

# Cooperative Catalysis and Critical Decomposition Distances between Molecular Water Oxidation Catalysts Incorporated in a Polymer Membrane

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Activity of a pentaamminechlororuthenium(III) ( $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ ) complex as a water oxidation catalyst was investigated in a homogeneous aqueous solution (AS) as well as in a heterogeneous Nafion membrane (HM). In the AS, the apparent catalytic activity ( $k_{\text{app}}/\text{s}^{-1}$ ) decreased monotonically with the concentration. In competition with water oxidation catalysis, dinitrogen ( $\text{N}_2$ ) evolution by oxidation of its ammine ligands was also observed, whose rate is second order with respect to its concentration, showing that a bimolecular decomposition of the complexes takes place at high concentrations. The bimolecular decomposition was suppressed remarkably by incorporating the complex into a HM. In the HM,  $k_{\text{app}}$  increased with the catalyst concentration at low concentrations below  $1.5 \times 10^{-2}$  M, indicating that four-electron water oxidation is cooperatively catalyzed by two complex molecules. The  $k_{\text{app}}$  was strikingly higher for HM than for AS in the whole concentration range, which was ascribed to both a favorable interaction for the cooperative catalysis and the suppression of the bimolecular decomposition by immobilization of the complex. The effect of intermolecular distance distribution of the complex in the membrane on  $k_{\text{app}}$  was analyzed in terms of cooperative catalysis distance ( $r_{\text{co}}/\text{nm}$ ) and critical decomposition distance ( $r_{\text{d}}/\text{nm}$ ) to give  $r_{\text{co}} = 1.21$  nm and  $r_{\text{d}} = 0.84$  nm. The  $r_{\text{co}}$  value obtained might suggest cooperative catalysis through hydrogen bonds between water and ammine ligands.

## Introduction

The activity of a molecule-based catalyst in heterogeneous matrixes such as clays,<sup>1</sup> ion-exchange resins,<sup>2–4</sup> intercalation compounds,<sup>5</sup> inorganic particles,<sup>6</sup> and polymer membranes<sup>7–10</sup> has been studied extensively for the application of the catalyst to practical use including fundamental research in electrochemistry and photochemistry. To optimize the catalysis, it is important to study factors affecting the activity and stability and to establish activity models involving these factors. Water oxidation is one of the most important fundamental reactions in nature.<sup>11a</sup> Many heterogeneous water oxidation catalyst systems have been reported.<sup>11b–d</sup> However, there has been no report on an activity model in a heterogeneous water oxidation catalysis except our earlier work on a trinuclear Ru complex confined onto Pt black<sup>6</sup> or in a Nafion membrane.<sup>7,8</sup>

In our earlier work,<sup>7</sup> a trinuclear ruthenium complex, Ru-red ( $[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{6+}$ ), which is capable of four-electron water oxidation by one catalyst molecule, underwent a bimolecular decomposition to deactivate at high concentrations in a homogeneous aqueous solution. However, the bimolecular decomposition was remarkably suppressed by incorporating the catalyst into a Nafion membrane. The catalyst activity and stability in the membrane were analyzed in terms of a critical decomposition distance ( $r_{\text{d}}/\text{nm}$ ) between the catalysts based on intermolecular distance distribution.

We have reported<sup>12</sup> that a mononuclear ruthenium complex,  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ , works as a water oxidation catalyst in both homogeneous aqueous solution and heterogeneous clay suspension systems. We have proposed that four-electron water oxidation is cooperatively catalyzed by two complex molecules, which is a two-electron oxidation catalyst based on  $\text{Ru}^{\text{III/IV}}$  oxidation states.<sup>12</sup> However, detailed studies on its activity as

a heterogeneous catalyst have remained open. In the present paper, the activity of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  in a Nafion membrane as a water oxidation catalyst is studied and its activity model proposed based on its intermolecular distance distribution. The effect of immobilization of the complex into a polymer membrane on its catalytic activity will be discussed.

