Analysis of Catalytic Water Oxidation by *cis*-Tetraamminedichlororuthenium(III) Complex Incorporated in a Polymer Membrane

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cis-Tetraamminedichlororuthenium(III) (*cis*-$[Ru(NH_3)_4Cl_2]^+$) complex was found to work as a very active water oxidation catalyst to evolve dioxygen (O_2) in an aqueous solution as well as in a Nafion membrane. The initial O_2 evolution rate (V_{O_2} (mol s^{-1})) was first-order with respect to the complex concentration in both the solution and membrane. The catalyst undergoes a bimolecular decomposition to deactivate at high complex concentrations. The first-order rate constant (k_{O_2} (s^{-1})) for O_2 evolution and the second-order rate constant (k_{deact} (dm^3 mol^{-1} s^{-1})) for bimolecular decomposition were obtained from the kinetic analysis based on the competition between both processes. The k_{O_2} (1.4×10^{-2} s^{-1}) in the Nafion membrane is much higher than that (2.3×10^{-3} s^{-1}) in the solution. The k_{deact} (5.1×10^{-1} dm^3 mol^{-1} s^{-1}) in the membrane was slightly higher than that (2.0×10^{-1} dm^3 mol^{-1} s^{-1}) in the solution. The catalytic activity in the Nafion membrane was analyzed in terms of the intrinsic activity (k_{O_2} (s^{-1})) and critical decomposition distance (r_d (nm)) on the basis of the intermolecular distance distribution to obtain $k_{O_2} = 1.5 \times 10^{-2}$ s^{-1} and $r_d = 0.88$ nm. The k_{O_2} was compared with the earlier results on $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5Cl]^{2+}$; the k_{O_2} of the complexes was in the order *cis*-$[Ru(NH_3)_4Cl_2]^+ > [Ru(NH_3)_5Cl]^{2+} > [Ru(NH_3)_6]^{3+}$. The structural effect on the catalytic activity was discussed.

Introduction

Water oxidation to evolve dioxygen (O_2) catalyzed at the oxygen-evolving center (OEC) in photosynthesis is one of the most important and fundamental chemical processes in nature.[1,2] Electrons are provided to the whole photosynthetic system by this process, which is the origin of all the biological activities. It is important to investigate molecule-based water oxidation catalysts[3−10] not only for understanding and simulating photosynthetic OEC but also for constructing an artificial photosynthesis which is attracting a great deal of interest for the conversion of solar energy into fuels.[11−13]

Analysis of the catalytic activity involving factors which affect the activity and stability of the catalyst is important to evaluate its intrinsic activity as well as to optimize the catalysis. However, there have been only a few reports on activity analyses of molecule-based water oxidation catalysts except our earlier works.[6−9]

We have studied water oxidation catalyses by mononuclear ammine−ruthenium complexes, $[Ru(NH_3)_6]^{3+}$ [7] and $[Ru(NH_3)_5Cl]^{2+}$,[8] both of which work as a 2-electron oxidation catalyst and catalyze 4-electron water oxidation by two complex molecules. The intrinsic activity of the $[Ru(NH_3)_5Cl]^{2+}$ was higher than that of $[Ru(NH_3)_6]^{3+}$ by 2 orders of magnitude.[7] This intrinsic activity increased on substitution by a chloro ligand, which gave an important suggestion for the design of more active molecule-based catalysts and encouraged us to study the water oxidation catalysis by a *cis*-tetraamminedichlororuthenium(III) complex (*cis*-$[Ru(NH_3)_4Cl_2]^+$). In the present paper, it is found that *cis*-$[Ru(NH_3)_4Cl_2]^+$ works as a very active water oxidation catalyst in an aqueous solution as well as Nafion membrane, and its catalytic activity will be analyzed to discuss

the structural effect on the catalysis compared with $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5Cl]^{2+}$.

