Enhancing Effects of Amino Acid Residue Model Compounds on Catalytic Activity of an Artificial Oxygen Evolving Center

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ABSTRACT: Electrocatalytic water oxidation was studied for an artificial oxygen evolving center (OEC) model using Nafion (Nf) membrane-coated electrode incorporating Ru-red ($[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{6+}$) and an amino acid residue model compound. On the cyclic voltammogram (CV) of Ru-red in the presence of a Tyr residue model, *p*-cresol (*p*-Cre) or a His residue model, 4-methylimidazole (MIm), the anodic current in an oxidative scan is much higher than that without the model compounds. The amount of O_2 evolved in the potentiostatic electrolysis increased remarkably in the presence of p-Cre or MIm. The enhancing effect of the model compounds on the catalytic activity was analyzed in terms of the intrinsic activity, charge-transfer distance between the complexes, and their critical decomposition distance based on the intermolecular distance distribution. The charge-transfer distance was remarkably prolonged from 1.28 to 2.25 nm by the presence of *p*-Cre and to 1.60 nm by MIm, which strongly suggests that *p*-Cre and MIm work as mediators for charge transfer in an artificial OEC model.

Introduction

There has been considerable interest on long-range electron transfer.[1−4] Aromatic amino acid residues of proteins work in some cases as a mediator for electron transfer.[2,3] Long-range electron transfer is attractive also in a synthetic system.[5] Recently, we have reported on the mediation effect of a tryptophan residue model, 3-methylindole (Ind), on electron transfer from the photoexcited $Ru(bpy)_3{}^{2+}$ to methyl viologen (MV^{2+}) in a polymer membrane.[6]

Water oxidation at the oxygen evolving center (OEC) of a photosynthetic system, which provides electrons to the whole photosynthetic system, is one of the most important and fundamental catalyses in nature.[7,8] This process is important not only in the biological activity but also in a photochemical solar energy conversion system which is attracting much attention toward obtaining a renewable energy resource. It has been difficult to construct an active and stable artificial OEC model. We have proposed[9] that a mediated long-range charge transfer is important and essential for the design of an active and stable OEC model and found[10] that a Tyr residue model, *p*-cresol (*p*-Cre), works as a mediator for charge transfer in the electrochemical OEC model composed of Nafion (Nf) membrane incorporating Ru-red ($[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{6+}$) to increase remarkably the catalytic activity of the complex.

In a photosynthetic OEC, amino acid residues play an important role.[7,11−13] It has been reported that Tyr residue mediates electron transfer between OEC and P680 in the photosystem II[7,11,12] and that the oxidation of His residue is involved in the S_2 to S_3 transition in the OEC.[7,11,13] In the present paper, it was found that the catalytic activity of Ru-red in a Nafion membrane increased remarkably by the presence of *p*-Cre or a His residue model, 4-methylimidazole (MIm). The enhancing effect of amino acid residue model compounds on the catalytic activity of the complex will be analyzed on the basis of intermolecular distance distribution and discussed.

Experimental Section

Materials. Ru-red, *p*-Cre, and toluene (Tol) were purchased from Wako Pure Chemical Industries Ltd. MIm, Ind, and Nafion 117 solution (5 wt % alcoholic solution) were purchased from Aldrich Chemical Co. Inc. Ind was recrystallized from its ligroin solution. *p*-Cre and Tol were purified before use by distillation under reduced pressure. All the other materials are of commercially available purest grade.

Preparation of Nf-Coated Electrode Incorporating Ru-red and an Amino Acid Model Compound. A methanol solution of an amino acid model compound was first prepared, and then the solution was mixed with the same weight of a 5 wt % Nafion solution to prepare a mixture solution (the density is 0.83 g cm^{-3}) containing 5×10^{-4} to 1×10^{-3} M amino acid model compound and 2.5 wt % Nafion. A Nafion membrane (thickness 3 μm) was prepared by casting this mixture solution onto a basal plane pyrolytic graphite (BPG) electrode (0.17 cm^2) or a Pt plate electrode (1 cm^2). The Nafion-coated electrode was immersed in a 2 mL of 1.0×10^{-4} M aqueous Ru-red solution to adsorb the complex into the membrane. 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 adsorption of the complex. The concentrations of the complex and the model compound in the membrane were calculated from the amount of each compound in the membrane and the membrane volume.

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 (or a saturated calomel reference electrode (SCE)), and a platinum wire counter electrodes. A 0.1 M potassium nitrate aqueous solution (pH 5.4) was used as a supporting electrolyte solution and deaerated by bubbling argon gas for 1 h. The O_2 evolved in a potentiostatic electrolysis was analyzed by a Hitachi 163 gas chromatograph equipped with a 5 Å molecular sieve column using argon carrier gas at a 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 to correct the contamination from air.