## Experimental Section

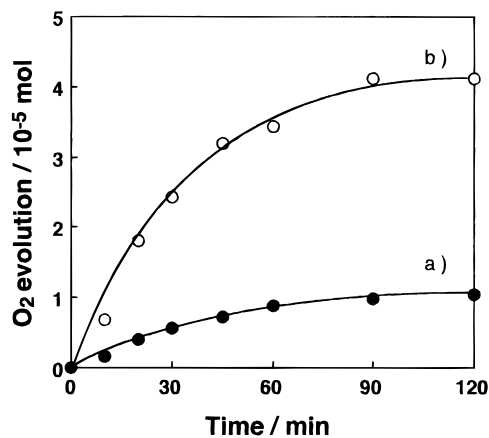
**Materials.** Pentaamminechlororuthenium(III) dichloride,  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2\text{Cl}_2$ , and a Nafion 117 membrane (thickness of 180  $\mu\text{m}$ ) were purchased from Aldrich Chemical Co. Inc. Cerium(IV) diammonium nitrate,  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ , was purchased from Wako Pure Chemical Industries Ltd. All the materials were of commercially available purest grade and used as received.

**Preparation of a Nafion Membrane Incorporating  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ .** The swollen membrane was immersed in a  $2.4 \times 10^{-4}$  to  $8.0 \times 10^{-3}$  M complex aqueous solution (5 mL) for ca. 5 h so that the complex is incorporated into the membrane by cation exchange.<sup>7</sup> The complex amount in the membrane was estimated from the decrease of the complex concentration in its aqueous solution, i.e., the absorbance change (at 328 nm) of the aqueous solution before and after adsorption of the complex. The membrane volume was estimated from the area and thickness (180  $\mu\text{m}$ ). The complex concentration in the membrane was calculated from the complex amount and the membrane volume.

**Dioxygen Evolution.** In a homogeneous aqueous solution (AS) system, excess  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  oxidant ( $6.0 \times 10^{-3}$  mol) was added quickly to  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-2}$  M complex aqueous solution (5.0 mL) in a reaction vessel. In the heterogeneous Nafion membrane (HM) system, the membrane ( $2.0 \times 10^{-4}$  mol) that incorporated  $1.0 \times 10^{-6}$  to  $4.0 \times 10^{-5}$  mol of the complex was put into pure water in a reaction vessel, and excess  $\text{Ce}^{\text{IV}}$  oxidant ( $6.0 \times 10^{-3}$  mol) was added quickly. In both the systems, the atmosphere in the reaction vessel was

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**Figure 1.** Time dependence of  $\text{O}_2$  evolved in (a) AS and (b) HM. The amounts are the following: complex,  $5 \times 10^{-6}$  mol;  $\text{Ce}^{\text{IV}}$  oxidant,  $6 \times 10^{-3}$  mol; membrane volume,  $2.0 \times 10^{-4}$  dm<sup>3</sup>; solution volume,  $1 \times 10^{-2}$  dm<sup>3</sup>.

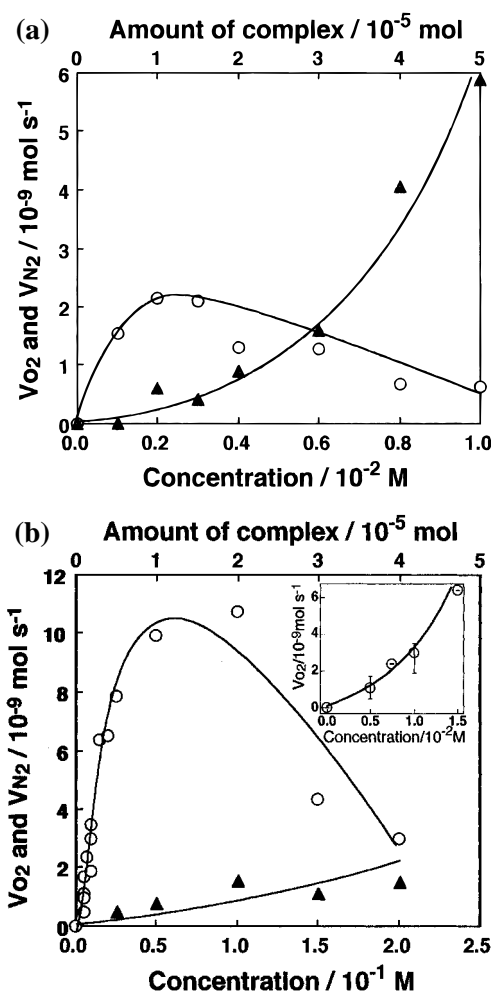
replaced with argon gas before the  $\text{Ce}^{\text{IV}}$  oxidant was added. For all the experiments, the vessel was kept at 25 °C. The pH during experiments is  $0.43 \pm 0.03$  without any buffer. The  $\text{O}_2$  evolved was analyzed on a gas chromatograph equipped with a 5 Å molecular sieve column using argon carrier gas (flow rate is 40 mL min<sup>-1</sup>) at 50 °C.