Experimental Section

Materials. *cis*-$[Ru(NH_3)_4Cl_2]Cl$ was synthesized and purified as described elsewhere.[14] A Nafion 117 membrane (thickness 180 μm) was purchased from Aldrich Chemical Co. Inc., and cerium(IV) diammonium nitrate 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 *cis*-[Ru-(NH$_3$)$_4$Cl$_2$]$^+$. Nafion membrane was swollen sufficiently by soaking in pure water for ca. 24 h. The swollen membrane was immersed in a 5.0×10^{-6} to ~8.0×10^{-3} mol dm^{-3} (M) complex aqueous solution (5 cm^3) for ca. 5 h so that the complex was incorporated into the membrane by cation exchange. The complex amount in the membrane was estimated from the absorbance change at 352 nm (molar absorption coefficient (ϵ) = 1600 M^{-1} cm^{-1}) 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.

Dioxygen Evolution. In a homogeneous aqueous solution system, excess Ce^{IV} oxidant (6.0×10^{-3} mol) was added quickly to 0 to ~1.5×10^{-2} M complex aqueous solution (5.0 cm^3) in a reaction vessel. In a heterogeneous Nafion membrane system, the membrane (membrane volume 2.0×10^{-4} dm^3) that incorporated 0 to ~3.7×10^{-5} mol of complex was put into pure water (5.0 cm^3) in a reaction vessel, and excess Ce^{IV} oxidant (6.0×10^{-3} mol) was added quickly. In both systems, the atmosphere in the reaction vessel was replaced with argon gas before the Ce^{IV} oxidant was added. For all the experiments, the vessel was kept at 25 °C. The O_2 evolved was analyzed on
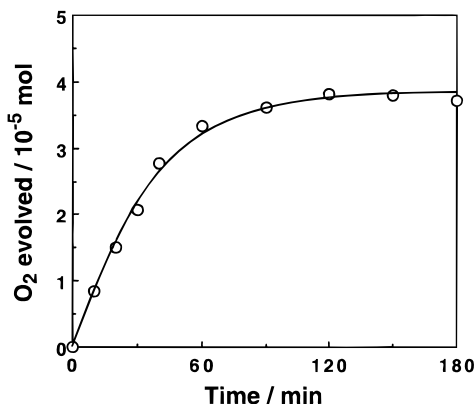
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Figure 1. Change of the amount of O_2 evolved in water oxidation using Ce^{IV} oxidant in an aqueous solution. The amounts of complex and oxidant are 5.0×10^{-6} and 6.0×10^{-3} mol in 5 cm^3 of water, respectively.

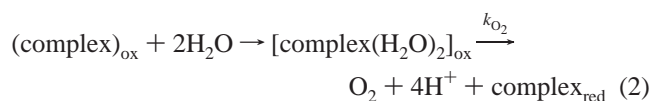a gas chromatograph equipped with a 5 Å molecular sieve column using argon carrier gas (flow rate 40 cm^3 min^{-1}) at 50 °C.

Results and Discussion

O_2 bubbles were observed when a large excess of a Ce^{IV} oxidant was added to an aqueous *cis*-[Ru(NH$_3$)$_4$Cl$_2$]$^+$ solution. The amount of O_2 evolved increased with time and saturated after ca. 120 min as shown in Figure 1. The initial O_2 evolution rate (V_{O_2} (mol s^{-1})) was obtained from the initial slope at time zero of the plots. The plots of V_{O_2} vs complex concentration in the aqueous solution are shown in Figure 2a. The V_{O_2} increased linearly at low concentrations with increasing complex concentration (in the inset of Figure 2a) and then deviated downward at high concentrations. The linear plots at low concentrations show that water oxidation proceeds as a first-order reaction with respect to the catalyst concentration.

