

Electrocatalysis of molecular aggregate composed of an osmium complex and a polymer membrane for dioxygen reduction

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Abstract

Electrocatalytic O₂ reduction was studied using a modified electrode coated with a Nafion® (Nf) membrane dispersing an osmium complex ([Os^{III}(bpy)₂Cl₂]Cl). When measuring cyclic voltammogram (CV) under O₂ atmosphere, growth of cathodic currents due to the O₂ reduction was found to take place on reducing Os^{III} into Os^{II} (below 0 V (versus Ag/AgCl)). Although a similar CV was also measured in acetonitrile containing the Os complex, no catalysis for O₂ reduction by the Os complex was observed on voltammetric aspect. Therefore, it appeared that the Os complexes aggregated in the polymer matrix are responsible for the electrocatalysis involving a multi-electron transfer. A selective and direct catalysis for O₂ reduction into H₂O was suggested from a ring-disk voltammogram to take place by the present system. In addition, the dependencies of both the catalytic currents for O₂ reduction ($-I_{\text{cat}}$) and the apparent diffusion coefficient of electron (D_{app}) on the complex concentration were investigated. Based on those results, the factor that affects the overall kinetics in the present catalysis system was discussed. © 2003 Elsevier B.V. All rights reserved.

Keywords: Oxygen reduction; Electrocatalysis; Molecular catalysis; Molecular aggregate; Polymer-coated electrode

1. Introduction

Four-electron transfer reduction of O₂, which corresponds to the cathode reaction in fuel cell, has been receiving much attention in view of basic science as well as technology [1]. Great efforts to design and develop molecular catalysts instead of conventional noble metals have been made, but there have been only few kinds of materials (e.g. phthalocyanines (Pc) [2–5], porphyrins (Por) [6–11], and cofacial metal complexes [12,13], etc.) capable of four-electron reduction of O₂. It has been realized that the fixed orientation of two active centers involved in catalyst structure is responsible for those catalyses resulting in the reductive cleavage of the O=O bonding (cf. also in case of the mononuclear Pc and Por complexes, the O₂ reduction catalysis into H₂O was often attributable to a dimer formation on an electrode surface [3,4,7]). However, the pioneering molecular catalysts of macrocyclic metal complexes (e.g. FePc, CoPor, etc.) are insufficient as far as both activity and stability concerned.

Moreover, as for the cofacial metal complexes, it has been a problem that such a complex is difficult to synthesize and obtained only in a low yield. New aspects need to be opened by designing and developing novel molecular catalysts and its catalysis systems, aiming at achieving an active and efficient O₂ reduction into H₂O.

We have recently reported that electrocatalytic O₂ reduction into H₂O takes place by mononuclear Ru amine complex embedded in a polymer matrix although the catalysis reaction itself is kinetically much slow [14]. The four-electron transfer reduction of O₂ was induced via the one-electron redox process of the complex (Ru^{III/II}), so that it was concluded that an aggregate formed in polymer matrix is responsible for the electrocatalysis resulting in the multi-electron transfer reduction. In order to create an efficient catalysis system by means of a molecular aggregate, it is important to investigate and accumulate fundamental knowledge for a complex capable of a potential catalysis. In the present work, a bipyridyl osmium complex ([Os^{III}(bpy)₂Cl₂]Cl) was applied to O₂ reduction catalyst. Polypyridyl Os complexes have been known to act as an efficient electron mediator [15,16]. In a typical result, the selective and direct O₂ reduction into H₂O was found to

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take place at a modified electrode coated with Nafion® (Nf) incorporating the complex. The electrocatalysis was investigated in terms of voltammetry. In addition, the factor that affects the overall kinetics in the present catalysis system will also be discussed.

2. Experimental

A 5 wt.% Nafion® alcoholic solution was purchased from Aldrich Chemical Co., Ltd. $[\text{Os}^{\text{III}}(\text{bpy})_2\text{Cl}_2]\text{Cl}$ was synthesized according to the previous procedures [17,18]. The purest grade reagents were used without further purification.

Electrode modification was carried out as follows. A methanol solution containing 2.5 wt.% Nf was at first prepared (the density of this solution is 0.83 g cm^{-3}). A $6 \mu\text{l}$ portion of this solution was cast onto a basal-plane pyrolytic graphite (BPG) electrode (effective area, 0.21 cm^2), followed by solvent evaporation under air. The membrane thickness was estimated to be ca. $3 \mu\text{m}$ by considering the density of the Nf membrane (2 g cm^{-3}) [19]. The Nf-coated BPG was dipped into deionized water for 30 min to improve its cation exchange ability. The introduction of the Os complex was carried out by a cation exchange method by dipping the Nf-coated BPG into water containing a known concentration of the complex, and the adsorbed amount was estimated by visible absorption spectral change before and after the adsorption. The visible absorption spectrum was measured using a Hitachi U-2010 spectrophotometer.

