Activity analysis of *trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$ incorporated into Nafion membrane for water oxidation catalyst

Hidenobu Shiroishi, Satoshi Yamashita, Masao Kaneko*

Faculty of Science, Ibaraki University, Mito, Ibaraki 310-8512, Japan

Abstract

Activity of *trans*-tetraamminedichlororuthenium(III) complex as water oxidation catalyst was studied both in a homogeneous aqueous solution (AS) and in a heterogeneous Nafion membrane (HM) using Ce(IV) oxidant. This *trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$ was more active than any other mononuclear ammine ruthenium complex studied before. In the AS, the rate of evolved dioxygen is second order with respect to the complex concentration, indicating that the complexes oxidize water molecules bimolecularly in low concentration regions. In high concentration regions, the activity of water oxidation decreased with the increase of the concentration, and at the same time dinitrogen (N$_2$) evolved by a bimolecular decomposition process. In the HM, the activity of the complex was remarkably high, and it was maintained for a long time at low concentrations (<0.02 mol dm^{-3}). At middle concentrations for the HM (0.02–0.05 mol dm^{-3}), the activity of the complex decreased with increasing concentration because of bimolecular decomposition. However, in high concentration regions the complex recovered the activity most probably due to polymerization of the complex. The activity in the HM was analyzed in terms of the cooperative catalysis, the bimolecular decomposition and the polymerization of the complex based on intermolecular distance distribution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water oxidation; Artificial photosynthesis; Nafion; *Trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$; Dioxygen evolution

1. Introduction

Artificial photosynthesis is attracting a great deal to produce renewable energy resource from solar energy and water [1–3]. There are many options of media and functional materials to construct an artificial photosynthetic system [1–8]. We selected polymer membrane and molecules as media as well as functional materials to construct an artificial photosynthetic system. For an artificial photosynthetic system it is of importance to use water as electron donor. To this objec-

tive efficient catalysis of water oxidation is important. However, there have been only very few active water oxidation catalyst except our earlier works [9–12]. An active water oxidation molecular catalyst should further be developed in this regard.

We found that Ru-red with ammine ligands and oxo-bridged trinuclear structure ([(NH$_3$)$_5$RuORu(NH$_3$)$_4$ORu(NH$_3$)$_5$]$^{6+}$) is active for water oxidation [9]. The Ru-red incorporated into a Nafion membrane is stabilized against bimolecular decomposition. To develop active catalysts for water oxidation, one of the candidates is a molecular catalyst with a similar structure as Ru-red. We have studied the activity of mono-, di-, and trinuclear ammine ruthenium complexes [7–12].

* Corresponding author. Tel.: +81-29-228-8374;
fax: +81-29-228-8374.
E-mail address: kanekom@mito.ipc.ibaraki.ac.jp (M. Kaneko).

In the present research, the activity of *trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$ for water oxidation catalyst has been investigated. It was found that its activity exceeds those of other Ru complexes investigated before and the activity was compared with those of Ru(NH$_3$)$_6$ and RuCl(NH$_3$)$_5$.

2. Experimental

2.1. Materials

Trans-Ru(NH$_3$)Cl$_2$ was synthesized by the method reported elsewhere [13]. Cerium(IV) diammonium nitrate was purchased from Wako Pure Chemical Industries, and a Nafion 117 membrane (thickness 178 μm) from Aldrich Chemical Co. Inc.

2.2. Preparation of Nafion membrane incorporating trans-[RuCl$_2$(NH$_3$)$_4$]$^+$

Nafion membrane was swollen sufficiently by soaking in distilled water for ca. 24 h. It was immersed in a *trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$ aqueous solution for more than 5 h under dark conditions to incorporate the complex by cation exchange into the membrane. The dark conditions were adopted in order to prevent the complex from isomerizing to *cis*-form. The amount of the complex incorporated into the membrane was estimated from the visible absorption spectral change of the aqueous solution before and after the incorporation of the complex. The complex concentration in the membrane was calculated from the complex amount and the membrane volume.

