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Analysis of cooperative catalysis by a molecular water oxidation catalyst adsorbed onto an inorganic particle matrix

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Abstract

Electrocatalytic water oxidation was carried out using a basal-plane pyrolytic graphite (BPG) electrode coated with electrodeposited Platinum black (Pt-black) adsorbing $[Ru(NH_3)_5Cl]^{2+}$. The amount of O_2 evolved (V_{O_2}, mol h^{-1}) remarkably increased by adsorbing the complex onto Pt-black. The plots of V_{O_2} vs. the complex amount on the Pt-black gave a sigmoidal curve, which was explained by both the cooperative catalysis by two molecules of the complex and their bimolecular decomposition. The electrocatalytic activity of the complex was analyzed in terms of its intrinsic activity, k (h^{-1}), cooperative catalysis distance, r_{co} (nm) and critical decomposition distance, r_d (nm) for both the void space adsorption model (VAM) and surface adsorption model (SAM) based on intermolecular distance distribution. $k = 940$ h^{-1}, $r_{co} = 1.21$ nm and $r_d = 0.97$ nm for VAM and 950 h^{-1} $r_{co} = 0.82$ nm and $r_d = 0.78$ nm for SAM were obtained, respectively. Remarkable high intrinsic activities are ascribed to the efficient charge transfer from the electrode to the complex attached to the Pt-black. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium complex; Pt black; Water oxidation catalyst; Intermolecular distance distribution

1. Introduction

The electrodes modified with inorganic particles, zeolite and intercalation compounds incorporating a functional molecule have been studied extensively for their application to practical use as well as to fundamental research in electrochemistry and photochemistry [1,2]. In order to optimize the molecular function, it is important to study factors affecting the activity and to establish activity analysis models involving these factors. However, there have been only a few reports on activity analysis model in such modified-electrode systems.

Water oxidation is one of the most important fundamental reactions in nature [3,4]. Many water oxidation catalyst systems have been reported [5–9]. However, the design of an active and stable water oxidation catalyst system has been difficult. Especially, the construction of an electrocatalytic system which is important for its application to an artificial photosynthetic system [10,11] has been difficult. We have found a highly active and stable electrocatalytic water oxidation system composed of a trinuclear ruthenium complex and Platinum black [12,13].

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$[Ru(NH_3)_5Cl]^{2+}$ is an interesting molecule-based water oxidation catalyst which works as a two-electron oxidation catalyst to catalyze four-electron water oxidation cooperatively by two complex molecules [14]. A Nafion membrane incorporating $[Ru(NH_3)_5Cl]^{2+}$ (Nafion-$[Ru(NH_3)_5Cl]^{2+}$) has been applied to an electrocatalytic water oxidation system [15], but the low turnover number of the complex has been a problem.

In the present paper, it was found that an efficient cooperative water oxidation catalysis by two molecules of $[Ru(NH_3)_5Cl]^{2+}$ takes place on electrodeposited Pt-black. The electrocatalytic activity of the complex on Pt-black will be analyzed in terms of its intrinsic activity, k (h^{-1}), cooperative catalysis distance, r_{co} (nm) and critical decomposition distance, r_d (nm) based on intermolecular distance distribution, and the results will be discussed compared with those in the $[Ru(NH_3)_5Cl]^{2+}$/Nafion system.

2. Experimental

2.1. Materials

$H_2PtCl_6 \cdot 6H_2O$ was purchased from Kanto Chemical and $[Ru(NH_3)_5Cl]Cl_2$ from Aldrich Chemical. All these materials were of commercially available purest grade and used as received.