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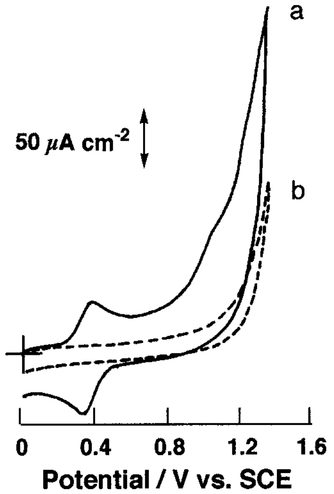

Figure 1. Cyclic voltammograms of BPG/Nf[Ru-red] (a) and BPG/Nf (b) at the scan rate of 50 mV s^{-1} in 0.1 M KNO_3.

Results and Discussion

The cyclic voltammogram (CV) of a basal plane pyrolytic graphite (BPG) electrode coated with a Nafion membrane incorporating Ru-red (abbreviated to BPG/Nf[Ru-red]) is shown in Figure 1a) for the cyclic scan between 0 and 1.4 V (vs SCE). The CV exhibited a couple of reversible redox peaks based on Ru-red ($Ru^{III}-Ru^{IV}-Ru^{III}$)/Ru-brown ($Ru^{IV}-Ru^{III}-Ru^{IV}$) around 0.4 V (vs SCE) and an irreversible anodic peak at 1.1 V. The Ru-red/Ru-brown redox couple was completely reversible and stable in a cyclic scan between 0 and 0.5 V (vs SCE). The anodic current at 1.4 V (vs SCE) in the presence of the complex is much larger than that without complex (Figure 1b), showing that electrocatalytic water oxidation takes place by Ru-red in the membrane.

The CVs of a Nf-coated BPG electrode containing Ru-red and an amino acid residue model compound (denoted as BPG/Nf[Ru-red, amino acid model] are shown in parts a of Figures 2–5, where *p*-Cre, MIm, Tol, and Ind are used as a model compound of Tyr, His, Phe, and Trp, respectively. In the each figure, part b is the CV of blank the Nf[amino acid model]. The anodic current above 1.2 V increased remarkably by Ru-red in the presence of *p*-Cre (Figure 2a) and MIm (Figure 3a), which indicates that *p*-Cre and MIm enhance the catalytic activity of Ru-red in the membrane. The anodic current did not increase by Ru-red in the presence of Tyr or His instead of *p*-Cre or MIm. The visible absorption spectral change of transparent ITO electrode coated by a Nafion membrane incorporating Ru-red and the model compound in the electrochemical redox reaction is the same as that without the model compound. *p*-Cre and MIm are known as a redox active compound, and actually, in both cases, a distinguished anodic peak was observed around 0.8 V (vs SCE) on the CV of their aqueous solution. However, the CV of the Nf-coated BPG containing *p*-Cre or MIm alone did not exhibit any anodic peak around 0.8 V (vs SCE), showing that both *p*-Cre and MIm are electroinactive in the membrane.

Electrocatalytic water oxidation under the potentiostatic conditions at 1.4 V (vs Ag/AgCl) was carried out using Nf-coated Pt plate (1 cm^2) containing Ru-red and a model compound. The turnover number (TN/h^{-1}) of the complex for the O_2 evolution was calculated by subtracting the amount of blank O_2 obtained at Nf[amino acid model] from the amount of O_2 evolved at Nf[Ru-red, amino acid model]. In the case of the Nf-coated Pt electrode containing Ru-red alone, the TN increased with the complex concentration at low concentrations (below 0.1M) as shown in Figure 6a, which is ascribed to facilitated charge transfer between the complexes by hopping.[9,14] A maximum TN (10.7 h^{-1}) was exhibited around 0.1 M, and then it decreased with the concentration. This TN decrease is ascribed to a bimolecular decomposition of the complex to yield N_2.[9,15] The TN of the complex in the membrane is determined by three factors, i.e., the intrinsic activity of the complex,

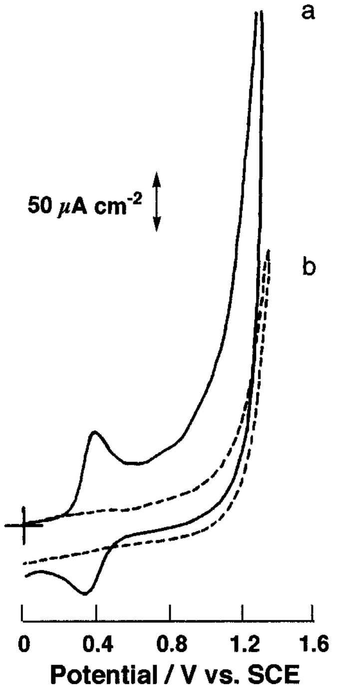

Figure 2. Cyclic voltammograms of BPG/Nf[Ru-red,*p*-Cre] (a) and BPG/Nf[*p*-Cre] (b) at the scan rate of 50 mV s^{-1} in 0.1 M KNO_3. The *p*-Cre concentration in the membrane is 1 × 10^{-1} M.

