Activity Analysis of $[(NH_3)_5RuORu(NH_3)_5]^{5+}$ Confined in a Coated-Polymer Membrane for Electrochemical Water Oxidation

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ABSTRACT: The activity of the electrochemical water oxidation catalyst, $[(NH_3)_5RuORu(NH_3)_5]Cl_5$, incorporated in an electrode-coated Nafion membrane was studied. The turnover number (TN) of the catalyst increased with the increase of its concentration in the membrane in low concentration regions because of facilitated charge transfer between the catalysts, while that decreased with the concentration in high concentration regions because of bimolecular decomposition of the catalyst. An activity model for the electrochemical catalyst in a membrane was applied based on intermolecular distance distribution, and the activity was analyzed in terms of a charge transfer distance (r_0/nm) and a critical decomposition distance (r_d/nm); their values were obtained as 1.14 nm and 1.09 nm, respectively. The activity was compared with other complexes. It was elucidated that the activity of the catalysts increased with the number of the metal ion present in one molecule.
KEY WORDS   Water Oxidation Catalyst / Artificial Photosynthesis / Ruthenium Complex / Nafion Membrane /

It is attractive to apply a functionalized polymer membrane containing nano-structured redox centers to sensors, energy conversion devices and electrocatalysis.[1-4] The subjects to be solved for developing polymer membranes with high performance are the arrangement of activity centers in a nano meter scale and its activity analysis in the polymer membrane. We have been investigating an artificial photosynthetic system by using a polymer membrane dispersing redox centers as an energy conversion device since the global environment and energy resource problems are becoming serious. In the photosynthesis water oxidation is one of the most important reactions that provides electrons to the whole system. The development of an active synthetic catalyst has been difficult since it is a 4-electrons reaction to evolve one O_2 molecule from two water molecules. We have been studying water oxidation catalysts, and found that $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$ called Ru-red is a very active catalyst.[1,2,5]

Our research on water oxidation was carried out by chemical and electrochemical methods.[1,2] The former method uses Ce^{4+} as oxidant as shown in Scheme 1, and the latter uses an electrode coated with a polymer membrane dispersing redox centers. It was shown that one molecule of Ru-red oxidizes two water molecules to evolve one O_2 molecule by a 4e⁻ process. However, the activity decreased with increasing the catalyst concentration, which was explained by bimolecular decomposition at high concentrations. We have successfully shown that it is of importance to fix them for instance in a polymer matrix so as to prevent contact with each other since bimolecular decomposition depends on the intermolecular distance between the catalyst molecules. It was found that bimolecular decomposition could be suppressed by incorporating the catalyst in a polymer membrane or other matrices and by controlling the intermolecular distance in a nanometer scale. In such an electrocatalytic system using a polymer-coated electrode, it is important to convey charges from the electrode to the catalyst molecule, which often takes place by charge hopping between the molecules.[6-12]

Such charge hopping can take place only within a distance between the two molecules. Therefore, it is important to arrange the catalyst molecules to have a proper distance between the neighboring molecules both for retarding bimolecular decomposition and for facilitating charge hopping between the molecules.

Now, investigation of the catalytic activity of a dinuclear Ru complex, $[(NH_3)_5RuORu(NH_3)_5]Cl_5$ (abbreviated to Ru-2) is of great interest and importance for understanding the effect of the polynuclear structure. For instance, if coordination of two water molecules to adjacent Ru metal ions in a polymer complex is most essential for one O_2 evolution by one catalyst molecule, the activity of Ru-red and Ru-2 might not differ much. The activity of the water oxidation catalyst, Ru-2, will be studied electrochemically in the present paper. The activity will be investigated in terms of intermolecular distance distribution that ranges in a nanometer scale. The activity of various oxidation catalysts will also be compared.
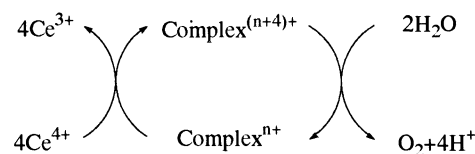
Scheme 1.