## Results and Discussion

The dependencies of the amount of  $\text{O}_2$  evolved on reaction time are shown in Figure 1 for the AS and HM systems. The amount of  $\text{O}_2$  evolved was remarkably higher for the HM than for the AS despite the same complex amount in the reaction system. The relationship between the initial  $\text{O}_2$  evolution rate ( $V_{\text{O}_2}/\text{mol s}^{-1}$ ) and the catalyst concentration in the AS is shown in Figure 2a.  $V_{\text{O}_2}$  increased with the concentration at low concentrations, a maximum  $V_{\text{O}_2}$  was exhibited at  $2.0 \times 10^{-3}$  M, and then it decreased with the concentration. Dinitrogen ( $\text{N}_2$ ) evolution was observed over  $2.0 \times 10^{-3}$  M. This  $\text{N}_2$  can result only from oxidation of the ammine ligands of the complex, since no  $\text{N}_2$  was detected without  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ . The initial  $\text{N}_2$  evolution rate,  $V_{\text{N}_2}/\text{mol s}^{-1}$ , is second order with respect to the complex concentration, indicating a bimolecular decomposition of the complexes. The  $V_{\text{O}_2}$  decrease at higher concentrations is ascribable to the decomposition.

The plots of  $V_{\text{O}_2}$  and  $V_{\text{N}_2}$  versus the complex concentration in the HM are shown in Figure 2b. The  $V_{\text{O}_2}$  value for the HM is much higher than that for the AS in the whole concentration range. The  $V_{\text{O}_2}$  increased with the concentration at low concentrations as shown in the inset of Figure 2b and decreased at high concentrations after passing a maximum value. The  $V_{\text{O}_2}$  at low concentrations was second order with respect to complex concentration, indicating that  $\text{O}_2$  evolution is a bimolecular reaction of the complex. The complex  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  could work only as a two-electron oxidant, since the maximum valence state of Ru is V in a usual case. Actually, we observed two oxidation waves at 1.06 and 1.28 V vs SCE in the cyclic voltammogram (CV) of a Nafion-coated graphite electrode incorporating  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ ,<sup>12b</sup> showing also that the complex acts as a two-electron oxidation catalyst.

The standard redox potential (1.77 V vs NHE) of  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  for producing  $\text{H}_2\text{O}_2$  from water is higher than that (1.71 V) of  $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ . To further investigate both potentials in the present Nafion membrane system, we analyzed the cyclic voltammograms of  $\text{H}_2\text{O}_2$  and  $\text{Ce}^{\text{IV}}$ . The potential (1.04 vs SCE) at the current rise using the Nafion-coated electrode was almost same as that (1.02 vs SCE) using the naked electrode, showing that



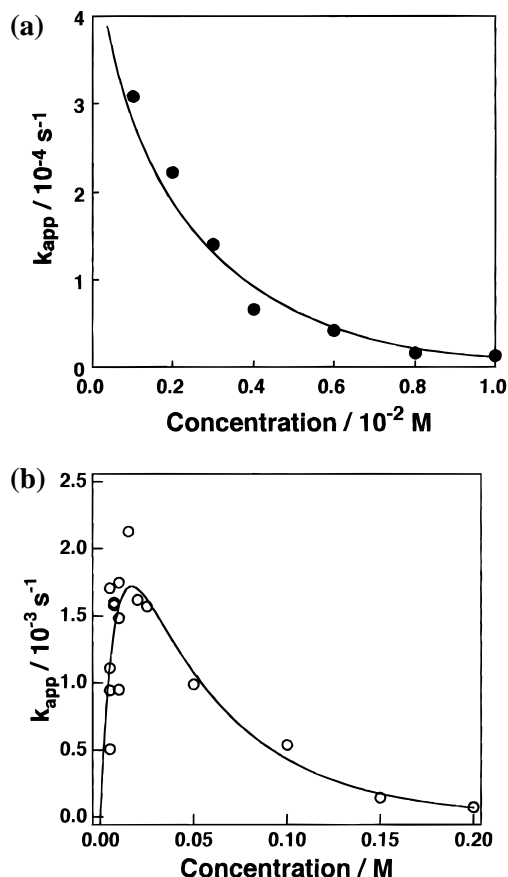
**Figure 2.** (a) Plots of the rates of gas evolution ( $V_{\text{O}_2}(\bigcirc)$  and  $V_{\text{N}_2}(\blacktriangle)$ ) versus complex concentration and complex amount for the AS. The amounts are the following:  $\text{Ce}^{\text{IV}}$  oxidant,  $6 \times 10^{-3}$  mol; solution volume,  $5 \times 10^{-3}$  dm<sup>3</sup>. (b) Plots of the rates of gas evolution ( $V_{\text{O}_2}(\bigcirc)$  and  $V_{\text{N}_2}(\blacktriangle)$ ) versus complex concentration and complex amount for the HM. The inset illustrates the plots at low concentrations. The amounts are the following:  $\text{Ce}^{\text{IV}}$  oxidant,  $6 \times 10^{-3}$  mol; membrane volume,  $2.0 \times 10^{-4}$  dm<sup>3</sup>; liquid-phase volume,  $5 \times 10^{-3}$  dm<sup>3</sup>.

