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Analysis of Water Oxidation Catalysis by Dinuclear Ruthenium Complex $[(NH_3)_5Ru–O–Ru(NH_3)_5]^{4+}$ Incorporated in a Nafion® Membrane

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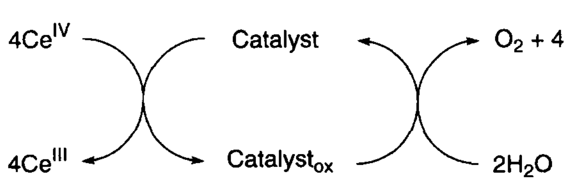
Catalytic activity of a dinuclear ammine ruthenium complex, $[(NH_3)_5Ru–O–Ru(NH_3)_5]^{4+}$, for water oxidation to evolve O_2 was investigated both in homogeneous aqueous solution and in heterogeneous Nafion® membrane systems using Ce^{IV} oxidant. It was suggested that the complex works as a four-electron water oxidation catalyst and that the water oxidation by the complex is in competition with a bimolecular decomposition between the complexes. The first-order rate constant (k_{O_2} (s^{-1})) for O_2 evolution and second-order rate constant (k_{deact} (M^{-1} s^{-1})) for bimolecular decomposition were obtained by a kinetic analysis. It was found that k_{deact} decreased by one order of magnitude by incorporating the complex in the membrane; this was ascribed to the suppression of the bimolecular decomposition. The critical decomposition distance (r_d (nm)) between the catalysts was analyzed to be 1.06 nm based on an intermolecular distance distribution.

Heterogeneous polymer membrane systems incorporating functional molecules such as a sensitizer,[1] redox center,[2,3] probe,[4] and catalyst[5—8] have been extensively studied for designing molecule-based photoelectric devices.[9] It is important to elucidate the factors affecting functions of the molecule and to derive an activity model involving these factors in order to optimize the functions of the molecule-based devices.

Water oxidation catalyst is one of the interesting candidates as a functional molecule because water oxidation is not only a fundamental catalysis process in nature, but is also important in photochemical solar energy conversion systems.[10] Many heterogeneous water oxidation catalyst systems have been reported.[11—13] However, there has been no report on an activity model, in which the factors affecting the catalyst activity are evaluated and involved in the theoretical equation, except our reports.[8,14,15]

We have reported heterogeneous water oxidation catalyses by mononuclear ruthenium complexes, $[Ru(NH_3)_5Cl]^{2+}$[14a] and $[Ru(NH_3)_6]^{3+}$[14b], and a trinuclear ruthenium complex, Ru-red ($[(NH_3)_5Ru–O–Ru(NH_3)_4–O–Ru(NH_3)_5]^{6+}$)[15] using Ce^{IV} oxidant as shown in Scheme 1. It is of great interest to analyze the catalyst activity of a dinuclear ruthenium complex for water oxidation and to compare it with the mono- and trinuclear ruthenium complexes reported earlier[14,15] for designing an active and stable molecule-based catalyst. In the present work, $[(NH_3)_5Ru–O–Ru(NH_3)_5]^{4+}$ ($RuORu^{4+}$) was found to be an active 4-electron water oxidation catalyst. The activity of the $RuORu^{4+}$ catalyst in a Nafion® membrane will be analyzed based on intermolecular distance distribution, and the effect of the multinuclear structure on multi-electron behavior will be presented.



Scheme 1. Chemical water oxidation catalysis.

Experimental

Materials and Preparation. $[(NH_3)_5Ru–O–Ru(NH_3)_5](PF_6)_4$ complex was prepared according to the procedure of Meyer et al.[16] by oxidation of $[Ru(NH_3)_5H_2O](PF_6)_2$ using $LiClO_4$ as oxidant in acetone containing $[N(n\text{-}C_4H_9)_4](PF_6)$. Cerium(IV) diammonium nitrate was purchased from Wako Pure Chemical Industries, and $[Ru(NH_3)_5Cl]Cl_2$ and Nafion® 117 membrane (thickness 180 μm) from Aldrich Chemical Co. Inc..