Analysis of Charge Propagation and Catalytic Activity

Charge transport in a polymer membrane containing redox molecules coated on an electrode is divided into two mechanisms. One is a charge hopping mechanism that takes place by self-exchange of the charges between the two redox centers[6-12], and the other is physical diffusion of the redox centers in the polymer matrix.[13] Dahms and Ruff reported the relation between these two mechanisms and an apparent diffusion coefficient.[14,15] The charges are mainly transported by physical diffusion of redox centers in a solution, since the physical diffusion of redox centers is very fast. We can neglect the contribution by charge hopping in a solution.

However, the physical diffusion of redox centers in a

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polymer membrane is much slower in comparison with a solution system. When redox centers are fixed to the polymer chain either by a covalent bond, coordination bond or by strong electrostatic binding, physical diffusion can be neglected, so that charge propagation in the polymer matrix is predominated by a charge hopping mechanism.
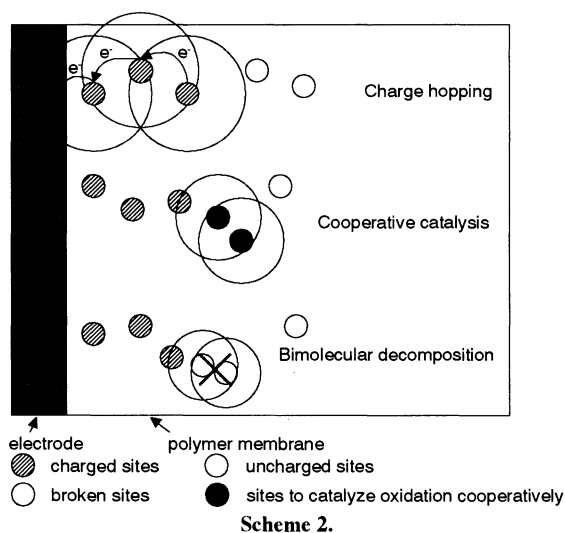
Saveant et al. derived the relation between an apparent diffusion coefficient and charge hopping distance.[16,17] The present authors analyzed a charge hopping distance based on the probability of distance distribution between the nearest-neighbor molecules by measuring the fraction of the charge transported (R_{CT}).[6-12] In analyzing the activity of the catalysts confined in a polymer membrane, the concept of the intermolecular distance is also important since the charges should at first be transported to the catalyst molecule. When bimolecular decomposition of the catalysts occurs in high concentrations, not only charge transfer but also bimolecular decomposition are important which depend on the intermolecular distance if the catalysts are immobilized in the membrane.[1,2,5,18]

Further, we found another important factor when the activity of [Ru(NH$_3$)$_5$Cl]$^+$ for water oxidation was investigated. This catalyst oxidized two water molecules cooperatively by two molecules. Such a cooperative catalysis depends also on the intermolecular distance between the catalysts. These factors are shown in Scheme 2.

The probability density $P(r)$ in a Poisson distribution is represented by the following equation:[6,7,19,20]

$$P(r) = 4\pi r^2 N_A \alpha c \times 10^{-24} \exp[-4\pi(r^3 - s^3)N_A \alpha c \times 10^{-24}/3] \quad (1)$$

where c (moldm^{-3}) is the concentration of the complex in the membrane, N_A is the Avogadro's number, r (nm) is the distance between the nearest neighboring molecules, α is the degree of the localization of the catalyst (in the present Nafion membrane estimated as 5.1)[7], and s (nm) represents the contact distance between the complexes. As an example of the probability distribution of the nearest neighbor molecules, refer Figure 4 mentioned later. The complexes present within the decomposition distance (r_d) do not work as a catalyst when the catalyst molecules are fixed in the matrix. Only the complexes located between the bimolecular decomposition distance(r_d) and the charge hopping distance (r_{co}) can work as a catalyst.

electrode   polymer membrane
▨ charged sites   ◯ uncharged sites
◯ broken sites   ● sites to catalyze oxidation cooperatively

Scheme 2.

EXPERIMENTAL

Materials

[Ru(NH$_3$)$_5$ORu(NH$_3$)$_5$]Cl$_5$ was prepared according to the procedures reported elsewhere.[21] An Nafion 117 solution (5 wt % alcohol solution) was purchased from Aldrich Chemical Co. Inc. and diluted to 2.5 wt % with methanol before use.

