Activity analysis of mononuclear ruthenium ammine complex dispersed in a polymer membrane as an electrochemical water oxidation catalyst

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Abstract

The activity of an electrochemical water oxidation catalyst based on pentaamminechlororuthenium(III) ($[Ru(NH_3)_5Cl]^{2+}$) complex incorporated in an electrode-coated Nafion membrane was investigated. The complex worked as an active electrochemical catalyst, and an optimum concentration for the turnover number (TN) of the catalyst in the O_2 evolution was exhibited. The TN increased with the concentration at low concentrations, which was ascribed either to charge transfer between the catalysts or to cooperative catalysis by the complex. The TN decrease at high concentrations was ascribed to bimolecular decomposition of the catalyst. The catalyst activity (TN) was analyzed in terms of a charge transfer distance between the catalysts (r_0/nm), a cooperative catalysis distance by the complex (r_{co}/nm), and a critical decomposition distance of the catalyst (r_d/nm) based on intermolecular distance distribution. It was suggested that the activity was controlled mainly by r_{co} and r_d, and the values $r_{co} = 1.26$ nm and $r_d = 0.82$ nm were obtained. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Mononuclear ruthenium ammine complex; Polymer membrane; Electrochemical water oxidation catalyst

1. Introduction

Catalysis in heterogeneous matrixes such as ion exchange resins [1–3], clays [4], inorganic particles [5,6] and polymer membranes [7–10], have been studied extensively. Study of the factors affecting the heterogeneous catalyst activity as well as its activity analysis are important in order to optimize the catalysis. Water oxidation is an important process not only in photosynthesis but also in a photochemical solar energy conversion system which is attracting much attention to obtain a renewable energy resource [11]. Many heterogeneous water oxidation catalyst systems have been reported [12–14]. There have been little research about activity analysis on water oxidation catalyst in het-

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erogeneous matrixes except our earlier works [5–7,15,16].

In our earlier paper [15], it was reported that an optimum concentration is exhibited for the activity of a chemical water oxidation catalyst based on $[Ru(NH_3)_5Cl]^{2+}$ incorporated in a Nafion membrane using Ce^{IV} oxidant. This optimum concentration was explained by two factors of a cooperative catalysis by the complex and a bimolecular decomposition of the catalyst. They are conflicting conditions as to intermolecular distance between the catalysts; i.e., shorter distance is better for the catalysis in view of cooperative catalysis and longer distance is better in view of bimolecular decomposition. The activity was analyzed in terms of a cooperative catalysis distance (r_{co}/nm) and a critical decomposition distance (r_d/nm) based on static intermolecular distance distribution.

In an electrocatalytic water oxidation catalysis by a trinuclear ruthenium complex, we found that the activity of the catalyst incorporated in a Nafion membrane depends on the charge transfer between the catalyst and on their bimolecular decomposition showing an optimum concentration [16]. A short distance between the catalysts is favorable for the activity in view of a charge transfer, but a long distance is favorable because of suppression of the bimolecular decomposition. TN of the catalyst was analyzed in terms of charge transfer distance (r_0/nm) and critical decomposition distance (r_d/nm) based on an intermolecular distance distribution.

From the previous studies on the activity analysis of a water oxidation catalyst using Ce^{IV} oxidant, the activity of $[Ru(NH_3)_5Cl]^{2+}$ in a membrane as an electrochemical water oxidation catalyst is supposed to depend on charge transfer between the catalysts, cooperative catalysis by the complex and bimolecular decomposition of the catalyst. In order to elucidate this, the electrocatalytic activity of the water oxidation catalyst, $[Ru(NH_3)_5Cl]^{2+}$ was studied, and an optimum concentration for its activity was found. An activity analysis in terms of charge transfer distance, cooperative catalysis distance

and bimolecular decomposition distance will be demonstrated, and the factors affecting the activity will be discussed.