It was confirmed that V_{O_2} is saturated under high Ce^{IV} concentrations in the trinuclear ruthenium ammine complex[6a] and [(bpy)$_2$(H$_2$O)Ru$-$O$-$Ru(OH$_2$)(bpy)$_2$]$^{4+}$ (bpy = 2,2′-bipyridine) catalyst systems.[9] The reactions in the present paper have also been carried out under such saturated conditions (Ce^{IV} concentration $>$1.2 mol dm^{-3}). Two mechanistic possibilities to explain the first-order dependency with respect to the catalyst concentration are considered.

One is that, after the redox equilibrium between the complex and complex^{n+} (redox intermediate; probably Ru(IV) or Ru(V) species), slow further oxidation of complex^{n+} to complex$^{(n+m)+}$ (catalytically active form) by Ce^{IV} occurs, followed by fast water oxidation by complex$^{(n+m)+}$.

The other possibility is that after oxidation of the complex by Ce^{IV} to form complex$_{ox}$ (eq 1), water oxidation (eq 2) by one molecule of complex$_{ox}$ is the rate-determining step on the

$$4Ce^{IV} + complex_{red} \xrightarrow{k_{ox}} 4Ce^{III} + complex_{ox} \quad (1)$$

$$(complex)_{ox} + 2H_2O \rightarrow [complex(H_2O)_2]_{ox} \xrightarrow{k_{O_2}}$$
$$O_2 + 4H^+ + complex_{red} \quad (2)$$

basis of the very large excess Ce^{IV} conditions (molar ratios of Ru complex/Ce^{IV} are more than 900) employed in the inset of Figure 2. It has been reported in earlier works that V_{O_2} in this case can be expressed by eq 3 using a steady-state method,[6a,9] where k_{ox} (M^{-4} s^{-1}) and k_{O_2} (s^{-1}) are the rate constants for the oxidation of the complex by Ce^{IV} and water oxidation by
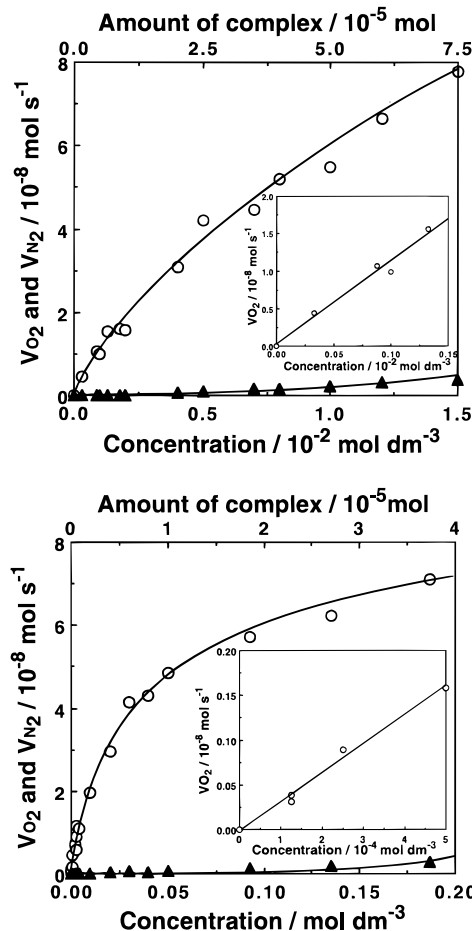
Figure 2. (a, top) Initial O_2 evolution rate, V_{O_2} (mol s^{-1}) (○), and initial N_2 evolution rate, V_{N_2} (mol s^{-1}) (▲), vs complex concentration in an aqueous solution system: amount of Ce^{IV} oxidant, 6.0×10^{-3} mol; liquid-phase volume, 5 cm^3. (b, bottom) Initial O_2 evolution rate, V_{O_2} (mol s^{-1}) (○), and initial N_2 evolution rate, V_{N_2} (mol s^{-1}) (▲), vs complex concentration in the Nafion membrane: amount of Ce^{IV} oxidant, 6.0×10^{-3} mol; membrane volume, 2.0×10^{-4} dm^{-3}; liquid-phase volume, 5 cm^3.