An electrochemical cell was equipped with the modified working electrode, a spiral Pt counter and a silver/silver chloride (Ag/AgCl, in saturated KCl electrolyte) reference electrode. All of the electrochemical study was run in a pH 2.0 aqueous phosphate buffer solution. The electrochemical study was carried out by using a potentiostat (HOKUTO DENKO, HA-301) equipped with a function generator (HOKUTO DENKO, HB-104), a coulomb meter (HOKUTO DENKO, HF-201) and a recorder (GRAPHTEC, WX-4000).

Electrochemical study by rotating ring-disk electrode (RRDE) was also carried out according to a conventional method. A platinum ring-graphite disk electrode (effective area of disk, 0.3 cm^2) was used as a working electrode. The graphite disk was polished with $0.05 \mu\text{m}$ alumina paste prior to use. Preparation of the modified RRDE was the same as the BPG system (e.g. Nf coating onto the graphite disk was carried out to be $3 \mu\text{m}$ thickness). The intrinsic collection efficiency (N) at the ring electrode was determined to be 0.39, where a redox couple of $\text{Fe}(\text{CN})_6^{3-/4-}$ was used in measuring a rotating ring-disk voltammogram. The N -value was in good agreement with the calculated value (N_0) based on the geometry of the ring-disk electrode. The RRDE apparatus (Nikko Keisoku, RRDE-1) was controlled by using a dual potentiostat (Nikko Keisoku, DPGS-1) equipped with a function generator, and a recorder. In the modified RRDE system, the cell constitution was similar to the BPG system.

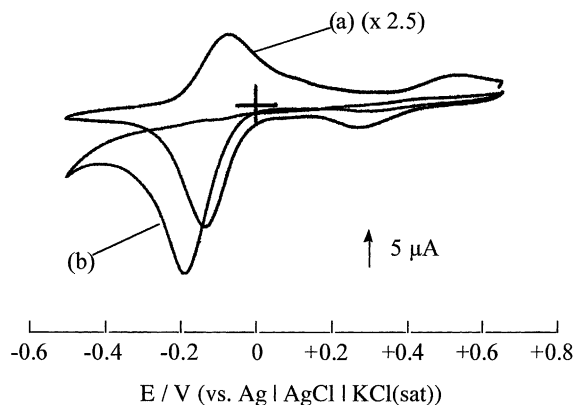


Fig. 1. CVs at BPG/Nf[Os] under Ar (a) and O_2 (b) atmospheres—scan rate, 5 mV s^{-1} ; complex concentration in Nf membrane: (a) $1.5 \times 10^{-1} \text{ mol dm}^{-3}$; (b) $4.6 \times 10^{-2} \text{ mol dm}^{-3}$.

3. Results and discussion

Fig. 1 shows cyclic voltammogram (CV) at BPG coated with Nf incorporating $[\text{Os}^{\text{III}}(\text{bpy})_2\text{Cl}_2]$ (BPG/Nf[Os]) under Ar (a) and O_2 (b) atmospheres. In Fig. 1(a), a redox couple of $\text{Os}^{\text{III/II}}$ was observed at around -0.1 V (versus Ag/AgCl), corresponding to previous knowledge [18]. When measuring CV at the BPG/Nf[Os] under O_2 atmosphere (Fig. 1(b)), the growth of catalytic current due to O_2 reduction started to take place on reducing Os^{III} into Os^{II} (below 0 V) (the O_2 reduction products will be discussed later). A similar CV measurement was also carried out in acetonitrile containing the Os complex (Fig. 2), compared with Fig. 1. However, the redox peak for $\text{Os}^{\text{III/II}}$ couple was found to appear at $\sim +0.05 \text{ V}$ even when employing the O_2 atmosphere. Based on the results of Figs. 1 and 2, it appears that the Os complex can exhibit the electrocatalysis for O_2 reduction by embedding it into the polymer matrix. Considering that the electrocatalytic O_2 reduction involving a multi-electron transfer (into H_2O and/or H_2O_2) is induced via the one-electron redox process of the complex, the electrocatalysis could be attributed to formation of an aggregate in the polymer matrix.