2. Experimental

2.1. Materials

Pentaamminechlororuthenium(III) dichloride, $[Ru(NH_3)_5Cl]Cl_2$, and a Nafion 117 solution (5 wt.% alcoholic solution) ware purchased from Aldrich Chemical. The Nafion solution was diluted to 2.5 wt.% with methanol before use. All the materials were of commercially available purest grade and used as received.

2.2. Preparation of a Nafion membrane incorporating $[Ru(NH_3)_5Cl]^{2+}$

A Nafion membrane (thickness 3 μm) was first prepared by casting 30 μl of a 2.5 wt.% Nafion solution onto a platinum plate electrode (1×1 cm^2). The Nafion membrane coated on a Pt electrode was immersed in a 5.0×10^{-4} M $[Ru(NH_3)_5Cl]^{2+}$ aqueous solution (2 ml) to adsorb the complex into the membrane. The amount of the complex in the membrane was estimated from the visible absorption spectral change of the aqueous solution before and after the adsorption. The complex concentration in the membrane was obtained from the amount of the complex in the membrane and the membrane volume.

2.3. Measurements

A BAS CV-27 cyclic voltammograph and a Rikadenki RW-21 recorder were used for electrochemical experiments. A conventional single-compartment cell was equipped with a modified working, a Ag/AgCl reference and a platinum wire counter electrode. A supporting electrolyte solution (pH 5.4) of 0.1 M potassium nitrate was deaerated by bubbling argon gas for 1 h. The dioxygen (O_2) evolved in a potentio-

static electrolysis was analyzed by a Hitachi 163 gas chromatograph equipped with a 5 Å molecular sieve column using argon carrier gas. The amount of the O_2 evolved was obtained by subtracting the amount of the O_2 detected for a blank experiment without electrolysis.

3. Results and discussion

$[Ru(NH_3)_5Cl]^{2+}$ was incorporated electrostatically into a Nafion membrane by cation exchange. The complex is supposed to be present in hydrophilic regions formed by the sulfonate groups of Nafion. The maximum complex concentration in the membrane was 0.72 M. The concentration of the sulfonate group in the membrane was estimated by elemental analysis as 1.4 M. At the ratio of the maximum concentration ($[Ru(NH_3)_5Cl]^{2+}$/sulfonate group $= 1/1.9$), the charges in the membrane are almost neutralized between the cationic $[Ru(NH_3)_5Cl]^{2+}$ and the anionic sulfonate groups $(1-)$.

The plots of the catalyst turnover number (TN) for the O_2 evolution vs. the catalyst concentration in the membrane are shown in Fig. 1. An optimum concentration for the TN was exhibited around 0.15 M. The TN increased with
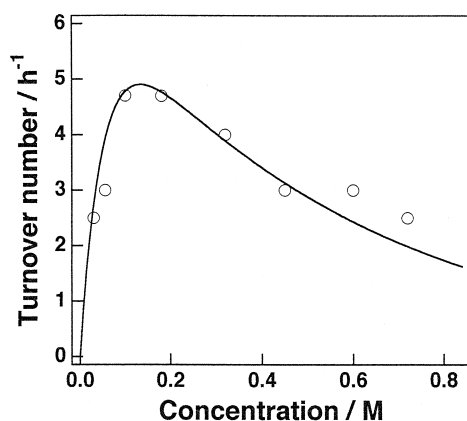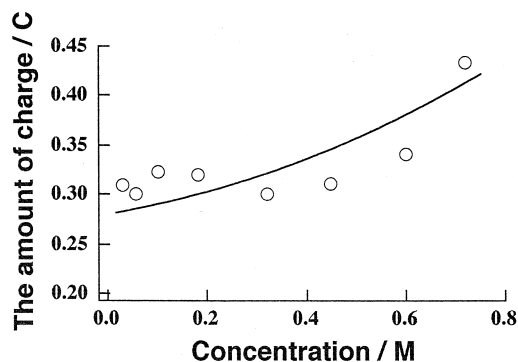