$$V_{O_2}/v = \frac{k_{O_2}c}{1 + k_{O_2}/\{k_{ox}[Ce^{IV}]^4\}} \quad (3)$$

complex$_{ox}$, respectively, v (dm^3) is the volume of the reaction system, c (mol dm^{-3}) is the catalyst concentration, $[Ce^{IV}]$ is the concentration of Ce^{IV}. The V_{O_2} can be given by eq 4, which

$$V_{O_2} = k_{O_2}cv \quad (4)$$

shows a linear dependence of V_{O_2} against c under large excess Ce^{IV} conditions.[6a,9] We have found that the dependency of V_{O_2} on the catalyst concentration is second-order with respect to the concentration in mononuclear Ru complex systems such as [Ru(NH$_3$)$_6$]$^{3+}$ [7] and [Ru(NH$_3$)$_5$Cl]$^{2+}$,[8] but first-order dependency was observed in multinuclear Ru complex systems such as [(NH$_3$)$_5$Ru$-$O$-$Ru(NH$_3$)$_4$$-O-$Ru(NH$_3$)$_5$]$^{4+}$ [6a] and [(NH$_3$)$_3$Ru-(μ-Cl)$_3$Ru(NH$_3$)$_3$]$^{2+}$.[6b] On considering these results, we believe that the present concentration dependency of V_{O_2} is most likely understood by the mechanism that water oxidation in eq 2 is rate-determining. Therefore, the present first-order dependency (inset of Figure 2) was analyzed by eq 4. The k_{O_2} in the aqueous solution was estimated as 2.2×10^{-3} s^{-1} from the slope of the linear plots in the inset of Figure 2 according to eq 4.

The cyclic voltammogram (CV) of a Nafion-coated graphite electrode incorporating *cis*-[Ru(NH$_3$)$_4$Cl$_2$]$^+$ was measured in an

aqueous KNO₃ solution to evaluate the oxidation process and oxidized species. Reversible waves based on Ru$^{III/II}$ at -0.25 V (vs SCE) and small but distinguishable oxidative shoulders were observed at 1.15 and 1.34 V. These redox responses are close to but not as clear as those observed for [Ru(NH₃)₅Cl]²⁺ (Ru$^{II/III}$ = -0.25 V, Ru$^{III/IV}$ = 1.06 V, Ru$^{IV/V}$ = 1.28 V vs SCE for [Ru(NH₃)₅Cl]²⁺)[15] and [Ru(NH₃)₆]³⁺ (Rn$^{II/III}$ = -0.22 V, Ru$^{III/IV}$ = 1.04 V, Ru$^{IV/V}$ = 1.32 V vs SCE for [Ru(NH₃)₆]³⁺).[16] Any distinguishable anodic wave could not be observed at higher potential because an anodic current rises steeply due to water oxidation. We investigated the oxidation of *cis*-[Ru(NH₃)₄Cl₂]⁺ by Ce^{IV} oxidant using UV−vis spectrophotometry, but reliable results could not be obtained because of a strong absorption band by Ce^{IV} around 295 nm.

The unimolecularity of the present water oxidation might be explained in several ways. One is a direct water oxidation by the oxidized catalyst as represented by eq 2. On the basis of the previous works on the reaction to evolve O₂ from hypochlorite ion (2ClO⁻ → O₂ + 2Cl⁻) catalyzed by many transition metal ions such as Ni^{II}, Cu^{II}, Mn^{II}, and Fe^{II},[17] there might exist another possible mechanism by oxidation of two chloro ligands to hypochlorite to form *cis*-[Ru(NH₃)₄(ClO)₂]⁺ as an intermediate in the catalysis. The hypochlorite ligands are allowed to disproportionate by intramolecular coupling to produce O₂. However, we have no direct evidence for the oxidation of the chloro ligands to hypochlorite, so we point out that the mechanism is still unclear.