2.2. Preparation of modified electrodes

Pt-black was electrodeposited from a 1.0×10^{-2} mol dm^{-3} (M) H_2PtCl_6 aqueous solution containing 2.0×10^{-4} M lead (II) acetate onto the surface of a BPG electrode (the effective area is 0.17 cm^2) by cathodic polarization of the electrode under galvanostatic conditions at 20 mA cm^{-2} with stirring to obtain a BPG electrode coated with electrodeposited Pt-black (abbreviated to BPG/Pt-black). The BPG/Pt-black obtained was rinsed with pure water and then polarized cathodically in a 0.1 M sulfuric acid aqueous solution to complete the electrodeposition. The amount of the deposited Pt-black was estimated from the optical absorbance change at 450 nm ($\varepsilon = 47.3$ cm^{-1} M^{-1}) of the H_2PtCl_6 aqueous solution before and after the electrodeposition. It was observed by a scanning electron microscope that the electrodeposited Pt-black is composed of Pt particles of a similar size of average 33-nm diameter. A $[Ru(NH_3)_5Cl]^{2+}$ aqueous solution (6.2×10^{-4} M) was cast onto the surface of the BPG/Pt-black and then the electrode was air-dried for about 12 h at room temperature to obtain a BPG electrode coated with the deposited Pt-black adsorbing $[Ru(NH_3)_5Cl]^{2+}$ (denoted as BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$]).

2.3. Measurements

A potentiostat (Hokuto Denko, HA-301), a function generator (Hokuto Denko, HB-104), coulometer (Hokuto Denko, HF-201) and an *X-Y* recorder (Rikadenki, RW-21T) 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 (0.1 M KNO_3, pH 6.8) was deaerated by bubbling argon gas for 1 h. The O_2 evolved in a potentiostatic electrolysis was analyzed by a gas chromatograph (Shimazu GC-8A) equipped with a 5 Å molecular sieve column using argon carrier gas at 40 ml min^{-1} flow rate. The amount of the evolved O_2 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 absorbed stably on Pt-black and not desorbed even by dipping the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] into an aqueous electrolyte solution. Its adsorption onto the Pt-black would be due to physical interaction

between the complex and the Pt-black [13]. The maximum molar ratio ($\eta = [Ru(NH_3)_5\text{-}Cl]^{2+}$/Pt-black) of the complex adsorbed and Pt-black is 3.5×10^{-3}. When the η exceeds this value, dissolution of the complex into water was observed.

The time–current curves in a potentiostatic electrolysis at 1.3 V (vs. Ag/AgCl) using the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] or BPG/Pt-black are shown in Fig. 1. The anodic current density (3.8 mA cm^{-2}) in the steady state at the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] was about 4.6 times as high as that (0.82 mA cm^{-2}) at the BPG/Pt-black.

The amount (V_{O_2}, mol h^{-1}) of the O_2 evolved after potentiostatic electrolysis for 1 h was remarkably higher in the whole potential range at the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] than at the BPG/Pt-black and a bare BPG electrode, and the potential to start O_2 evolution was significantly lower at the former than at the latter blank electrodes as shown in Fig. 2. The O_2 (1.2×10^{-4} dm^3) evolved at the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] at 1.30 V (vs. Ag/AgCl) was 6.6 times as high as that (1.8×10^{-5} dm^3) at the BPG/Pt-black. Turnover number of the complex was 300 h^{-1} for the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] under the conditions employed. It should be noted that the catalytic activity of the complex supported on the Pt-black is remarkably high when considering its maximum turnover number (4.7 h^{-1} at 1.4 V vs. Ag/AgCl) [15] in a Nafion membrane.

The plots of V_{O_2} vs. the $[Ru(NH_3)_5Cl]^{2+}$ amount are shown in Fig. 3, where the complex

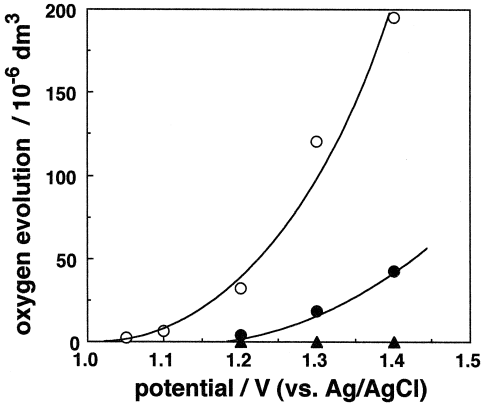

Fig. 2. Relationship between the amount of O_2 evolved (V_{O_2}, mol h^{-1}) and applied potential in potentiostatic electrolyses for 1 h using various electrodes. (○) BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$]; (●) BPG/Pt-black; (▲) bare BPG; The amount of Pt-black and $[Ru(NH_3)_5Cl]^{2+}$ on the electrode is 6.0×10^{-6} and 1.4×10^{-8} mol, respectively.