2.3. Dioxygen evolution

In a homogeneous aqueous solution (AS) system, excess Ce(NH$_4$)$_2$(NO$_3$)$_6$ oxidant (3.1×10^{-3} mol) was added quickly to into an aqueous solution (5 cm^3) of the complex in a reaction vessel under dark. In a heterogeneous Nafion membrane (HM) system, a membrane (54 mm^3 volume) incorporating the complex was put into pure water (5 cm^3), and excess Ce(IV) oxidant (3.1×10^{-3} mol) was added quickly. In both the systems, the atmosphere in the reaction vessel was replaced with argon gas before Ce(IV) oxidant was added. No buffer solution was used, and the pH was

about 0.8 during the experiments. The O$_2$ evolved was analyzed on a gas chromatograph equipped with a 5A molecular sieve column using argon carrier gas (flow rate 40 cm^3 min^{-1}) at 50°C.

3. Results and discussion

Fig. 1 shows the dependencies of the amount of O$_2$ evolved on the reaction time for the AS and HM systems with the same amount of the catalyst. The rate of O$_2$ evolved in the HM is much higher than that in the AS. The O$_2$ evolution in the AS saturated after ca. 50 min most probably due to decomposition of the catalyst [9–12] despite the excess amount of Ce(IV), while that in the HM continued even after 120 min. It is suggested that the fixation in Nafion membrane prevents the complex from decomposing [9–12]. The initial O$_2$ evolution rate (V_{O_2}, mol s^{-1}) and N$_2$ evolution rate (V_{N_2}, mol s^{-1}) were obtained from the initial slope at time zero. The plots of V_{O_2} and V_{N_2} versus the complex concentration in the AS are shown in Fig. 2. The V_{O_2} is second order with respect to the complex concentration at low concentrations as shown in the inset of Fig. 2, indicating that two complex molecules works for O$_2$ evolution. N$_2$ evolution is attributed to a bimolecular decomposition of the complex due to
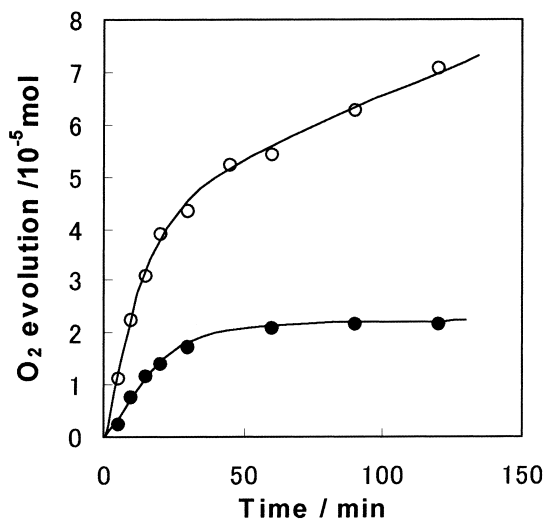

Fig. 1. Time dependence of O$_2$ evolved in AS (●) and HM (○): the used amounts are complex, 1×10^{-6} mol; Ce(IV) oxidant, 3×10^{-3} mol; membrane volume, 5.4×10^{-5} dm^{-3}; water, 5 cm^3.
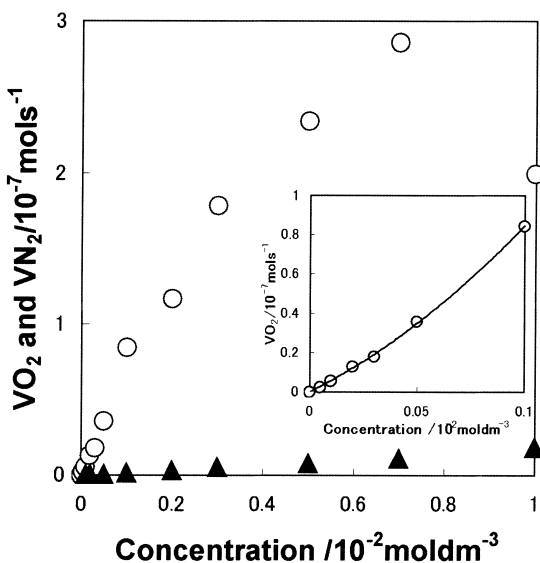
Fig. 2. Dependence of initial rate of evolved O_2 ($\bigcirc$) and N_2 ($\blacktriangle$) evolution on catalyst concentration in AS: Ce(IV) oxidant, 3×10^{-3} mol; water, 5 cm^3. The inset shows the rate of O_2 evolution in lower concentrations, and the solid line is a fitted curve based on second order of the concentration.