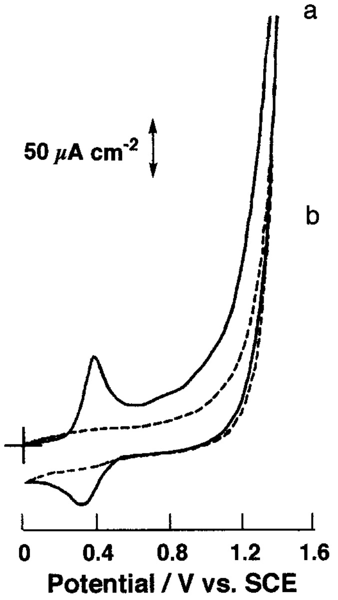

Figure 3. Cyclic voltammograms of BPG/Nf[Ru-red,MIm] (a) and BPG/Nf[MIm] (b) at the scan rate of 50 mV s^{-1} in 0.1 M KNO_3. The MIm concentration in the membrane is 1 × 10^{-1} M.

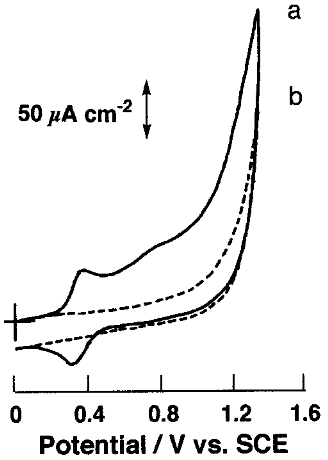

Figure 4. Cyclic voltammograms of BPG/Nf[Ru-red,Tol] (a) and BPG/Nf[Tol] (b) at the scan rate of 50 mV s^{-1} in 0.1 M KNO_3. The Tol concentration in the membrane is 1×10^{-1} M.

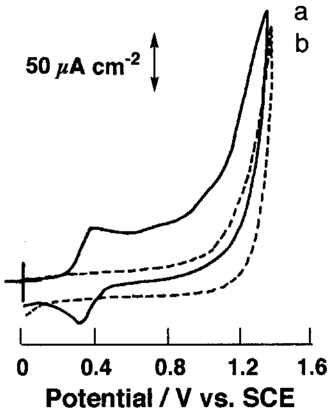

Figure 5. Cyclic voltammograms of BPG/Nf[Ru-red,Ind] (a) and BPG/Nf[Ind] (b) at the scan rate of 50 mV s^{-1} in 0.1 M KNO_3. The Ind concentration in the membrane is 1×10^{-1} M.

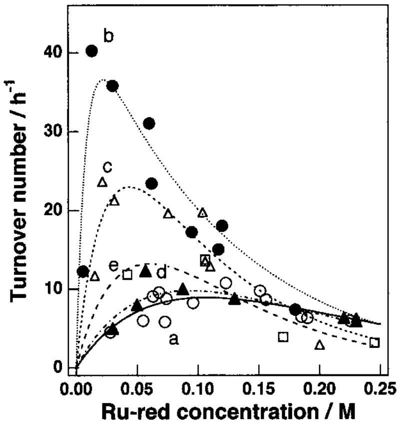

Figure 6. Relationships between turnover number (TN) of the Ru-red for O_2 evolution and the complex concentration in the membrane in the absence of any amino acid model compound (a) and in the presence of 5.0×10^{-2} M *p*-Cre (b), 5.0×10^{-2} M MIm (c), 5.0×10^{-2} M Tol (d), and 5.0×10^{-2} M Ind (e). The solid lines are the calculated curves based on eq 1 (a) or 2 (b−e). The data of a, b, and d were cited from ref 10.

charge transfer between the complexes, and their bimolecular decomposition.[9]

In the presence of *p*-Cre or MIm (Figure 6b or c), the TN increased remarkably at low complex concentrations compared with that without the model compound (Figure 6a). Maximum TNs are 40.2 and 23.6 h^{-1} for *p*-Cre and MIm, respectively. In the presence of Tol or Ind (Figure 6d or e), almost no change of TN was observed. These TN results corresponded to CV data described above. We have reported that TN enhanced by *p*-Cre is ascribable to their mediation effect for charge transfer between the complexes in the membrane.[10] On the basis of our earlier report, it is most probable that MIm can work also as a mediator for the charge transfer between the complexes in the Nf[Ru-red, MIm] system, but Tol and Ind cannot. This is supported by the activity analysis described later. As for the charge mediating effect, we assume some overlapping of the wave functions of the charge donating and accepting catalyst molecules by the help of the wave function of the mediator (*p*-Cre and MIm), which could enhance charge propagation in the membrane.