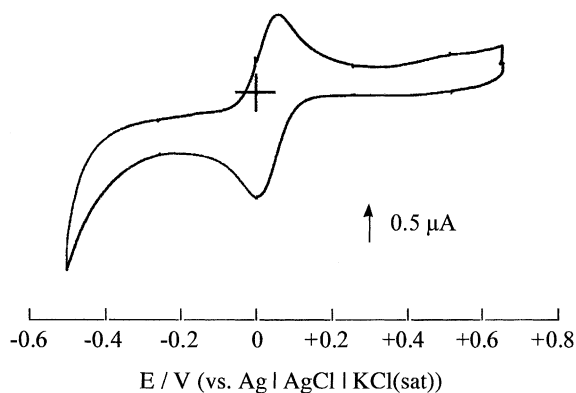


Fig. 2. CV at a BPG electrode in acetonitrile containing $[\text{Os}^{\text{III}}(\text{bpy})_2\text{Cl}_2]^+$ (under O_2)—scan rate, 5 mV s^{-1} ; electrolyte, $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ tetra-*n*-butylammonium perchlorate; complex concentration, $1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

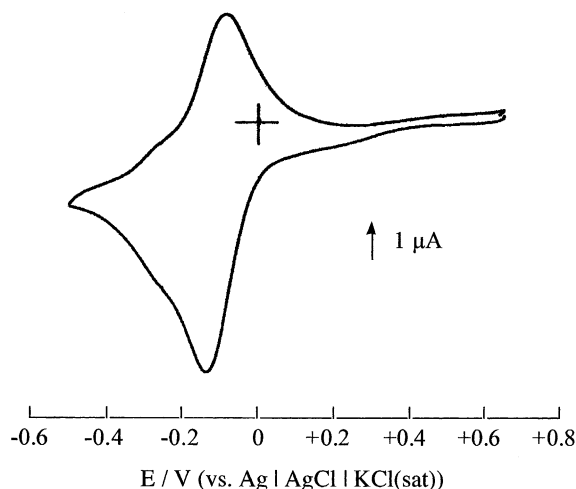


Fig. 3. CV at BPG/Nf[Os] in the presence of H_2O_2 (under Ar)—scan rate, 5 mV s^{-1} ; complex concentration in Nf membrane, $1.7 \times 10^{-1} \text{ mol dm}^{-3}$.

The BPG/Nf[Os] system was also applied to electrocatalyst for H_2O_2 reduction (see Fig. 3). CV was measured by adding H_2O_2 into the electrolyte solution (the H_2O_2 concentration was controlled equal to the saturated O_2 concentration in an aqueous phase ($\sim 1.45 \times 10^{-3} \text{ mol dm}^{-3}$) [20]). An electrocatalytic H_2O_2 reduction by the Nf[Os] would take place because the reoxidation peak from the active species (Os^{II}) is not perfectly recovered (i.e. ratio of the area of the anodic peak to the cathodic one is not unity). Comparing the CV of Fig. 3 with that of Fig. 1(b), it is noted that the catalysis by the Nf[Os] is much faster in O_2 reduction than in H_2O_2 one. That is, there is only a small possibility of H_2O formation via H_2O_2 intermediate, owing to a poor catalysis for H_2O_2 reduction by the Nf[Os]. Therefore, it is most probable that the Nf[Os] catalyzes a two-electron reduction of O_2 into H_2O_2 and/or a direct H_2O formation in one-step.

The O_2 reduction products in the present system were investigated by measuring a voltammogram at a rotating Pt ring-graphite disk electrode (denoted as RRDE), and a typical result is shown in Fig. 4. The voltammogram at the disk electrode was measured by reductive potential scan from $+0.65 \text{ V}$ (scan rate, 50 mV s^{-1} ; rotation speed, $3.3 \times 10^1 \text{ rps}$). The anodic currents (I_{R}) at the ring electrode, which arises from reoxidation of H_2O_2 produced by O_2 reduction, were simultaneously recorded by applying a constant potential of $+0.75 \text{ V}$ (versus Ag/AgCl). The cathodic current at disk electrode (I_{D}) started to appear at around -0.1 V , and it then reached a plateau below -0.25 V . The wave appeared at ca. $+0.2 \text{ V}$ is attributed to the reduction of the impurity (i.e. quinone) contained in the graphite. According to the following equation (Eq. (1)), ratio of H_2O formation in the O_2 reduction was calculated:

$$\text{H}_2\text{O} (\%) = \frac{(I_{\text{D}} - I_{\text{R}})/N}{(I_{\text{D}} + I_{\text{R}})/N} \times 100 \quad (1)$$