Preparation of Nafion Membrane Incorporating $RuORu^{4+}$. Nafion® membrane was sufficiently swollen by soaking in distilled water for ca. 24 h. The swollen membranes were immersed in aqueous complex solutions (3 ml) with different concentrations for ca. 5 h to incorporate the complex into the membrane by cation exchange. The theoretical cation-exchange capacity of the Nafion® membrane is estimated to be 3.5×10^{-1} mol dm^{-3} for the $RuORu^{4+}$ with four valence since the concentration of sulfonate group in a Nafion® membrane is reported to be 1.4 mol dm^{-3}.[15] The degree of cation-exchange by the $RuORu^{4+}$ was calculated to be 0.26—33% under the present concentration conditions. The complex amount in the membrane was estimated from the absorbance change of the aqueous solution before and after adsorption of the complex. The complex concentration in the membrane was calculated from the complex amount and the membrane volume before swelling. The complex incorporated in the membrane was not dissolved into water during catalysis using Ce(IV) oxidant.

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Measurements. In a homogeneous aqueous solution system, excess $Ce(NH_4)_2(NO_3)_6$ oxidant (6.0×10^{-3} mol) was added quickly to 5.0×10^{-5}—9.0×10^{-3} M complex aqueous solution (5.0 ml) in a reaction vessel (1 M = 1 mol dm^{-3}). In the heterogeneous Nafion® membrane system, the membrane (1.1×10^{-4} dm^3) that incorporated 1.0×10^{-7}—1.25×10^{-5} mol complex was put into pure water in a reaction vessel, and excess Ce^{IV} oxidant (4.0×10^{-3} mol) was added quickly. In both the systems, the atmosphere in the reaction vessel was replaced with argon gas before adding the Ce^{IV} oxidant. For all the experiments, the vessel was kept at 25 °C. The pH was 0.43 without any buffer under the whole complex concentration range under the typical conditions, and the pH change was less than 0.03 before and after the O_2 evolution experiment. The O_2 evolved was analyzed on a gas chromatograph equipped with a molecular sieve 5A column using argon carrier gas (flow rate is 40 ml min^{-1}) at 50 °C. The sensitivity and accuracy of gas chromatography are 100 ppm and ±1%, respectively, and ca. 1 μl of O_2 evolved is exactly detected under the present conditions. O_2 from atmospheric contamination can be negligible because O_2 and N_2 were not at all detected in control experiments without the catalyst. In the present system, bubbles of O_2 can be observed.

Results and Discussion

A typical time dependence of the amount of O_2 evolved in the Nafion® membrane system is shown in Fig. 1. The O_2 evolved increased linearly with time at the initial stage (up to ca. 45 min) as shown in the inset of Fig. 1, and then gradually declined but did not saturate even after 8 h. The initial O_2 evolution rate (V_{O_2} (mol s^{-1})) was obtained from the initial slope.

When assuming that 4-electron water oxidation to evolve O_2 is catalyzed by one molecule of the complex which has 4-electron oxidation ability, the overall O_2 evolution consists of oxidation of the $(\text{catalyst})_{\text{red}}$ (the reduced form of catalyst) by the 1-electron Ce^{IV} oxidant (Eq. 1) and 4-electron water oxidation by one $(\text{catalyst})_{\text{ox}}$ (their oxidized form) (Eq. 2).

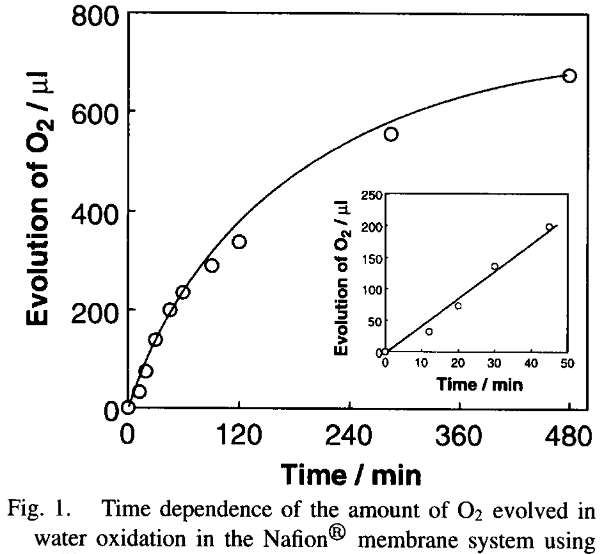

Fig. 1. Time dependence of the amount of O_2 evolved in water oxidation in the Nafion® membrane system using Ce^{IV} oxidant. The inset shows the data in the initial stage. The amounts of catalyst and oxidant are 5.0×10^{-7} mol and 4.0×10^{-3} mol, respectively, in 10.0 cm^3 water. Membrane volume, 1.1×10^{-4} dm^3.

