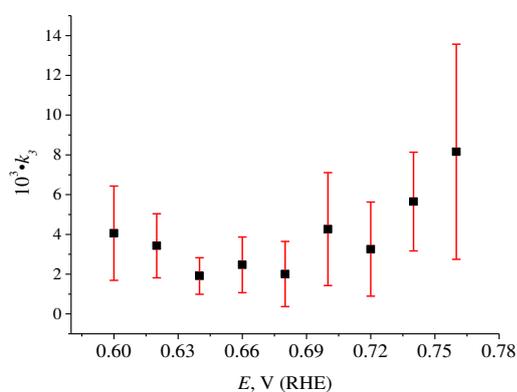

Figure 4. Dependence of the constant k_3 on the potential of oxygen reduction on Ru PC in 1.0 M KOH.

the growth of the ratio k_1/k_2 at $E > 0.62$ V [13].

The Koutecký–Levich analysis [14] also showed that the oxygen reduction occurs by the combined mechanism. Figure 5 depicts the theoretical dependences of the reverse current on the reverse angular rate for four- and two-electron reactions and the experimental points for the potential of 0.70 V. The number of electrons that take part into the reduction is more than 2 but less than 4. These data are in good agreement with the results obtained earlier on the disc electrode [7].

Experimental

Ruthenium phthalocyanine was synthesized in the Laboratory of New Physico-Chemical Problems, IPCE RAS, according to the published procedure [15]. The resulting complex was characterized by IR, UV-*vis*, and EPR spectra, which confirmed its structure and the oxidation state of the central atom.

The polarization curves were registered on a PINE Instruments biopotentiostat using a glassy-carbon disc electrode (0.196 cm^2) with a platinum ring (0.110 cm^2). Prior to the measurement, the platinum ring was activated by cycling the polarization potential from the hydrogen adsorption region (0 V RHE) to the oxygen adsorption region (+1.4 V RHE) in 0.5 M H$_2$SO$_4$ under an argon atmosphere. The measured roughness factor of platinum (the ratio of the real surface to the geometric
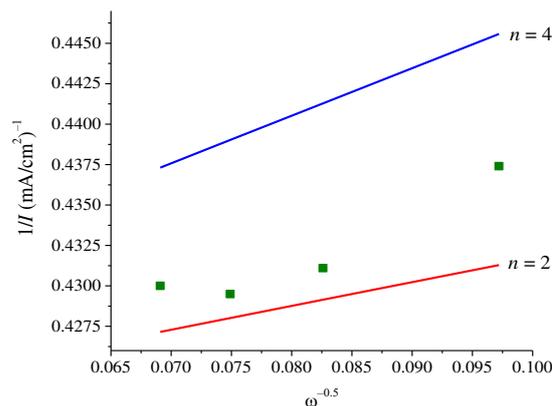

Figure 5. Theoretical (straight lines) and experimental (discrete points) dependences of the disc reverse current on the reverse angular rate of electrode rotation (ω, s^{-1}); n is the number of electrons in ORR.

one) after the activation composed 100–120. The value of the real surface area was determined by the adsorption of atomic hydrogen [16].

1.0 M KOH solution was prepared every day by diluting a concentrated solution of KOH using titrimetric definition of the concentration. After registration of each five polarization curves, the working solution in a cell was changed in order to avoid accumulation of hydrogen peroxide and reduction in the efficiency of the platinum catalyst for hydrogen peroxide oxidation on the ring electrode.

The complex (1 mg) was dissolved in an ethanol–chloroform mixture (1:1 by volume) upon ultrasonic treatment for 30 min in the presence of 5% ethanol solution of nafion (1 μL, Nafion^{TM}, Aldrich). An aliquot of the resulting solution (1 μL) was applied to the surface of the glassy-carbon disc and dried in air for 30 min. The amount of the complex on the electrode surface was calculated on the assumption of plane filling of the electrode surface with the adsorbed complex molecules. This value ranged from 30 to 70 monolayers.

The measurements were started after reaching a stationary potential of the electrode in solution under oxygen blow. During registration of a polarization curve, oxygen was passed over the solution in order to avoid additional uncontrollable mixing and violation of the conditions for equal access of the electrode surface. The measurements were carried out at the rotation rate of 1000, 1400, 1700, and 2000 rpm and the potential scanning rate of 10 mV/s.

The measurements were performed relative to a silver chloride reference electrode in saturated KCl solution connected with the working volume through a glass diaphragm and a salt bridge filled with 1.0 M KOH. All the potentials are presented relative to the reverse hydrogen electrode.

Conclusions

The investigation by RRDE method showed that the unsubstituted ruthenium phthalocyanine catalyzes the oxygen reduction in an alkaline solution. Furthermore, in the range of the first wave potentials, it allows for the partial realization of the direct four-electron reduction of OH$^-$ ions with the rate comparable to that of the formation of HO$_2^-$.

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