Fig. 2. Relationship between the amount of charge and complex concentration in Nafion membrane after the potentiostatic electrolysis at 1.4 V (Ag/AgCl) for 1 h.

the concentration at low concentrations. $[Ru(NH_3)_5Cl]^{2+}$ is a 2-electron water oxidation catalyst, so that cooperative catalysis by two complexes is needed to achieve 4-electron water oxidation to evolve O_2 [15,17]. Actually, the activity of $[Ru(NH_3)_5Cl]^{2+}$ for water oxidation in the membrane using Ce^{IV} oxidant increased with its concentration in the range of low concentrations [15]. On the other hand, in the present electrochemical water oxidation, charge hopping between the redox centers confined in the membrane is important to provide charges to the catalyst. In the electrochemical Nafion/Ru-red system [16], charge hopping is facilitated by the catalyst concentration increase, so that electrochemical activity of Ru-red in a membrane increased with complex concentration. The TN increase in the low concentration region of the present $[Ru(NH_3)_5Cl]^{2+}$ system is therefore ascribable either to cooperative catalysis by the complex or to charge transfer between the catalysts.

The TN decreased over 0.15 M in Fig. 1. However, the amount of the charge passed increased monotonously with the concentration as shown in Fig. 2, indicating that charges are transported to the catalyst. We have reported that dinitrogen (N_2) which results from oxidation of the ammine ligands of the $[Ru(NH_3)_5Cl]^{2+}$ evolves by a bimolecular decomposition in a chemical water oxidation system

Fig. 1. Dependence of turnover number (TN) of the catalyst for O_2 evolution on the complex concentration in Nafion membrane after the potentiostatic electrolysis at 1.4 V (Ag/AgCl) for 1 h. The solid line is a calculated curve based on Eq. (6).

using Ce^{IV} oxidant [15]. The decreasing TN at high concentrations in Fig. 1 is ascribable to the bimolecular decomposition of the complex. Thus, the activity of the present catalyst should be determined by either charge transfer between the catalysts or cooperative catalysis, and by their bimolecular decomposition.

Based on this, we analyzed the electrochemical activity of the present catalyst in the membrane. The charge transfer between the catalysts, cooperative catalysis and bimolecular decomposition should depend on the intermolecular distance between the catalysts immobilized in the membrane, so that intermolecular distance distribution rather than average intermolecular distance has been taken into account to analyze the activity. In a random dispersion, distance distribution between the nearest-neighbor molecules is represented by Eq. (1) [7,15,16,18–20];

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

$$\left. \times N_A \alpha c \times 10^{-24}/3\right] \tag{1}$$

where $P(r)/nm^{-1}$, N_A/mol^{-1}, $c/mol\ dm^{-3}$, r/nm, s/nm and α are probability density, Avogadro's number, complex concentration in a membrane, distance between the nearest-neighbor molecules, the contact distance (0.75 nm) [15] between the catalysts, and the degree (5.1) [19] of the localization of the catalyst in the present Nafion membrane, respectively.

According to Eq. (1), the probability distribution curves are depicted in Fig. 3 as a function of the nearest intermolecular distance for various concentrations. The charges on the complex can be transferred mainly by hopping between the molecules present within a charge transfer distance (r_0/nm). Molecules present within a cooperative catalysis distance (r_{co}/nm) can catalyze water oxidation cooperatively. As we have already proposed [7,15,16], we define critical decomposition distance (r_d/nm) within which bimolecular decomposition takes place between the molecules. When $r_0 < r_{co}$, O_2 evolution is
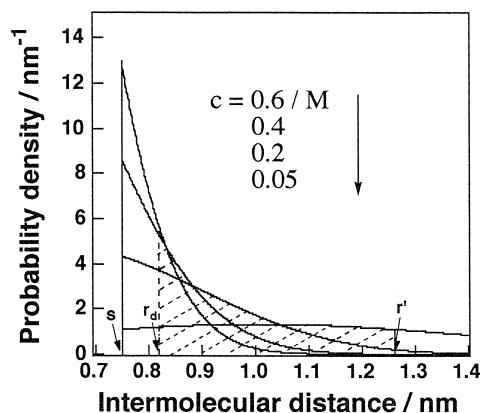