$$4Ce^{IV} + (\text{catalyst})_{\text{red}} \xrightarrow{k_{\text{OX}}} 4Ce^{III} + (\text{catalyst})_{\text{ox}}. \tag{1}$$

$$(\text{catalyst})_{\text{ox}} + 2H_2O \xrightarrow{k_{O_2}} O_2 + 4H^+ + (\text{catalyst})_{\text{red}}. \tag{2}$$

The O_2 evolution rate is given by the Eq. 3 using a steady-state method when assuming that the reaction rate in Eq. 1 is expressed by k_{OX} $[Ce^{IV}]^4$ [catalyst];[15]

$$\frac{d[O_2]}{dt} = (V_{O_2}/v) = \frac{k_{O_2}k_{\text{OX}}[Ce^{IV}]^4[\text{catalyst}]}{k_{\text{OX}}[Ce^{IV}]^4 + k_{O_2}} = \frac{k_{O_2}[\text{catalyst}]}{1 + k_{O_2}/(k_{\text{OX}}[Ce^{IV}]^4)}, \tag{3}$$

where v (dm^3) is the aqueous solution volume or membrane volume, k_{OX} (M^{-4} s^{-1}) and k_{O_2} (s^{-1}) are the rate constant for the reaction in Eq. 1 and the pseudo first order rate constant for the reaction in Eq. 2, respectively.

The V_{O_2} increased with the increase in the Ce^{IV} concentration, and then was saturated beyond ca. 100 molar ratio of Ce^{IV}/complex. The almost constant V_{O_2} value saturated beyond this molar ratio of Ce^{IV}/complex shows that the term $k_{O_2}/(k_{\text{OX}}\,[Ce^{IV}]^4)$ is negligible in the Eq. 3, i.e., the value of $k_{\text{OX}}\,[Ce^{IV}]^4$ is large enough in comparison with the k_{O_2} value, so that the reaction in Eq. 2 is a rate determining-step for O_2 evolution under the large excess Ce^{IV} conditions. Therefore, V_{O_2} at a large excess of Ce^{IV} oxidant (beyond ca. 100 of the molar ratio of Ce^{IV}/complex) is given as

$$\frac{d[O_2]}{dt} = (V_{O_2}/v) = k_{O_2}[\text{catalyst}], \tag{4}$$

showing that the V_{O_2} is first order with respect to the complex concentration according to Eq. 4 under the large excess Ce^{IV} conditions. All the O_2 evolution experiments were carried out under the conditions of a large excess Ce^{IV} oxidant (the molar ratio of Ce^{IV}/complex was at least 130).

The plots of V_{O_2} vs. complex concentration in the aqueous solution and membrane systems are shown in Fig. 2 (a) and (b), respectively. These plots increased with the concentration, then exhibited an optimum V_{O_2}, and thereafter decreased with the concentration. These plots gave a linearity at low concentrations for both the systems, as shown in the insets of Fig. 2 (a) and (b), showing that water oxidation is first order with respect to the complex concentration. The k_{O_2} values in the present aqueous solution and membrane systems were estimated as 1.5×10^{-2} s^{-1} and 1.3×10^{-2} s^{-1}, respectively, from the slope in the insets of Fig. 2 (a) and (b) according to Eq. 4, showing that the intrinsic catalytic activity in the membrane is almost the same as the aqueous solution system.