Preparation of Nafion Membrane Incorporating Ru-2

A Nafion membrane (thickness ca. 3 μm) was first prepared by casting 30 mm^3 of a 2.5 wt % Nafion solution onto a platinum plate electrode (1 x 1 cm^2). The Nafion membrane coated on a Pt electrode was immersed in a catalyst aqueous solution to adsorb the complex. The modified electrode was abbreviated to Pt/Nf[Ru-2]. The amount of the complex in the membrane was estimated from the absorption spectral change of the aqueous solution before and after the adsorption. The complex concentration was obtained from the amount of the complex in the membrane and the membrane volume.

Measurements

An electrochemical study was carried out by using a potentiostat (Fuso Seisakujo, 1100L) with a function generator (Fuso Seisakujo, 1104), a coulomb meter (Hokuto Denko, HF-201) and an X-Y recorder (Rikadenki, RW-21). A single compartment electrochemical cell was equipped with a modified working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode. A supporting electrolyte solution (pH 5.4) of 0.1 moldm^{-3} potassium nitrate was deaerated by bubbling an argon gas stream for 1 h. Dioxygen (O$_2$) evolved in a potentiostatic electrolysis was analyzed by a Shimadzu GC-4A gas chromatograph equipped with a 5 Å (1 Å =0.1nm) molecular sieve column using an Ar carrier gas.

RESULT AND DISCUSSION

Figure 1 shows a cyclic voltammogram of Ru-2 in a 0.1 M (1 M = 1 mol dm^{-3}) KNO$_3$ aqueous solution. An irreversible oxidation wave was observed around 1.1 V (vs. Ag/AgCl) followed by an increase of anodic current due to catalytic water oxidation.

The activity of Ru-2 incorporated in the membrane for O$_2$ evolution is shown in Figure 2 as a function of the applied potential. The amount of O$_2$ evolved was higher in the presence of the catalyst than that in its absence at higher potentials than 1.3 V (vs. Ag/AgCl). It shows for example that half of the O$_2$ is evolved via the catalyst at 1.4 V (vs. Ag/AgCl). The mechanism of water oxidation in Nafion membrane does not differ from that in aqueous solution because the complex was adsorbed in hydrophilic region of Nafion membrane.[1]

The plot of the catalyst turnover number (TN) for the O$_2$ evolution vs. the catalyst concentration in the membrane is shown in Figure 3. Although the plots are scattered, the TN increased with the concentration in low concentration regions and then exhibits an optimum point around 0.15 M followed by a decrease with the increase of the concentration. This behavior of Ru-2 resembled with that of
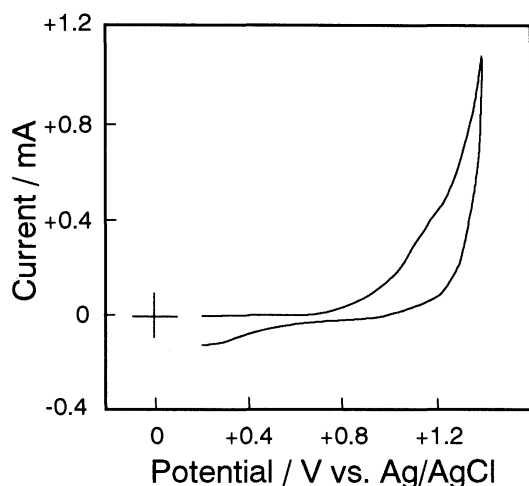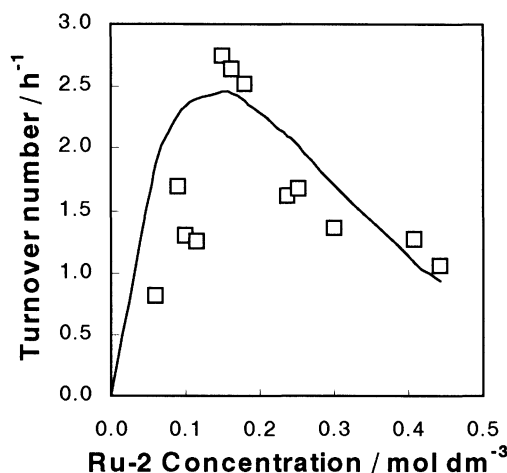
Figure 1. Cyclic voltammogram of Pt/Nf[Ru-2] electrode at a scan rate 20 mV/s in 0.1 mol dm^{-3} KNO$_3$ aqueous solution in the potential region from 0.2 V (vs. Ag/AgCl) to 1.4 V (vs. Ag/AgCl).
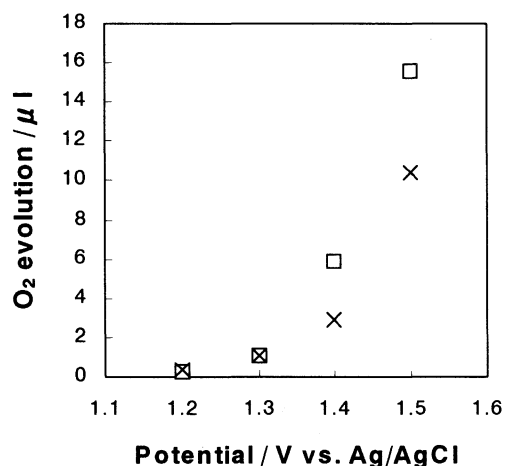