N₂ was evolved at high concentrations in a solution as shown in Figure 2a. Since no N₂ was detected in an aqueous solution containing the same amount of Ce^{IV} oxidant without the complex, this N₂ evolved can result only from the oxidation of the ammine ligands of the complex. The initial N₂ evolution rate (V_{N_2} (mol s⁻¹)) was second-order with respect to complex concentration, so that it can be concluded that a bimolecular decomposition of the complex takes place in the solution. The downward-deviated curve of the V_{O_2} vs complex concentration at high concentrations in Figure 2a is ascribed to the bimolecular decomposition.

The relationship between the V_{O_2} and the complex concentration in the Nafion membrane is shown in Figure 2b. The plots of V_{O_2} vs complex concentration at low concentrations gave a straight line, showing that the complex catalyzes water oxidation by one molecule in the membrane. The k_{O_2} value in the Nafion membrane was obtained from the slope of the straight line as 1.6×10^{-2} s⁻¹, which is much larger than that (2.2×10^{-3} s⁻¹) in the aqueous solution. N₂ was evolved at high concentrations, showing that the bimolecular decomposition between the adjacent complexes also takes place in the Nafion membrane.

To analyze the catalytic activities of the complex in the aqueous solution and Nafion membrane, an apparent first-order rate constant of O₂ evolution (k_{app} (s⁻¹)) was defined as

$$k_{app} = V_{O_2}/n_{Ru} \qquad (5)$$

where n_{Ru} (mol) is the amount of the complex in the solution or membrane. On the basis of the dependencies of k_{app} on the complex concentration, the comparison between the aqueous solution and membrane systems is possible as shown in Figure 3. In both the aqueous solution and Nafion membrane, the k_{app} decreased with the increase of the complex concentration. However, k_{app} in the Nafion membrane is much higher than that in the aqueous solution in the whole concentration range.

On the basis of the mechanism that the first-order water oxidation by the oxidized complex is in competition with its second-order bimolecular decomposition, eq 6 was derived to
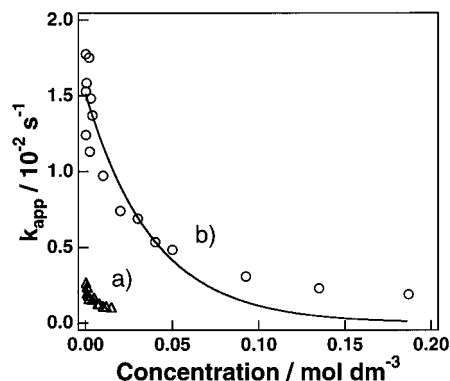

Figure 3. k_{app} vs concentration in the aqueous solution (a) and the Nafion membrane (b). The solid line is a calculated curve based on eq 7.
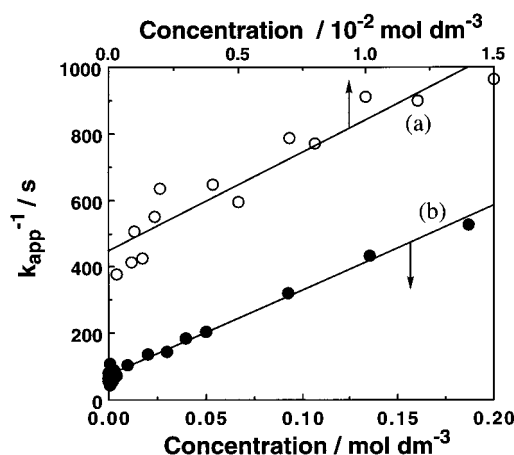

Figure 4. k_{app}^{-1} vs complex concentration in the aqueous solution (a) and Nafion membrane (b). The solid linear lines are based on eq 6.