We have studied the water oxidation catalyses by various mono- and multinuclear complexes. In the $[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{6+}$ system,[15] the plots of V_{O_2} vs. complex concentration at low concentrations gave a linear relationship under the conditions of much excess Ce^{IV} oxidant, while in the mononuclear complex systems such as $[Ru(NH_3)_5Cl]^{2+}$[14a] and $[Ru(NH_3)_6]^{3+}$[14b], these plots gave clearly second-order dependency with respect to the complex concentration. This indicates that even in the presence of much excess of Ce^{IV}, the mechanism is reflected in the dependency of V_{O_2} on the catalyst concentration. It is

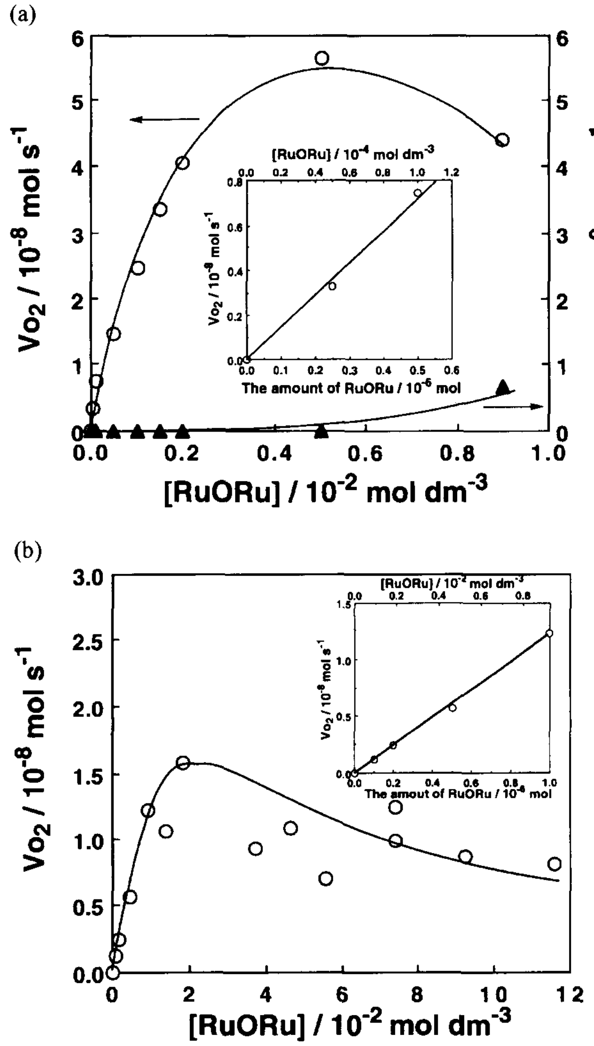

Fig. 2. (a) Dependencies of initial O_2 evolution rate, V_{O_2} (mol s^{-1}), (○) and N_2 evolution rate, V_{N_2} (mol s^{-1}), (▲) on complex concentration in aqueous solution system. The inset shows data in low concentration regions. liquid volume, 5.0 cm^3; Ce^{IV}, 6.0×10^{-3} mol. (b) Dependence of initial O_2 evolution rate, V_{O_2} (mol s^{-1}), (○) on complex concentration in Nafion® membrane system. The inset shows data in low concentration regions. Membrane volume, 1.1×10^{-4} dm^3; Ce^{IV}, 4.0×10^{-3} mol in 10.0 cm^3 water.

reasonable, based on the redox reactions of these complexes, that the difference in the concentration dependencies of V_{O_2} is explained by the difference in the ability of catalytic water oxidation (4- or 2-electron oxidation). Most probably, the linear plots of V_{O_2} vs. complex concentration in the insets of Fig. 2 (a) and (b) would show that the present dinuclear complex works as a 4-electron oxidation catalyst. Multinuclear structure must be an important factor to construct a four-electron water oxidation catalyst.