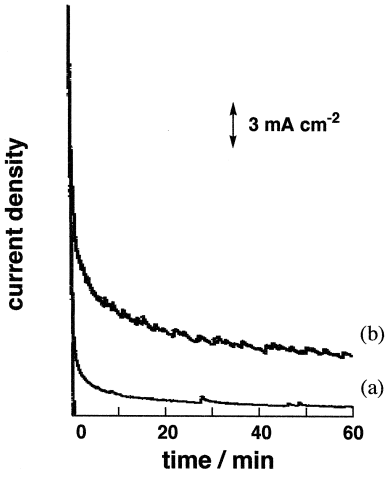

Fig. 1. Time–current curves in potentiostatic electrolyses at 1.3 V (vs. Ag/AgCl) for 1 h in an aqueous 0.1 M KNO_3 (pH 6.8). (a) BPG/Pt-black, (b) BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$]; Pt-black and $[Ru(NH_3)_5Cl]^{2+}$ are 6.0×10^{-6} and 1.4×10^{-8} mol, respectively.

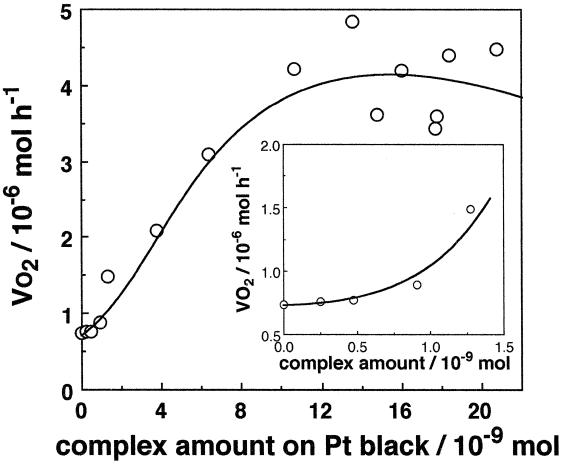

Fig. 3. Dependency of the rate of O_2 evolved (V_{O_2}, mol h^{-1}) on the $[Ru(NH_3)_5Cl]^{2+}$ amount in potentiostatic electrolyses at 1.3 V (vs. Ag/AgCl) for 1 h in an aqueous 0.1 M KNO_3 (pH 6.8) using a BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$]. The Pt-black amount is 6.0×10^{-6} mol.

amount is a measure of its concentration on the Pt-black. The V_{O_2} increased with the complex amount at low amounts and decreased with its amounts after passing a maximum value. The V_{O_2} increase at low amounts was second order with respect to the complex amount (i.e., concentration) as shown in the inset of Fig. 3, indicating that O_2 evolution is a bimolecular reaction with respect to the complex. Distinguishable redox waves based on the complex were not observed in the cyclic voltammogram (CV) of the BPG/Pt-black [$[Ru(NH_3)_5Cl]^{2+}$] because of the high capacitive currents due to the Pt-black. However, we observed actually two oxidation waves at 1.06 V and 1.28 V vs. SCE in the CV of a Nafion-coated graphite electrode incorporating $[Ru(NH_3)_5Cl]^{2+}$ [16], showing that the complex acts as a two-electron oxidation catalyst. Thus, the four-electron water oxidation to evolve O_2 should be cooperatively catalyzed by two molecules of the complex on the Pt-black.

The V_{O_2} decreased when the complex amount exceeds 1.4×10^{-8} mol per 6.0×10^{-6} mol Pt-black. We found that $[Ru(NH_3)_5Cl]^{2+}$ undergoes bimolecular decomposition to deactivate at high complex concentrations in an aqueous solution as well as in a polymer membrane in the chemical water oxidation system using a Ce^{IV} oxidant [14]. In these cases, dinitrogen evolution resulting from the oxidation of its ammine ligands was observed following its activity decrease [14]. The activity decrease in the present system at its high complex loading region can be ascribed to the bimolecular decomposition of the complex. The η at the optimum conditions for the catalysis is 2.3×10^{-3}.

Such water oxidation catalysis system composed of a complex adsorbed on metal particles has not been studied yet except our earlier paper [13]. In the present system, four-electron water oxidation takes place by cooperative catalysis of the complexes, which undergo bimolecular decomposition to become inactive. In a system where catalysts are immobilized in (or on) a matrix as the present case, the distance between the catalyst molecules are important for bimolecular catalysis and decomposition. Therefore, the intermolecular distance between the immobilized complex molecules is an important factor for analyzing the catalysis. It is designated here that cooperative catalysis takes place only within a cooperative catalysis distance, r_{co} (nm) and that the catalysts present within a critical decomposition distance, r_d (nm) undergo a bimolecular decomposition without catalysis.