the redox potential of  $\text{O}_2/\text{H}_2\text{O}_2$  in the Nafion membrane is almost the same as that in an aqueous solution. Considering this result, we could expect that the redox potential of  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  in the membrane would not be appreciably different from that in an aqueous solution. On the other hand, the potential of  $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$  under the present conditions was 1.53 V vs NHE (pH = 0.43), which is much smaller than the redox potential (1.74 V vs NHE, pH 0.43) of  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ . Thus, the potential of  $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$  would not be sufficient to oxidize water to  $\text{H}_2\text{O}_2$  under the present conditions. Therefore, it is most probable that four-electron oxidation to produce  $\text{O}_2$  (the standard redox potential is 1.23 V vs NHE) rather than the two-step oxidation process to produce  $\text{H}_2\text{O}_2$  takes place in the present system.

The bimolecular decomposition of the complex is also observed to take place in HM at high concentrations. However, the  $\text{N}_2$  evolution is suppressed to a great extent in comparison with the AS, and the concentration for the maximum  $V_{\text{O}_2}$  is ca. 50 times as high as that for the AS.

To study the catalysis in the present system, the apparent catalyst activity ( $k_{\text{app}}/\text{s}^{-1}$ ), which means turnover number of the catalyst, was defined as

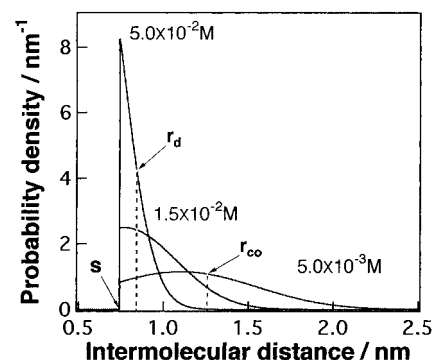
$$k_{\text{app}} = V_{\text{O}_2}/m_{\text{Ru}}$$



**Figure 3.** (a) Relationship between  $k_{app}$  and complex concentration in the AS. (b) Relationship between  $k_{app}$  and complex concentration in the HM. The curve shows a calculated value based on eq 4.

where  $m_{Ru}/\text{mol}$  is the amount of the complex present in the reaction system either in the solution or in the membrane. The complex incorporated in the membrane is not desorbed into the water. Therefore,  $m_{Ru}$  in HM is the complex amount in the membrane, and  $m_{Ru}$  in AS is the complex amount in the aqueous solution. The dependencies of  $k_{app}$  on the complex concentration for the AS and HM are shown in parts a and b of Figure 3, respectively. In the AS,  $k_{app}$  decreased monotonically with the concentration, which is ascribed to a bimolecular decomposition of the complex. On the other hand, in the HM, the  $k_{app}$  increased with the concentration when the concentration is low and decreased with the concentration after passing a maximum value ( $1.5 \times 10^{-2} \text{ M}$ ). Two molecules of the complex are required for this catalysis (vide supra). The increase of  $k_{app}$  with the concentration in the initial stage can be explained by a cooperative catalysis by two molecules of the complex. An isolated complex in the membrane could not work for this cooperative catalysis. As the complex concentration increases, the fraction of the adjacent complexes capable of cooperative catalysis increases to result in the  $k_{app}$  increase. When the concentration increases further, the fraction of the complex that undergoes a bimolecular decomposition would increase to result in the  $k_{app}$  decrease. In the Nafion/Ru-red system reported by us earlier,<sup>7</sup> four-electron water oxidation is catalyzed by one catalyst molecule but bimolecular decomposition of the catalyst takes place at high concentrations so that  $k_{app}$  for HM decreased monotonically with the concentration.