The active species might be Ru^V–Ru^V in the 4-electron water oxidation by one molecule. The redox reaction of RuORu^{4+} was reported by Meyer to indicate the reversible redox of RuORu^{4+}/RuORu^{5+} at 0.32 V (vs. saturated sodium chloride calomel electrode) and irreversible further oxidation to RuORu^{6+} at 1.67 V in the cyclic voltammogram (CV) of RuORu^{4+} in an acetonitrile solution, though the second oxidation is not well-defined.[16] In our earlier report on the CV of a Nafion® membrane-coated Pt electrode incorporating RuORu^{5+} in the potential range of 0.2 V to 1.4 V vs. Ag/AgCl, no redox response other than an unclear irreversible oxidative wave at 1.1 V could be observed before the increased catalytic current on water oxidation.[17] We have reported the CV of a Nafion® membrane-coated ITO electrode incorporating $[Ru(NH_3)_5Cl]^{2+}$ in which two oxidative peaks at 1.06 and 1.28 V vs. SCE (1.30 and 1.52 V vs. NHE) were observed based on Ru^{III}/Ru^{IV} and Ru^{IV}/Ru^V, respectively.[18] Since the real redox potential (in the order of 1.6 V) of the Ce^{IV}/Ce^{III} under the present conditions is higher than that (1.52 V vs. NHE) of Ru^{IV}/Ru^V, it is possible that the Ru^V state of $[Ru(NH_3)_5Cl]^{2+}$ is formed by a Ce^{IV} oxidant. The potential for forming the Ru^V–Ru^V state of the present RuORu^{4+} is considered, at least, to be lower than that of Ru^{IV}/Ru^V in $[Ru(NH_3)_5Cl]^{2+}$ because of the delocalization of charges, and therefore, the Ru^V–Ru^V state is possible to be formed in the present system.

N_2 was evolved at high concentrations only in the aqueous solution system (Fig. 2(a)). Since no N_2 was detected in an aqueous solution containing the same amount of Ce^{IV} without the complex, this N_2 evolved can result only from the oxidation of the ammine ligands of the catalyst. V_{N_2} is second order with respect to the complex concentration (Fig. 2(a)), showing that bimolecular decomposition of the complexes takes place as described in Eq. 5,

$$2(\text{catalyst})_{\text{ox}} \xrightarrow{k_{\text{deact}}} (\text{decomposed products}), \tag{5}$$

where k_{deact} (M^{-1} s^{-1}) represents the second-order rate constant for the bimolecular decomposition. This will be supported by a kinetic analysis described later.

In order to analyze the catalyst activities in the aqueous solution and membrane systems, an apparent first-order rate constant of O_2 evolution (k_{app} (s^{-1})) was defined as

$$k_{\text{app}} = V_{O_2}/n_{\text{Ru}}, \tag{6}$$

where n_{Ru} (mol) is the amount of the complex. The comparison of k_{app} between the aqueous solution and membrane systems is possible based on the dependencies of k_{app} on the catalyst concentration as shown in Fig. 3. In both the aqueous solution and membrane systems, the k_{app} decreased with the increase of the catalyst concentration. However, decreasing tendency of the k_{app} is much lower for the membrane system than for the aqueous solution, which can be ascribed to stabilization of the catalyst against bimolecular decomposition due to adsorption of the complex in the membrane.

On the basis of the consideration that the first-order water oxidation by the high oxidation state complex (Eq. 2) is in competition with the bimolecular decomposition of the complex (Eq. 5), Eq. 7 was derived to analyze k_{app};[15]

$$k_{\text{app}}^{-1} = 1/k_{O_2} + (k_{\text{deact}}/k_{O_2}^2)[\text{RuORu}]. \tag{7}$$

According to Eq. 7, plots of k_{app}^{-1} vs. [RuORu] are shown

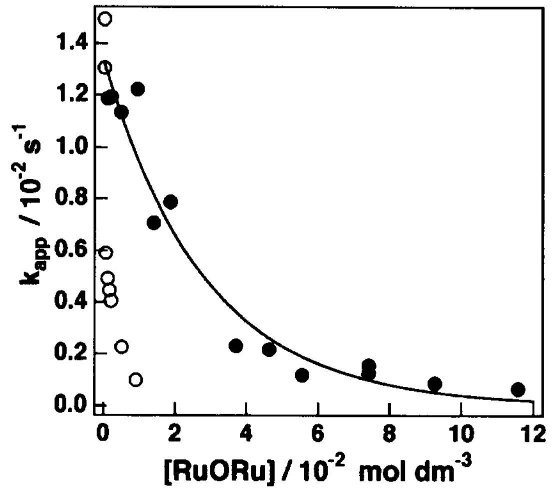

Fig. 3. Relationship between apparent catalytic activity (k_{app} (s^{-1})) and complex concentration in the aqueous solution (○) and the membrane systems (●). The solid line is the calculated curve based on Eq. 8.