We now propose two activity models. One is a void space adsorption model (VAM) for which the catalyst is adsorbed into the void space between the Pt particles, and another is a surface adsorption model (SAM) for which the catalyst is adsorbed on the surface of the Pt particles.

In the VAM, the distance distribution between the nearest-neighbor molecules in the void space is given by Eq. (1) [13,17]:

$$P_v(r) = 4\pi r^2 N_A c \times 10^{-24} \exp\left[-4\pi \times \left(r^3 - s_v^3\right) N_A c \times 10^{-24}/3\right], \quad (1)$$

where $P_v(r)$ (nm^{-1}), c (mol dm^{-3}), s_v (nm) and N_A (mol^{-1}) are the probability density that the center-to-center distance between the nearest-neighbor molecules is r (nm), complex concentration in the void space among the Pt particles, contact distance between the complexes for the VAM, and Avogadro's number, respectively. As for s_v, the diameter (0.75 nm) of the sphere of the complex was approximately used [14]. When assuming a closest packing of the Pt particles, the void space volume, V (dm^3 mol^{-1}) among the particles per 1 mol Pt-black is calculated from $M_W p \times 10^{-3}/d$ to be 2.4×10^{-3} dm^3 per mol Pt-black, where M_W is the atomic weight (195.08 g mol^{-1}) of platinum, p is the fractional void (void volume/(void volume + particle volume) = 0.26) and d is the density (21.45 g cm^{-3}) of platinum. When the modified electrode is dipped in an aqueous solution of the complex, the complex is incorporated into the void space, and c can be calculated by η/V.

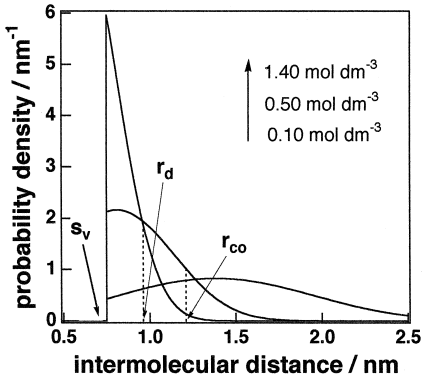

Fig. 4. Distance distribution between the nearest-neighbor complexes for various complex concentrations in the void space model (VAM) among the Pt particles according to Eq. (1).

The distance distribution was calculated according to Eq. (1) as shown in Fig. 4 for different c.

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 fractions of the complex which works as a cooperative catalyst (R_{co}) and the fraction which undergoes a bimolecular decomposition (R_{dec}) are expressed as follows:

$$R_{co} = \int_{s_v}^{r_{co}} P_v(r)\mathrm{d}r = 1 - \exp\left[-4\pi \times \left(r_{co}^3 - s_v^3\right) N_A c \times 10^{-24}/3\right], \quad (2)$$

$$R_{dec} = \int_{s_v}^{r_d} P_v(r)\mathrm{d}r = 1 - \exp\left[-4\pi \times \left(r_d^3 - s_v^3\right) N_A c \times 10^{-24}/3\right]. \quad (3)$$

The amount of the effective complex for the water oxidation is represented by $m(R_{co} - R_{dec})$ where m (mol) is the total complex amount. The V'_{O_2} which is the amount of O_2 evolved via the complex is proportional to $m(R_{co} - R_{dec})$, and therefore Eq. (4) is derived:

$$V'_{O2} = km(R_{co} - R_{dec}) = km\left[\exp\left\{-4\pi\left(r_d^3 - s_v^3\right)N_A c \times 10^{-24}/3\right\} - \exp\left\{-4\pi\left(r_{co}^3 - s_v^3\right)N_A c \times 10^{-24}/3\right\}\right], \quad (4)$$

where k (h^{-1}) is a constant representing an intrinsic catalyst activity (turnover number of the catalyst). V'_{O_2} was calculated by subtracting V_{O_2} without the complex from V_{O_2}. Eq. (4) was fitted to the experimental V'_{O_2} data, and the best fitting was obtained as shown in Fig. 5a when $k = 940\ h^{-1}$, $r_{co} = 1.21$ nm and $r_d = 0.97$ nm.