Figure 2. Relationship between the amount of O$_2$ evolved and applied potential in a potentiostatic electrolysis for 1 h in 0.1 M KNO$_3$ (pH 5.5). □,Pt/Nf[Ru-2]; ×,blank Pt/Nf.

Figure 3. Dependence of turnover number(TN) of the catalyst for O$_2$ evolution by Pt/Nf[Ru-2] on the catalyst concentration in potentiostatic electrolysis for 1h at 1.4 V(vs.Ag/AgCl). The curve is the best fitted one according to eq. (5).
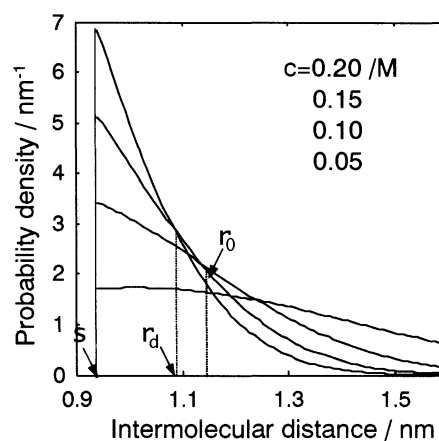
Figure 4. Intermolecular distance distribution of Ru-2 between the nearest-neighbor molecules for various concentrations. s is the contact distance between the catalysts, r_0 is the charge transfer distance, and r_d is the critical decomposition distance between the catalysts.

Ru-red.[2] It was shown that two water molecules were oxidized with one Ru-2 molecule using Ce^{IV+} as an oxidant in our previous research.[22] Therefore, the increase of the activity in the low concentration regions can be ascribed to charge propagation taking place by a charge hopping mechanism. The decrease of the activity in the high concentration regions can be explained by bimolecular decomposition because dinitrogen evolution could be observed similarly to Ru-red using Ce^{IV+} as an oxidant. We could not observe nitrogen evolution in the present system owing to the slower reaction rate than Ru-red.

Such charge propagation and bimolecular decomposition should depend on the intermolecular distance, since the complex is immobilized in the polymer membrane. In a random dispersion, the distance distribution between the nearest-neighbor molecules is represented by eq. 1 as mentioned before. For the s value (contact distance), the diameter (s = 0.94 nm) of a sphere, which has the same volume (0.43 nm^3) as the Ru-2 molecule (approximated as a cylinder of diameter 0.75 nm and 1.12 nm length) was adopted.[21]

According to eq.1, the probability distribution curves of Ru-2 as a function of the nearest neighboring intermolecular distance are depicted in Figure 4. We can assume now that the Ru-2 molecules existing between the charge hopping distance (r_0) and the critical decomposition distance (r_d) are able to catalyze water oxidation. The fraction of the complex able to transport charges is expressed by eq. 2.[1,2]

$$R_{CT} = \int_s^{r_0} P(r)dr = 1 - \exp(-4\pi(r_0{}^3 - s^3)\alpha c N_A \times 10^{-24}/3) \quad (2)$$