in Fig. 4 for the aqueous solution and membrane systems. They show linear relationships, supporting the competition between the first-order O_2 evolution and the bimolecular decomposition. The k_{O_2} and k_{deact} for both the aqueous solution and membrane systems were obtained from the intercept and slope of the straight lines in the Fig. 4, respectively. These values are listed in Table 1. The k_{O_2} values in both the systems are almost the same as those obtained from the initial slope in the insets of Fig. 2 (a) and (b), respectively. The k_{deact} value in the membrane system is lower than that in the aqueous solution system by one order of magnitude. In the present system, the cationic complex is electrostatically attached to anionic sulfonate groups on the Nafion® chain, so that there is a strong restriction for the complex to move from site-to-site in the membrane, although smaller counter cations can move in the membrane. The bimolecular decomposition was suppressed by the restriction to result in a much lower k_{deact} value in the membrane system. This also shows that free diffusion of the catalyst is prohibited in the matrix. Therefore, the bimolecular decomposition could be analyzed by a static mechanism rather than a dynamic one which involves diffusion and collision of the complex in the membrane.

We have reported that the catalytic activity of a molecule-based catalyst in a polymer membrane can be analyzed by using intermolecular distance distribution.[14,15] When assuming that the catalysts existing within a critical decomposition distance, r_d (nm), undergo a bimolecular decomposition, k_{app} is represented by Eq. 8 :

$$k_{app} = k \times \exp\{-4\pi(r_d^3 - s^3)\alpha c N_A \times 10^{-24}/3\}, \qquad (8)$$

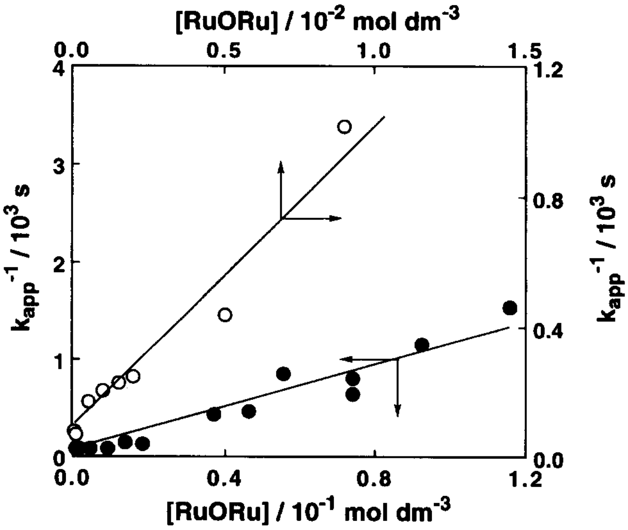

Fig. 4. Plots of k_{app}^{-1} versus catalyst concentration in the aqueous solution (○) and the membrane systems (●) according to Eq. 7.

Table 1. Rate Constants k_{O_2} and k_{deact} Obtained from Fig. 4 and Eq. 7

System	k_{O_2} / 10^{-2} s^{-1}	k_{deact} / dm^3 mol^{-1} s^{-1}
Aqueous solution	1.3 (1.5)[a]	20.7
Nafion® membrane	1.3 (1.3)[a]	1.9

[a] Obtained from inset of Fig. 2 (a) and (b).

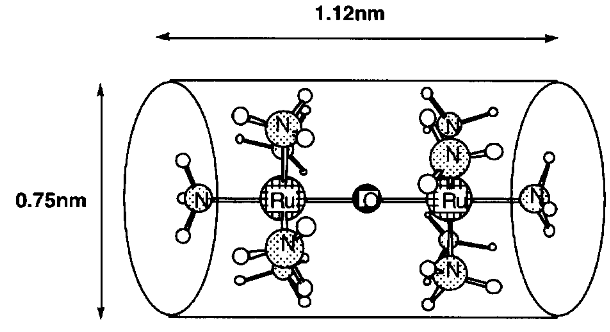

Fig. 5. Steric chemical structure and molecular size of $RuORu^{4+}$ complex.