In the SAM, the distance distribution between the nearest-neighbor molecules on the Pt particle surface can be given by Eq. (5) when assuming a random dispersion:

$$P_s(r) = \left\{2\pi r N_A \gamma \times 10^{-14}\right\} \times \left\{\exp\left[-\pi\left(r^2 - s_s^2\right)N_A \gamma \times 10^{-14}\right]\right\}, \quad (5)$$

where $P_s(r)$ (nm^{-1}), γ (mol cm^{-2}) and s_s (nm) is the probability density, the surface complex

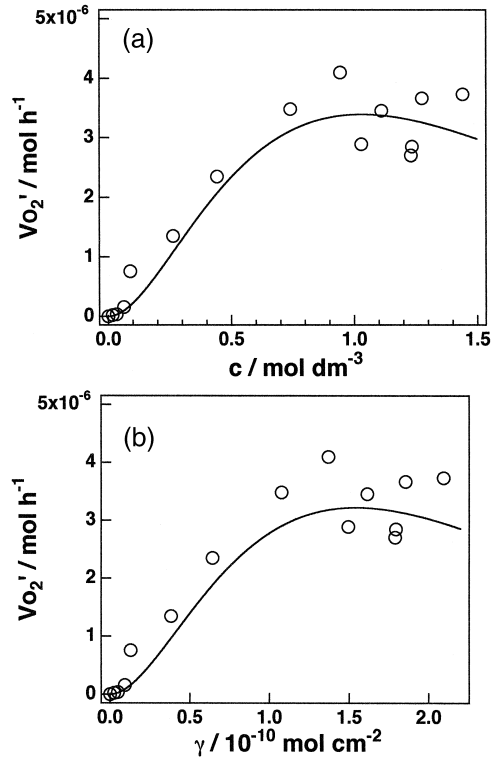

Fig. 5. Plots of the rate of O_2 evolved via the complex (V'_{O_2}) vs. the complex concentration (c) or surface complex concentration (γ). The solid line is the calculation curves based on Eq. (4) for VAM.

concentration and the contact distance between the complex for SAM, respectively. The surface area per 1 mol Pt particle, S (cm^2 mol^{-1}) is calculated to be 1.65×10^7 cm^2 mol^{-1} from the average particle size (33 nm) and d (21.45 g cm^{-3}) and M_W (195.08 g mol^{-1}) of the platinum, and γ is obtained by η/S. The s_s value is the diameter (0.75 nm) of a complex projected on a flat surface assuming the complex as a sphere [14].

The R_{co} and R_{dec} for the SAM are given by Eqs. (6) and (7):

$$R_{co} = \int_{s_s}^{r_{co}} P_s(r)\mathrm{d}r = 1 - \exp\left[-\pi\left(r_{co}^2 - s_s^2\right)N_A\gamma \times 10^{-14}\right], \quad (6)$$

$$R_{dec} = \int_{s_s}^{r_d} P_s(r)\mathrm{d}r = 1 - \exp\left[-\pi\left(r_d^2 - s_s^2\right)N_A\gamma \times 10^{-14}\right]. \quad (7)$$

Eq. (8) is then derived similarly to the VAM:

$$V'_{O2} = km(R_{co} - R_{dec}) = km\left[\exp\left\{-\pi\left(r_d^2 - s_s^2\right)N_A\gamma \times 10^{-14}\right\} - \exp\left\{-\pi\left(r_{co}^2 - s_s^2\right)N_A\gamma \times 10^{-14}\right\}\right]. \quad (8)$$

The best fitting of Eq. (8) to the experimental V'_{O_2} data was obtained as shown in Fig. 5b when $k = 950$ h^{-1}, $r_{co} = 0.83$ nm and $r_d = 0.78$ nm, respectively.