Fig. 3. Relationship between k_{app} and concentration in AS ($\bullet$) and HM ($\bigcirc$). The solid line is the calculated curve based on Eq. (7) (vide infra) and the dashed line is the calculated curve based on Eq. (5). The inset illustrates the plots for AS at low concentrations.

oxidation of the ammine ligands [9–12] because V_{N_2} is second order with respect to the complex concentration in the AS and that the rate of evolved O_2 decreased at high concentrations.

Fig. 3 shows the dependence of the apparent first-order rate constant of O_2 evolution (k_{app}, s^{-1}) on concentration in the AS and HM. The rate constant k_{app} is defined by the following equation:

$$k_{app} = \frac{V_{O_2}}{n_{Ru}} \quad (1)$$

where n_{Ru} (mol) is the amount of the complex in the solution or membrane. In the HM, the value of k_{app} increases linearly with the concentration at low concentrations. This initial linear increase is attributable to the cooperative oxidation of water by two catalyst molecules. In the middle concentration regions, the activity of the complex decreased sharply due to bimolecular decomposition. The activity of the catalyst in the HM is remarkably higher than that in the AS. This could be attributed to a proper configuration of the complexes in the Nafion membrane which could facilitate cooperative water oxidation, in addition to
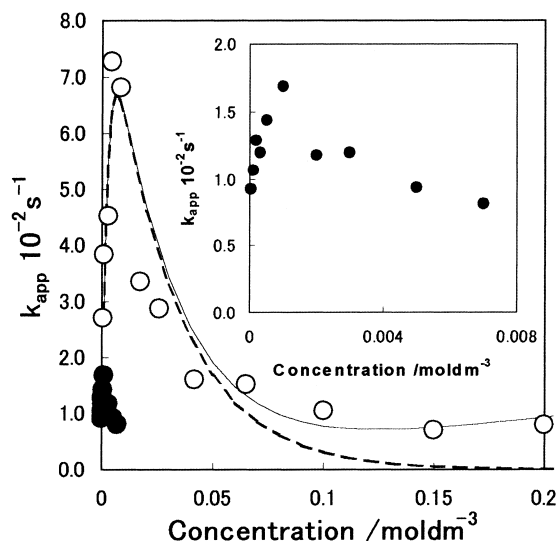
suppression of a bimolecular decomposition due to the fixation of the catalyst in the membrane.

The activity of the complex in the HM was analyzed based on intermolecular distance distribution as follows. The probability density $P(r)$ in a Poisson distribution is represented by the following equation:

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

where c (mol dm^{-3}) is the concentration of the complex in the membrane, N_A the Avogadro's number, r (nm) the distance between the nearest neighboring molecules, α the degree of localization of the catalyst (in the present Nafion membrane estimated as 40) [9] and s (nm) represents contact distance between the complexes. The complex volume was estimated from the distance, angle of the atoms and the van der Waal's radius of hydrogen and chlorine atoms. Fig. 4 shows the intermolecular distance distribution at various complex concentrations in the membrane. It is assumed that the catalyst existing between the cooperative catalysis distance (r_{co}, nm) and the critical decomposition distance (r_d, nm) are able to oxidize water molecules [9–12].
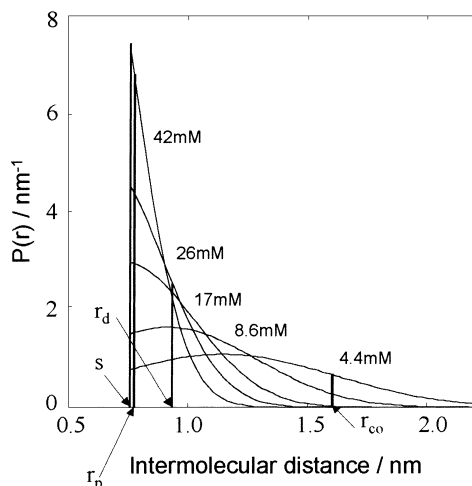
Fig. 4. Intermolecular distance distribution between the nearest-neighbor complexes in the membrane at various complex concentrations.