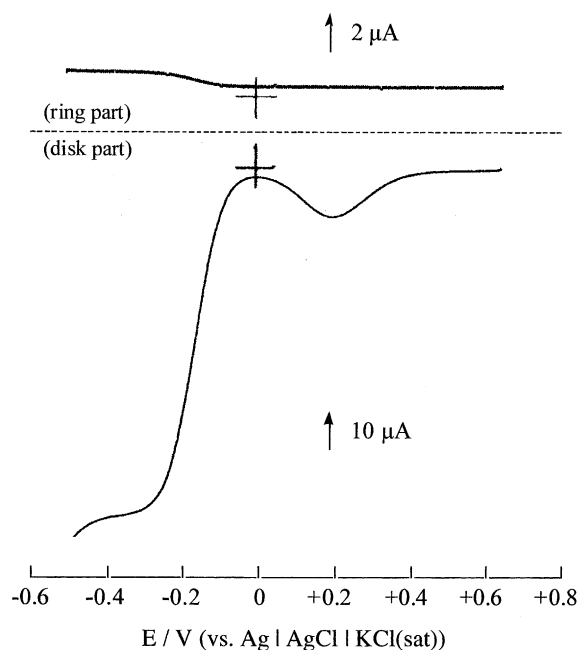


Fig. 4. A graphite disk-Pt ring voltammogram under O_2 atmosphere. The part of graphite disk was modified with Nf[Os]. A graphite disk electrode was used as working (effective area, $\sim 0.3 \text{ cm}^2$)—scan rate, 50 mV s^{-1} ; complex concentration in Nf membrane, $2.2 \times 10^{-1} \text{ mol dm}^{-3}$; rotating speed, $3.3 \times 10^1 \text{ rps}$.

The ratio for H_2O formation was calculated to be $>97\%$ (e.g. at -0.2 V). The selectivity for H_2O formation was almost independent of potentials (below -0.15 V), catalyst concentration and rotating rate, showing that a constant catalysis by the Nf[Os] takes place. Considering the voltammetric characteristics as shown before, the selective H_2O formation by the Nf[Os] can be concluded to take place via four-electron transfer in one-step.

In order to investigate the catalysis characteristics of Nf[Os] for O_2 reduction, the electrocatalysis was examined on voltammetric aspect (i.e. CV at BPG/Nf[Os] was measured with respect to the catalyst concentration in Nf membrane). Typical CVs in a high catalyst concentration are shown in Fig. 5. It was noted that the catalytic currents decrease with increasing the concentration. Moreover, part of the reoxidation peak of Os^{II} noticeably appeared especially in the higher concentration ((b) in Fig. 5). These voltammetric behaviors evidently show that the electrocatalysis by the Nf[Os] is lowered in the region of high catalyst concentrations. In Fig. 6, the relationship between the catalytic currents ($-I_{\text{cat}}$) for O_2 reduction (at -0.15 V) and the catalyst concentration is summarized. The $-I_{\text{cat}}$ initially increased with the increase of catalyst concentration (region I). However, as indicated in Fig. 5, a downward dependence of the $-I_{\text{cat}}$ on the concentration was found above 0.2 mol dm^{-3} (region II). In the following part, the details for the present catalysis will be discussed on kinetic aspects.

The overall kinetics in molecule-based catalysis reaction is often affected by electron propagation via catalyst

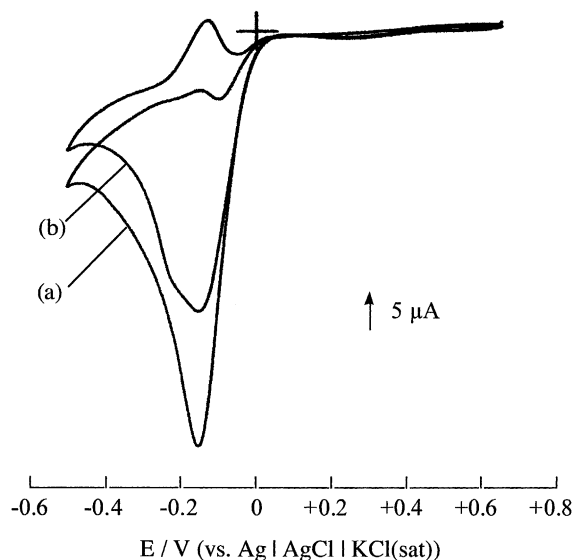


Fig. 5. CV at BPG/Nf[Os] in high catalyst concentrations (under O_2)—scan rate, 5 mV s^{-1} ; complex concentration in Nf membrane: (a) $2.1 \times 10^{-1} \text{ mol dm}^{-3}$; (b) $4.0 \times 10^{-1} \text{ mol dm}^{-3}$.