The analysis results are summarized in Table 1 together with our previous results for which Ce^{IV} was used as an oxidant to oxidize water [14]. The k values in the present system, which are almost the same for VAM and SAM, are 5×10^3 times larger than the turnover number (1.8×10^{-1} h^{-1}) of the Pt-black alone obtained from the slope of a linear relation of V_{O_2} vs. Pt-black amount at the BPG/Pt-black, showing that water oxidation at the BPG/Pt-black $[Ru(NH_3)_5Cl]^{2+}$ is catalyzed mainly by the complex. Polymer-coated electrodes are often used in an electrocatalysis. These k values in the present system are larger than that (6.7 h^{-1} at 1.4 V vs. Ag/AgCl) [15] at the Nafion membrane coated Pt electrode incorporating the complex (Pt/Nafion $[Ru(NH_3)_5Cl]^{2+}$) by two orders of magnitude. In the Nafion $[Ru(NH_3)_5Cl]^{2+}$ system, the charge transport from the electrode to the complex takes place via charge transfer between the complexes which is a relatively slow process. While, in the present system, the charge would be directly injected to the complex via Pt-black. Such efficient charge transport from the electrode to the complex would be important for the electrocatalytic activity.

The r_d values for VAM (0.97 nm) and SAM (0.78 nm) are close to those (0.82 nm and 0.84 nm) in electrochemical and chemical Nafion $[Ru(NH_3)_5Cl]^{2+}$ systems and reasonable when considering the molecular size (0.75 nm) of the complex, showing that the bimolecular decom-

Table 1
Summary of k, s, r_{co} and r_d values in water oxidation catalyst system

System	Applied potential (V vs. Ag/AgCl)	Analysis model	k [h^{-1}]	r_{co} [nm]	r_d [nm]
Electrochemical system					
BPG/Pt-black $[Ru(NH_3)_5Cl^{2+}]$	1.3	VAM	940	1.21	0.97
(present study)		SAM	950	0.82	0.78
Pt/Nafion $[Ru(NH_3)_5Cl^{2+}]$[a]	1.4	–	6.7	1.26	0.82
Chemical system using Ce^{IV} oxidant					
Nafion $[Ru(NH_3)_5Cl^{2+}]$[b]		–	9.7[c]	1.21	0.84

VAM: void-space adsorption model; SAM: surface adsorption model.
[a]Ref. [15], [b]Ref. [14], [c]estimated from the data per second (2.7×10^{-3} s^{-1}).

position takes place between the complexes in close proximity with each other on the Pt-black.

The r_{co} value (0.82 nm) for SAM is shorter than that (1.21 nm) for VAM. When comparing these values with the r_{co} (1.26 and 1.21 nm) in the electrochemical and chemical Nafion $[Ru(NH_3)_5Cl]^{2+}$ systems, the VAM model would be more reasonable than the SAM model. We have proposed from the r_{co} value (1.21 nm) obtained in a chemical Nafion $[Ru(NH_3)_5Cl]^{2+}$ system a possible mechanism of a cooperative catalysis via an intermediate formed through hydrogen bonds between water and its ammine ligands (Ru–N–H · · · O–O · · · H–N–Ru) in the membrane [14]. The r_{co} value in the present system supports also such the possibility of an intermediate mechanism.

4. Conclusion

Highly active electrocatalytic water oxidation system to evolve dioxygen (O_2) was established using electrodeposited platinum black adsorbing $[Ru(NH_3)_5Cl]^{2+}$. The amount of O_2 evolved (V_{O_2}, mol h^{-1}) increased remarkably by adsorbing the complex onto the Pt-black. The plots of V_{O_2} vs. the complex amount on Pt-black gave a sigmoidal curve, which was explained by both a cooperative catalysis by two complex molecules and their bimolecular decomposition. The electrocatalytic activity of the complex was analyzed in terms of its intrinsic activity, k (h^{-1}), cooperative catalysis distance, r_{co} (nm) and critical decomposition distance, r_d (nm) for both the void space adsorption model (VAM) and surface adsorption model (SAM) based on intermolecular distance distribution. The analysis results are summarized in Table 1, and compared with those in a Pt/Nafion $[[Ru(NH_3)_5Cl]^{2+}]$. The intrinsic activities (940 h^{-1} for VAM, 950 h^{-1} for SAM) in the present system are larger than that (6.7 h^{-1} at 1.4 V vs. Ag/AgCl) in the Pt/Nafion $[[Ru(NH_3)_5Cl]^{2+}]$ by two orders of magnitude, which is ascribed to the efficient charge transfer from the electrode to the complex on Pt-black.

Acknowledgements

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