The  $k_{app}$  values for the HM are much higher than those for the AS in the whole concentration range (compare parts a and b of Figure 3); the  $k_{app}$  value in HM is higher by 140 times than that in AS at the same complex concentration ( $1.0 \times 10^{-2} \text{ M}$ ). The diffusion of the complex is suppressed by incorporat-



**Figure 4.** Intermolecular distance distribution between the nearest-neighbor molecules for the various concentrations according to eq 1.  $s$ ,  $r_d$  and  $r_{co}$  are contact distance, critical decomposition distance, and cooperative catalysis distance between the catalysts, respectively.

ing it into the membrane, which is favorable for a cooperative catalysis, and also decreases the bimolecular decomposition, leading to the higher  $k_{app}$  values for the HM. In the Nafion/Ru-red system where a bimolecular decomposition is also suppressed, the  $k_{app}$  values for the AS and HM are very close to each other at low concentrations.<sup>7</sup> However, in the present Nafion/[Ru(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> system, the  $k_{app}$  value at low concentrations is much higher in the HM than in the AS. This cannot be explained merely by suppression of the bimolecular decomposition; favorable interaction of the complex in the membrane for the cooperative catalysis must be an important factor. The complex concentration in the membrane under the present experimental conditions is much higher than that in aqueous solution so that most complexes are close to each other, making cooperative catalysis possible. The fixed catalysts in the membrane are favorable for cooperative catalysis. Complexes interacting via two water molecules would form an intermediate in this cooperative catalysis. The intermediate would be stabilized thermodynamically by immobilization of the complex in the membrane to increase the catalytic activity.

Both the cooperative catalysis and the bimolecular decomposition in the membrane strongly depend on the intermolecular distance between the complexes. It is important to take the intermolecular distance distribution of the complex into account rather than the average intermolecular distance. We do not think that the catalysts interact directly with each other. They can work cooperatively only with coordinated two-water molecules bridging the catalysts only when the complex is oxidized by Ce<sup>IV</sup>. If they directly cooperate before oxidation, they undergo bimolecular decomposition after oxidation by Ce<sup>IV</sup>. Therefore, the uptake of the catalyst that is carried out before adding Ce<sup>IV</sup> should be on a molecular level. Therefore, a random distribution of the complex in the membrane was assumed in the following analysis. In a random dispersion, an intermolecular distance distribution between the nearest-neighbor complexes in the membrane is given by the following equation<sup>6-8,13-16</sup>

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

where  $P(r)/\text{nm}^{-1}$ ,  $N_A/\text{mol}^{-1}$ ,  $c/\text{mol dm}^{-3}$ ,  $r/\text{nm}$ ,  $s/\text{nm}$ , and  $\alpha$  are the probability density, Avogadro's number, complex concentration in the membrane, the distance between the nearest-neighbor molecules, contact distance between them, and the degree of localization of the complex in the membrane, respectively. The complex was approximated as a sphere, and its diameter ( $0.75 \text{ nm} = s$ ) was calculated from the distance and the angle of the atoms (Ru-N, 0.210 nm; N-H, 0.101 nm;  $\angle \text{H-N-Ru}$ ,  $110^\circ$ )<sup>17</sup> as well as the van der Waals radius (0.12

nm) of hydrogen. In the present system where the complex is adsorbed from its solution into a preformed membrane, the complex can be present only in hydrophilic regions of the membrane to result in localization of the complex.<sup>15</sup> The degree ( $\alpha$ ) of this localization was estimated as 40,<sup>7</sup> meaning that the fraction of the hydrophilic region where the complex is present is 2.5% of the total membrane volume.