molecule through matrix [21–23]. Therefore, the heterogeneous electrocatalysis should be discussed in combination with the electroreduction process of the Os^{III} complex. The potential-step chronoamperometry was carried out at BPG/Nf[Os] according to Cottrell's equation (Eq. (2)) [24,25] based on a semi-infinite diffusion process:

$$j = -\frac{nFc(D_{app})^{1/2}}{(\pi t)^{1/2}} \quad (2)$$

where D_{app} ($\text{cm}^2 \text{ s}^{-1}$) is the apparent diffusion coefficient of the electron, j (A cm^{-2}) the current density, n the number of electron (present case, 1), c the total concentration of the Os complex in the polymer membrane, and F is the Faraday's constant ($9.65 \times 10^4 \text{ C mol}^{-1}$). The electron propagation

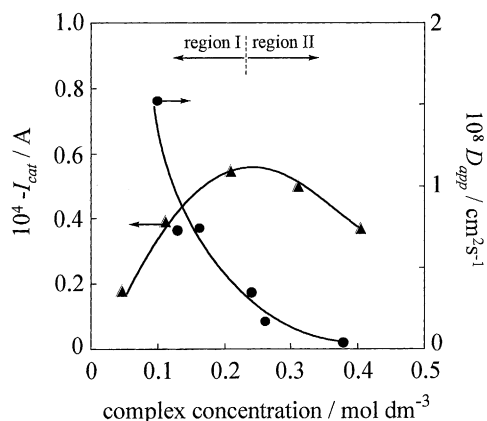


Fig. 6. Dependence of both $-I_{cat}$ (▲) and D_{app} (●) on the complex concentration. As for the latter, the chronoamperometry to obtain the $j-t^{-1/2}$ plot was carried out by stepping the potential from $+0.3$ to -0.5 V (under Ar). The $-I_{cat}$ values were obtained by measuring a similar CV to Figs. 1(b) and 5.

was studied by potential-steps from $+0.3$ to -0.5 V under Ar. The relationship between j and $t^{-1/2}$ was linear and applicable to the Cottrell's equation. From the slope, D_{app} value was estimated as a function of the complex concentration. As also shown in Fig. 6, the D_{app} value decreased with increasing the concentration. Such a dependence of D_{app} on concentration means that electron transport by a molecule takes place not by a hopping mechanism but by a physical diffusion mechanism [26]. We have experienced some examples concerning the downward dependence of D_{app} on concentration in electron reduction process [14,21–23,27]. The decline of the D_{app} is attributable to the effect that the diffusion of the complex is prohibited by increasing the concentration. However, in the course of the electron transport analysis in Fig. 6, it was found that the slope obtained from the j versus $t^{-1/2}$ plot (Cottrell's plot) increases with the total concentration, implying that the effective concentration essentially increases with the total one. Therefore, the present characteristic for the electron transport probably suggests that the ratio of the electroactive amount to the total one decreases with increasing the total concentration.

Finally, the characteristics of the present catalysis are discussed based on the result of Fig. 6. In order to achieve the selective and direct H_2O formation by the Os complex, it is of essence that the electrocatalysis reaction involving reductive cleavage of the $O=O$ bonding takes place by a bimolecular process. Although the active species ($Os^{III/II}$ complex) migrates during the electroreduction, the electrochemically generated Os^{II} species can be electrostatically concentrated in a hydrophilic column composed of sulfonic ion groups on the side chain of the Nf, and consequently, the catalytically active species is presumably oriented on the polymer side chain. On that occasion, a dimeric intermediate formation ($Os^{III} \cdots O_2^{2-} \cdots Os^{III}$) between adjacent Os^{II} species and an O_2 molecule through electrostatic interaction would be possible followed by further reduction. In the region II, the dependence of $-I_{cat}$ on the concentration is similar with D_{app} , showing that in such conditions the electrocatalysis is kinetically dominated by the electroreduction process of the Os complex. The markedly slow electron transport, attributable to the presence of a number of molecules not to participate in diffusion, kinetically affects the following steps (i.e. formation of the intermediate and succeeding reduction into H_2O (vide supra)), which would consequently lead to the appearance of reoxidation peak of the catalytically active species on the CVs of Fig. 5. In the region I, the $-I_{cat}$ shows an upward dependence on the concentration in spite of the decline of the D_{app} . Fig. 6 may suggest that the electroreduction process is the rate-determining step over the whole concentration region. The region I would be the condition that the D_{app} is not so small as the electroreduction process completely dominates the electrocatalysis, so that a bimolecular catalysis for O_2 reduction by the Os complexes could efficiently take place in that region.

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