TABLE 1: Summary of Rate Constants for O₂ Evolution (k_{O_2}) and Bimolecular Decomposition (k_{deact})

	$k_{O_2}/10^{-2}$ s⁻¹	$k_{deact}/10^{-1}$ dm³ mol⁻¹ s⁻¹
aqueous solution	0.23 (0.22)^a	2.0
Nafion membrane	1.4 (1.6)^b	5.1

^{a} Obtained from the slope of the inset of Figure 2a. ^{b} Obtained from the slope of the inset of Figure 2b.

$$k_{app}^{-1} = 1/k_{O_2} + (k_{deact}/k_{O_2}^{2})c \qquad (6)$$

analyze the dependencies of k_{app} on complex concentration c (mol dm⁻³);[6a] where k_{deact} (dm³ mol⁻¹ s⁻¹) is the second-order rate constant of the bimolecular decomposition. The plots of k_{app}^{-1} vs c in both the solution and membrane according to eq 6 are shown in Figure 4. They show linear relationships, which supports the assumption that eq 6, considering the competition between the O₂ evolution and the bimolecular decomposition, is reasonable. The k_{O_2} and k_{deact} were obtained from the intercept and slope of the straight lines, respectively. These values are summarized in Table 1. The k_{O_2} values in the solution (2.3×10^{-3} s⁻¹) and membrane (1.4×10^{-2} s⁻¹) are almost the same as those obtained from the initial slopes in the insets of parts a (2.2×10^{-3} s⁻¹) and b (1.6×10^{-2} s⁻¹), respectively of Figure 2. It is unusual that the k_{O_2} in the membrane is much larger than that in the solution by 6.1 times, showing that the intrinsic activity of the complex increases by incorporating it into the membrane. The more hydrophobic environment, i.e., lower polar medium surrounding the complex in the Nafion membrane compared with the aqueous solution, might decrease the outer-

TABLE 2: Summary of k and r_d Values as Well as the Catalytic Ability in Water Oxidation Catalysis by Mononuclear Ammineruthenium Complexes in a Nafion Membrane

complex	k/s^{-1}	r_d/nm	s/nm	catalytic ability
$[Ru(NH_3)_6]^{3+\ a}$	3.5×10^{-5}	0.82	0.75	2-electron oxidation
$[Ru(NH_3)_5]^{2+\ b}$	2.7×10^{-3}	0.84	0.75	2-electron oxidation
cis-$[Ru(NH_3)_4Cl_2]^+$	1.5×10^{-2}	0.88	0.75	4-electron oxidation

[a] Reference 7. [b] Reference 8.

sphere reorganization energy for the electron transfer in the water oxidation process to increase the intrinsic activity.

The k_{deact} in the membrane is slightly higher than that in the solution. We have reported[6-8] that the bimolecular decomposition is suppressed in systems where a complex is immobilized in a membrane, resulting in the lower k_{deact} because the complex cannot move freely. The bimolecular decomposition was also supposed to be suppressed in the present system since the complex is immobilized in the membrane. However, the bimolecular decomposition was more rapid in the membrane. The same enhancing effect by the hydrophobic environment could also work as for the k_{O_2} value. Even though the k_{deact} increased in the membrane, the enhancement of the k_{O_2} exceeds that of k_{deact}, which results in much more active O_2 evolution in the membrane than in the aqueous solution.

Intermolecular distance distribution between the complexes is important for the bimolecular decomposition of the complex immobilized in the membrane. We analyzed the catalytic activity of the complex in the membrane on the basis of the intermolecular distance distribution as follows. When assuming that the complexes existing within a critical decomposition distance, r_d (nm), undergo a bimolecular decomposition to deactivate, k_{app} is represented by eq 7,[6a] where k (s^{-1}), s (nm), α, and N_A

$$k_{app} = k \exp\{-4\Pi(r_d^3 - s^3)\alpha c N_A \times 10^{-24}/3\} \qquad (7)$$