Fig. 3. Intermolecular distance distribution between the nearest neighboring complex for various concentrations. s is the contact distance between the catalysts, r' is either the charge transfer distance (r_0) between the catalysts or cooperative catalysis distance (r_{co}) by the complex, and r_d is the critical decomposition distance of the catalyst. The shadow expresses the fraction effective for the catalysis.

controlled by r_0, so that the fraction (R_{eff}) of the effective catalyst is expressed by Eq. (2).

$$R_{eff} = \int_{r_d}^{r_0} P(r) dr \tag{2}$$

When $r_{co} < r_0$, O_2 evolution is controlled by r_{co} similarly, so that R_{eff} is expressed by Eq. (3).

$$R_{eff} = \int_{r_d}^{r_{co}} P(r) dr \tag{3}$$

Now, r' was used instead of the shorter distance of r_0 or r_{co}, so that R_{eff} is represented by Eq. (4).

$$R_{eff} = \int_{r_d}^{r'} P(r) dr = \exp\left\{-4\pi\left(r_d^3 - s^3\right)\right.$$

$$\left. \times \alpha c N_A \times 10^{-24}/3\right\}$$

$$- \exp\left\{-4\pi(r'^3 - s^3)\right.$$

$$\left. \times \alpha c N_A \times 10^{-24}/3\right\} \tag{4}$$

The TN which should be proportional to R_{eff} is given by Eq. (5).

$$TN = k_{O_2} \times R_{eff} \qquad (5)$$

where k_{O_2}/h^{-1} is a constant to express the intrinsic activity of the catalyst. Then Eq. (6) is derived from Eqs. (4) and (5).

$$TN = k_{O_2}\Big[\exp\{-4\pi(r_d^3 - s^3)\alpha c N_A$$
$$\times 10^{-24}/3\} - \exp\{-4\pi(r'^3 - s^3)\alpha c N_A$$
$$\times 10^{-24}/3\}\Big] \qquad (6)$$

The Eq. (6) was applied to the data of Fig. 1 using a nonlinear least-square method, and the best fitting was obtained when $k_{O_2} = 6.7$ h^{-1}, $r' = 1.26$ nm and $r_d = 0.82$ nm. The r_d (0.82 nm) is almost the same as the critical decomposition distance (0.84 nm) [15] in the chemical water oxidation system of $[Ru(NH_3)_5Cl]^{2+}/$ Nafion using Ce^{IV} oxidant and is reasonable considering the molecular size (diameter 0.75 nm) of the complex. The r' (1.26 nm) is close to the cooperative distance (1.21 nm) [15] obtained in the chemical system. In our studies, electron transfer distance (r_0) was obtained as 1.3–1.6 nm [18–21], e.g., 1.6 nm for the electrochemical charge transfer between [Ru-(bpy)$_3$]$^{2+}$ in a polymer membrane [21]. These results suggest strongly that O$_2$ evolution is controlled by r_{co} rather than r_0 in the present electrochemical system.

4. Conclusion

The activity of the mononuclear ruthenium complex ($[Ru(NH_3)_5Cl]^{2+}$) incorporated in a membrane as electrochemical water oxidation catalyst was studied. An optimum complex concentration for the catalytic activity was exhibited. The activity of the mononuclear complex was analyzed in terms of three factors, charge transfer distance (r_0) between the catalysts, cooperative catalysis distance (r_{co}) and bimolecular decomposition distance (r_d); r_{co} or $r_0 = 1.26$ nm and $r_d = 0.82$ nm were obtained. As for the predominant factor affecting the present electro-

chemical activity, cooperative catalysis was suggested rather than charge transfer.

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