The intermolecular distance distribution for various complex concentrations is depicted in Figure 4 according to eq 1. It is assumed now that the cooperative catalysis can take place only within a cooperative catalysis distance ( $r_{co}/nm$ ) and that the complexes present within a critical decomposition distance ( $r_d/nm$ ) undergo a bimolecular decomposition. Then the fraction of the complex that works as a cooperative catalyst ( $R_{co}$ ) and the fraction that undergoes a bimolecular decomposition ( $R_{dec}$ ) are expressed as follows:

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

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

The fraction of the effective complex for water oxidation is given by ( $R_{co} - R_{dec}$ ). The  $k_{app}$ , which should be proportional to ( $R_{co} - R_{dec}$ ), is therefore given by eq 4:

$$k_{app} = k_{O_2}(R_{co} - R_{dec}) = k_{O_2}[\exp\{-4\pi(r_d^3 - s^3)\alpha c N_A \times 10^{-24}/3\} - \exp\{-4\pi(r_{co}^3 - s^3)\alpha c N_A \times 10^{-24}/3\}] \quad (4)$$

where  $k_{O_2}/s^{-1}$  is a constant to express an intrinsic catalytic activity of the complex for the cooperative catalysis.

Equation 4 was applied to the relationship between  $k_{app}$  and concentration in Figure 3b using the nonlinear least-squares method. The best fitting was obtained as shown in the curve of Figure 3b when  $k_{O_2} = 2.7 \times 10^{-3} s^{-1}$ ,  $r_d = 0.84$  nm, and  $r_{co} = 1.21$  nm. This good fitting of eq 4 that assumes random distribution of the complex in the membrane supports the idea that this treatment is reasonable. The  $r_d$  value (0.84 nm) is reasonable when considering the molecular size (0.75 nm) of  $[Ru(NH_3)_5Cl]^{2+}$ , showing that the bimolecular decomposition takes place between the complexes in proximity to each other. The  $r_{co}$  value (1.21 nm) is larger than the calculated distance (0.58 nm) between the Ru centers in a presumed Ru—O—O—Ru intermediate binding (Ru—O, 0.214 nm;<sup>18</sup> O—O, 0.148 nm<sup>17</sup>). Two kinds of interpretations might be possible for this. One is that water-coordinated high oxidation state complexes move from their anchored positions in the membrane<sup>14,19,20</sup> (so-called bounded motion) to make the real interacted distance much shorter ( $\sim 0.58$  nm). We have reported that the bounded motion of the tris(2,2'-bipyridine)ruthenium(II) complex confined in a Nafion membrane is estimated as 0.3–0.6 nm.<sup>14,20</sup> Another interpretation is possible by considering a new mechanism for water coordination. Namely, water is not coordinated directly to the Ru center but interacts with ammine ligands through hydrogen bonds to form an intermediate such as Ru—N—H $\cdots$ O—O $\cdots$ H—N—Ru. The distance between the Ru centers in this bonding is estimated to be ca. 1.1 nm using the distance and the angle of the atoms (H $\cdots$ O, 0.279 nm;  $\angle$ N—H $\cdots$ O and  $\angle$ H $\cdots$ O—O, 180°; vide supra). This distance is close to the estimated  $r_{co}$  value (1.21 nm), suggesting a possible mechanism of a cooperative catalysis taking place through

hydrogen bonds between water and ammine ligands. Actually, we have found that the hexaammineruthenium(III) complex can also catalyze water oxidation to give O<sub>2</sub>.<sup>21</sup> Since the Ru—ammine binding is substitution-unlabile, this result might suggest the possibility of the latter ammine—water interaction mechanism rather than the former bounded motion mechanism.

## Conclusion

The activity of a mononuclear ruthenium complex ( $[Ru(NH_3)_5Cl]^{2+}$ ) as a water oxidation catalyst was studied in a homogeneous aqueous solution (AS) and a heterogeneous Nafion membrane (HM). A bimolecular decomposition of the complex was marked at high concentrations in the AS. This bimolecular decomposition was remarkably suppressed by incorporation into a Nafion membrane. An optimum complex concentration for the apparent catalyst activity ( $k_{app}/s^{-1}$ ) in the HM was exhibited, which was explained by both a bimolecular decomposition and a cooperative catalysis by two complex molecules. The  $k_{app}$  was remarkably higher in the HM than in the AS, which is ascribable to a favorable interaction for the cooperative catalysis by the immobilization of the complex as well as to the suppression of a bimolecular decomposition in the HM. The  $k_{app}$  for the HM was analyzed in terms of a cooperative catalysis distance ( $r_{co}/nm$ ) and a critical decomposition distance ( $r_d/nm$ ) based on the intermolecular distance distribution, and  $r_d = 0.84$  nm and  $r_{co} = 1.21$  nm were obtained. It was suggested that the cooperative catalysis takes place through hydrogen bonds between water and ammine ligands.

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