The fraction of the complex decomposing bimolecularly is expressed by eq. 3.

$$R_{dec} = \int_s^{r_d} P(r)dr = 1 - \exp(-4\pi(r_d{}^3 - s^3)\alpha c N_A \times 10^{-24}/3) \quad (3)$$

This equation does not take account of the orientation between the complexes on assuming that the orientation of the complex in Nafion membrane is averaged. The turnover number (TN) of the complex for O$_2$ evolution can be expressed by eq. 4,

$$TN = k_{O_2}(R_{CT} - R_{dec}) \quad (4)$$

Table I. Comparison of parameters for various ruthenium complexes

	k_{O2} /h⁻¹	r_O /nm	r_{co} /nm	r_d /nm	Molecular size /nm
[(NH₃)₅RuORu(NH₃)₄ORu(NH₃)₅]⁶⁺ (Ru-red)²⁾	54.8	1.28	-	1.21	1.40 / s=1.06 / 0.75
[(NH₃)₅RuORu(NH₃)₅]⁵⁺ (Ru-2)	18.5	1.14	-	1.09	1.12 / =0.94 / 0.75
Ru(NH₃)₅Cl	6.7	-	1.26	0.82	=0.75 / 0.75

where k_{O2}/h⁻¹ is a constant to express the intrinsic activity (TN) of the catalyst. Eq. 5 is obtained from eqs. 2-4.

$$TN = k_{O_2}[\exp\{-4\pi(r_d^3 - s^3)\alpha cN_A \times 10^{-24}/3\} -$$

$$\exp\{-4\pi(r_0^3 - s^3)\alpha cN_A \times 10^{-24}/3\}] \qquad (5)$$

We applied eq. 5 to analyze the data in Figure 4 using a nonlinear least-squares method[2], and the best fitting was obtained when k_{O2}=18.5 h⁻¹, r_0=1.14 nm and r_d=1.09 nm.

The r_d value (1.09 nm) is reasonable considering the molecular size (0.94 nm). It is suggested that bimolecular decomposition occurs between the complexes in close proximity with each other. The difference between the r_0 and r_d values is very small showing that a delicate condition exists to construct an efficient and stable artificial photosynthetic oxygen evolving center model.

The various catalysts parameters estimated in our laboratory are summarized in Table I as a comparison. First of all, the catalytic activity becomes higher with the number of metal centers in one molecule. It shows that it is advantageous as an oxygen evolving catalyst to have many metal centers in one molecule. Before the present analysis it was inferred that the activity of Ru-2 and Ru-red might not differ much if only the coordination of two water molecules to one catalyst molecule is an essential factor. However, the activity of Ru-red and Ru-2 differed substantially. This indicates that water oxidation is controlled not by coordination of water to the catalysts but by a thermodynamic factor. It is well known that four electron oxidation of water is most advantageous thermodynamically.[23] It is required that the oxidation number of the Ru atom becomes high to oxidize water by four electrons with one molecule. It was reported that [(bpy)₂(OH₂)RuORu(H₂O)(bpy)₂]⁴⁺ complex known as the water oxidation catalyst becomes Ru^V-O-Ru^V from Ru^{III}-O-Ru^{III}. The polynuclear structure would facilitate delocalization of the charges on the catalyst and therefore stabilize high oxidation state of the catalyst.[23,24]

When comparing the charge hopping (r_0) and decomposition distances (r_d) of the catalysts, these distances are longer for the complex comprising more metal centers. These values are reasonable when considering the molecular size.

CONCLUSION

We have analyzed the activity of the Ru-2 as the electrochemical water oxidation catalyst based on the intermolecular distance distribution. It was shown that the activity becomes higher in order of the number of Ru atoms present in one molecule, and that there is a correlation between the molecular size and the distance of both charge hopping and critical decomposition. It was suggested that the polynuclear structure containing more metal centers might enable us to make more active catalyst for water oxidation.

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