Fig. 5. Visible absorption spectral changes of Nafion membrane incorporating *trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$: (a) before the reaction; (b) after 2 min; (c) after 5 min of water oxidation.

The fraction of the complex able to oxidize water cooperatively is expressed by Eq. (3) as

$$R_{co} = \int_s^{r_{co}} P(r)\,dr$$
$$= 1 - \exp\left[-\frac{4\pi(r_{co}^3 - s^3)\alpha c N_A \times 10^{-24}}{3}\right] \quad (3)$$

The fraction of the complex decomposing bimolecularly is expressed by Eq. (4) as

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

The turnover number (TN) of the complex for O$_2$ evolution can then be expressed by Eq. (5) as follows:

$$k_{app} = k_{O_2}(R_{CT} - R_{dec}) \quad (5)$$

where k_{O_2} (h^{-1}) is a constant to express the intrinsic activity of the catalyst. We applied Eq. (5) to the data of Fig. 3 using a nonlinear least-squares method, and the calculated curve is shown as a dashed line in Fig. 3. The calculated curve fits well with the experimental dots at low to middle concentrations. However, the calculated curve does not agree with the experimental data at high concentrations where the activity
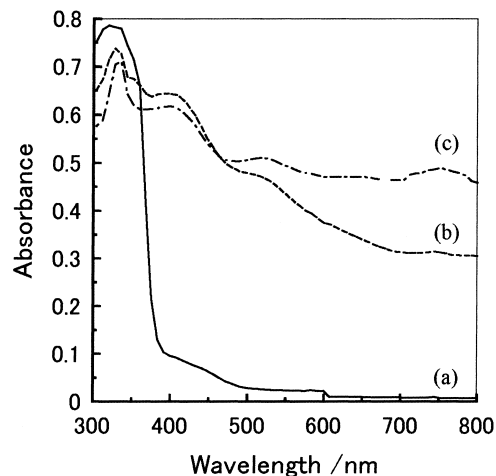
recovers against the prediction by using Eq. (5). This behavior is different from [Ru(NH$_3$)$_6$]$^{2+}$ [11] and [RuCl(NH$_3$)$_5$]$^{2+}$ [10].

Fig. 5 shows a visible absorption spectral change of a Nafion membrane incorporating the catalyst at high concentration (0.15 mol dm^{-3}) before adding Ce(IV) as well as after a few minutes of water oxidation reaction. The absorption rose immediately after beginning the reaction with the addition of Ce(IV). The absorption band around 530 nm appeared immediately that is attributable to the absorption by a trinuclear ruthenium (III–IV–III) as inferred from a close resemblance to that of Ru-red. Another new absorption appeared around 750 nm after 5 min that might be attributable to a polynuclear complex.

When assuming that the complexes existing within the distance r_p are polymerized, the fraction of the polymerized complex is expressed by Eq. (4).

$$R_p = \int_s^{r_p} P(r)\,dr$$
$$= 1 - \exp\left[-\frac{4\pi(r_p^3 - s^3)\alpha c N_A \times 10^{-24}}{3}\right] \quad (6)$$

Apparent first-order rate constant can then be expressed by the sum of the catalyses by the mononuclear and the polynuclear complexes.

$$k_{app} = k_{O_2}(R_{CT} - R_{dec}) + k' R_p \quad (7)$$

Table 1
Summary of the parameters of the ruthenium complexes for water oxidation in a Nafion membrane