Table 2. Values of Intrinsic Activity k and Critical Decomposition Distance r_d for Various Ammine Ruthenium Complexes as Water Oxidation Catalyst Incorporated into a Nafion® Membrane

Catalyst	k / 10^{-2} s^{-1}	r_d / nm	s / $nm^{a)}$	Mechamism	Reference
$[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$ (Ru-red)	4.4	1.23	1.06	4-Electron oxidation	Ref. 14
$[(NH_3)_5RuORu(NH_3)_5]^{4+}$	1.3	1.06	0.98	4-Electron oxidation	Present system
$[Ru(NH_3)_5Cl]^{2+}$	0.27	0.84	0.75	2-Electron oxidation	Ref. 15

a) Molecular diameter approximated as a sphere.

where k (s^{-1}), s (nm), α, c (mol dm^{-3}) and N_A (mol^{-1}) are an intrinsic activity of the catalyst, contact distance (0.98 nm) between the complexes, localization degree (40)[15] of the complex in the Nafion® membrane, complex concentration in the membrane and Avogadro's number, respectively. This s value was tentatively taken as the radius of a sphere which has the same volume as the complex volume with a cylindrical form (see Fig. 5) in the same way as in our earlier paper.[15] The exponential term of Eq. 8 expresses the fraction of the complex which does not undergo the bimolecular decomposition. Equation 8 was applied to the plots of k_{app} vs. c for the membrane system in Fig. 3 using a nonlinear least-square method, and the best fitting was obtained when k and r_d values were 1.3×10^{-2} s^{-1} and 1.06 nm, respectively. The k is the same as the k_{O_2} (1.3×10^{-2} s^{-1}) value calculated from the initial slope in the inset of Fig. 2(b).

The k and r_d values[14,15] in various ammine ruthenium complexes/Nafion® membrane are shown in Table 2. The order of the catalytic activity is as follows; Ru-red > $RuORu^{4+} \gg [Ru(NH_3)_5Cl]^{2+}$. The k_{O_2} values of di- and trinuclear complexes are remarkably larger than that of the mononuclear complex. These multinuclear complexes are highly active catalysts most probably because they could work as four-electron water oxidation catalyst, while the mononuclear complex needs two molecules for O_2 evolution. Multinuclear structure is important for constructing efficient artificial molecule-based catalysts. Further, the trinuclear complex is more active than $RuORu^{4+}$, suggesting that it is capable of forming a highly oxidized intermediate compared with that of $RuORu^{4+}$ due to delocalization of the charges. The order of r_d is as follows: Ru-red > $RuORu^{4+} > [Ru(NH_3)_5Cl]^{2+}$. This result is reasonable because this order is the same as that of the molecular size of the complex and the r_d values are close to the molecular size. This supports that static bimolecular decomposition takes place between the neighboring complexes in the membrane. It is important to separate the distance between the catalysts over 1.06 nm for the $RuORu^{4+}$ in the Nafion® membrane.

Conclusion

Catalytic water oxidation activity based on a dinuclear ruthenium complex, $[(NH_3)_5Ru–O–Ru(NH_3)_5]^{4+}$, was studied in a homogeneous aqueous solution and heterogeneous Nafion membrane using Ce^{IV} oxidant. It was suggested that the complex works as a four-electron water oxidation catalyst and the water oxidation by the complex is in competition with a bimolecular decomposition between the complexes. The second-order rate constant (k_{deact} (M^{-1} s^{-1})) for bimolecular decomposition decreased by one order of magnitude by incorporating the complex in the membrane, showing that the bimolecular decomposition is remarkably suppressed due to adsorption in the Nafion® membrane. The intrinsic catalytic activity (k (s^{-1})) and critical decomposition distance (r_d (nm)) of the complex in the membrane system were analyzed based on intermolecular distance distribution, and compared with those of mono- and trinuclear complexes. It was found that multinuclear structure is an important factor for an active artificial water oxidation catalyst. Control of the intermolecular distance between the complexes is important to optimize the water oxidation catalysis in the membrane.

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