(mol^{-1}) are the intrinsic activity of the catalyst, the contact distance (0.75 nm) between the catalysts, the localization degree (40)[6a] of the catalyst in the Nafion membrane, and Avogadro's number, respectively. The complexes were approximated as a sphere, and its diameter ($s = 0.75$ nm) was calculated in the same way as that in our earlier paper.[7,8] The exponential term of eq 7 expresses the fraction of the complex which does not undergo the bimolecular decomposition (the intermolecular distance is longer than r_d). Equation 7 was applied to the plots of k_{app} vs c in the membrane in Figure 3 using a nonlinear least-squares method, and the best fitting was obtained when k and r_d were 1.5×10^{-2} s^{-1} and 0.88 nm, respectively. The k is almost the same as the k_{O_2} (1.4×10^{-2} s^{-1}) calculated from the kinetic analysis based on the competition between water oxidation and bimolecular decomposition. The r_d value (0.88 nm) is reasonable when considering the molecular size (0.75 nm) of the complex. It is important to separate the distance between the complexes over 0.88 nm for the stable catalysis in the Nafion membrane.

The k and r_d values as well as the catalytic abilities of mononuclear ammine−ruthenium complexes are summarized in Table 2 including our earlier results on $[Ru(NH_3)_6]^{3+}$[7] and $[Ru(NH_3)_5Cl]^{2+}$.[8] The order of k is cis-$[Ru(NH_3)_4Cl_2]^+$ > $[Ru(NH_3)_5Cl]^{2+}$ > $[Ru(NH_3)_6]^{3+}$, showing that the intrinsic activity of the complex increases remarkably on the substitution of the ammine ligands by chloro ligands. The high catalytic activity of the present cis-$[Ru(NH_3)_4Cl_2]^+$ could be explained by its 4-electron oxidation ability, compared with $[Ru(NH_3)_6]^{3+}$ and

$[Ru(NH_3)_5Cl]^{2+}$, both of which work as only a 2-electron oxidation catalyst.[7,8]

Conclusion

cis-Tetraamminedichlororuthenium(III) (cis-$[Ru(NH_3)_4Cl_2]^+$) was found to be capable of oxidizing water to evolve O_2. It underwent a bimolecular decomposition to deactivate at high complex concentrations. The first-order rate constant (k_{O_2} (s^{-1})) for O_2 evolution and the second-order rate constant (k_{deact} (mol^{-1} dm^3 s^{-1})) for the bimolecular decomposition were obtained from the kinetic analysis based on the competition between both processes. The k_{O_2} (1.4×10^{-2} s^{-1}) in the Nafion membrane is much higher than that (2.3×10^{-3} s^{-1}) in the solution, which might be explained by the lower outer-sphere reorganization energy for the electron transfer in the water oxidation in the hydrophobic medium of the Nafion membrane. The k_{deact} (5.1×10^{-1} dm^3 mol^{-1} s^{-1}) in the membrane was slightly higher than that (2.0×10^{-1} dm^3 mol^{-1} s^{-1}) in the solution. The activity in the Nafion membrane was analyzed in terms of the intrinsic activity (k (s^{-1})) and critical decomposition distance (r_d (nm)) on the basis of the intermolecular distance distribution to obtain $k = 1.5 \times 10^{-2}$ s^{-1} and $r_d = 0.88$ nm. This r_d value indicates that the separation of the distance between the complexes over 0.88 nm is important for the complex to work stably in the Nafion membrane. The k value was compared with the earlier results on $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5Cl]^{2+}$, and the order of k_{O_2} is cis-$[Ru(NH_3)_4Cl_2]^+$ > $[Ru(NH_3)_5Cl]^{2+}$ > $[Ru(NH_3)_6]^{3+}$, which could be explained by the 4-electron oxidation ability of cis-$[Ru(NH_3)_4Cl_2]^+$. The contribution of Cl$^-$ ion to water oxidation is also interesting when compared with one or more Cl$^-$ ions known to be required in water oxidation at the OEC of photosynthesis.[1]

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