We have reported a catalytic activity analysis model based on intermolecular distance distribution assuming the random dispersion of a catalyst and mediator.[9,10,15] In the absence of a mediator, TN can be expressed by eq 1 [9] considering three factors, the intrinsic activity of

$$TN = k_{O_2}[\exp\{-4\pi(r_d^{\,3} - s^3)\alpha c N_A(10^{-24}/3)\} - \exp\{-4\pi(r_0^{\,3} - s^3)\alpha c N_A(10^{-24}/3)\}] \quad (1)$$

the complex, charge transfer between the complexes, and their bimolecular decomposition, where k_{O_2}/h^{-1} is a constant to express an intrinsic activity of catalyst, r_0/nm is a charge-transfer distance within which the charge can be transferred by hopping between complexes, and r_d/nm is a critical decomposition distance within which the bimolecular decomposition of complexes takes place. s/nm, α, c/(mol dm^{-3}), and N_A/mol^{-1} are the contact distance (1.06 nm)[15] between the complexes, degree of the complex localization (5.1)[16] in the Nafion membrane, the complex concentration in the membrane, and Avogadro's number, respectively. The first exponential term in the parentheses of eq 1 represents the fraction of the complex that does not undergo the bimolecular decomposition (the intermolecular distance between the nearest-neighbor complexes, r, is longer than r_d), and the second one representing the fraction of the complex that cannot accept charge by hopping between the complexes (r is longer than r_0).

In the presence of a mediator, TN can be represented by eq 2,[10] assuming that the charge on the complex is transferred via a mediator between the complexes present within a mediated charge-transfer distance (r_0'/nm) in addition to charge transfer between them present within r_0, where c_m and r_m are a mediator

$$TN = k_{O_2}[\exp\{-4\pi(r_d^{\,3} - s^3)\alpha c N_A(10^{-24}/3)\} - \exp\{-4\pi(r_0^{\,3} - s^3)\alpha c N_A(10^{-24}/3)\} + \{1 - \exp(-4\pi r_m^{\,3} N_A c_m(10^{-24}/3))\}\,[\exp\{-4\pi(r_0^{\,3} - s^3)\alpha c N_A(10^{-24}/3)\} - \exp\{-4\pi((r_0')^3 - s^3)\alpha c N_A(10^{-24}/3)\}]] \quad (2)$$

concentration in a membrane and a radius of a sphere in which model compounds work as a mediator.[5,10] When the model compounds are present in this sphere, they can work to mediate charge transfer. The third term in the large parentheses expresses the fraction of the complex that can accept charge by hopping via a mediator between the complexes.

Table 1. Summary of Fitting Parameters in Nf[Ru-red, Amino Acid Model Compound] Systems

mediator	k_{O_2}/h^{-1}	r_0/nm	r_d/nm	r_0'/nm
none[a]	54.8	1.28	1.21	
p-Cre[a]	60.1	1.29	1.24	2.25
MIm	55.0	1.27	1.28	1.60
Tol	50.3	1.30	1.22	1.31
Ind	59.8	1.29	1.23	1.33

[a] Cited from ref 10.

Equation 1 was applied to the system without a mediator, and eq 2 was applied to the systems in the presence of the model compound. Good fittings were obtained as shown in each curve of Figure 6. The parameters in the best fitting for the various systems are summarized in Table 1. The k_{O_2}, r_0, and r_d values are almost the same in the each system. The r_0' values in the presence of *p*-Cre or MIm are remarkably longer than r_0 without model compounds, though those in the presence of Tol or Ind are not appreciably different from the value without a mediator. These results show a charge mediation effect of MIm and *p*-Cre in the electrocatalytic water oxidation system based on Ru-red.

Conclusion

Cyclic voltammetry and potentiostatic electrolysis were carried out using a Nafion membrane-coated electrode incorporating Ru-red and a amino acid residue model compound. On the cyclic voltammogram (CV) of Ru-red in the presence of a Tyr residue model, *p*-cresol (*p*-Cre), or a His residue model, 4-methylimidazole (MIm), the anodic current in an oxidative scan is much higher than that without the model compound. The amount of O_2 evolved in a potentiostatic electrolysis increased remarkably in the presence of *p*-Cre or MIm. The enhancing effect of the model compound on the catalytic activity of the complex was analyzed in terms of the intrinsic activity, charge-transfer distance between the complexes, and their critical decomposition distance based on the intermolecular distance distribution. The charge-transfer distance was remarkably prolonged from 1.28 to 2.25 nm by the presence of *p*-Cre and to 1.60 nm by the presence of MIm, which shows that *p*-Cre and MIm work as a mediator for charge transfer in an artificial OEC model.

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