Complex	Catalytic ability	k_{O_2} (s^{-1})	r_d (nm)	r_{co} (nm)	k_p (s^{-1})	r_p (nm)	s (nm)	Reference
[Ru(NH$_3$)$_6$]$^{3+}$	Two-electron oxidation	3.5×10^{-5}	0.82	1.21	–	–	0.75	[9]
[Ru(NH$_3$)$_5$Cl]$^{2+}$	Two-electron oxidation	2.7×10^{-3}	0.84	1.26	–	–	0.75	[8]
Trans-[RuCl$_2$(NH$_3$)$_4$]$^+$	Two-electron oxidation	9.0×10^{-2}	0.93	1.66	8.7×10^{-1}	0.78	0.78	Present work
[{Ru(NH$_3$)$_5$}$_2$(μ-O)]$^{5+}$	Four-electron oxidation	1.1×10^{-2}	1.02	–	–	–	0.94	[10]
Ru-red	Four-electron oxidation	4.4×10^{-2}	1.23	–	–	–	1.06	[7]

where k' is the intrinsic activity of the polynuclear complex. Eq. (7) was applied to the k_{app} versus c data for the HM in Fig. 3 using the nonlinear least-squares method, and the calculated curve is shown as a solid line. The calculated curve fits well with the experimental data. The parameters obtained by the best fitting were summarized in Table 1 with other complexes reported [9–12]. For the present *trans*-[RuCl$_2$(NH$_3$)$_4$]$^+$, the activity of the assumed polynuclear complex is higher than the starting complex by one order of magnitude. The activity of the complex increased with substitution of the ammine ligands by chloro ligands. Chloro ligands of the complex would be substituted by water at the beginning of the reaction resulting in efficient water oxidation, but the details are open to the future investigation.

4. Conclusion

The activity of *trans*-tetraamminedichlororuthenium(III) complex as water oxidation catalyst was investigated in AS and in HM systems using Ce(IV) oxidant. The activity of the complex in the HM is much higher than that in the AS. In the middle concentration regions, the activity of the complex decreased sharply, but in high concentration regions, the activity recovered most probably due to polymerization of the complex. The substitution of the ammine ligands by chloro ligands improves the activity for water oxidation.

References

[1] K. Kalyanasundaram, E. Borgarello, M. Gratzel, Helvetica Chim. Acta 35 (1981) 64.
[2] W. Rüttinger, G.C. Dismukes, Chem. Rev. 95 (1997) 1.
[3] M. Kaneko, in: H.S. Nalwa (Ed.), Organic Conductive Molecules and Polymers: Photoelectric Conversion by Polymeric and Organic Materials, Vol. 4, Wiley, New York, 1997, p. 661.
[4] T. Matsubara, Y. Saito, T. Yamakawa, S. Shinoda, J. Mol. Catal. 66 (1991) 171.
[5] K. Uosaki, K. Okazaki, H. Kita, J. Chem. Soc., Chem. Commun. (1990) 195.
[6] K. Sayama, H. Arakawa, J. Phys. Chem. 97 (1993) 531.
[7] J. Yoshimura, Y. Ebina, J. Kondo, K. Domen, A. Tanaka, J. Phys. Chem. 97 (1993) 1970.
[8] J.A. Gilbert, D.S. Eggleston, W.R. Murphy Jr., D.A. Geselowitz, S.W. Gersten, D.J. Hodgson, T.J. Meyer, J. Am. Chem. Soc. 107 (1985) 3855.
[9] M. Yagi, S. Tokita, K. Nagoshi, I. Ogino, M. Kaneko, J. Chem. Soc., Faraday Trans. 92 (1996) 2457.
[10] M. Yagi, K. Nagoshi, M. Kaneko, J. Phys. Chem. B 101 (1997) 5143.
[11] M. Yagi, N. Sukegawa, M. Kasamatsu, M. Kaneko, J. Phys. Chem. B 103 (1999) 2151.
[12] K. Nagoshi, M. Yagi, M. Kaneko, Bull. Chem. Soc. Jpn. 73 (2000) 2193.
[13] W. P. Griffith, D. Pawson, J. Chem. Soc., Dalton Trans. (1973) 1315.