

Oxygen-evolving Centre utilizing Polymer Membrane and Trinuclear Ruthenium Complexes

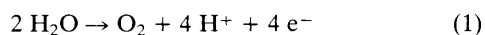
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Efficient and stable heterogeneous catalytic systems for water oxidation can be used to model the photosynthetic dioxygen-evolving centre using trinuclear ruthenium complexes (Ru-red and Ru-brown) and polymer membrane.

Multielectron transfer is an important reaction in biological systems especially in water oxidation in photosynthesis. In order to couple photoexcitation processes with electron-transfer reaction, electron transfer must be photoinduced from a water molecule to carbon dioxide in the photosynthetic process.^{1,2} In photosynthesis, a four-electron process of water oxidation to give dioxygen [eqn. (1)] is coupled with a one-electron process of photoexcitation occurring in chlorophyll.



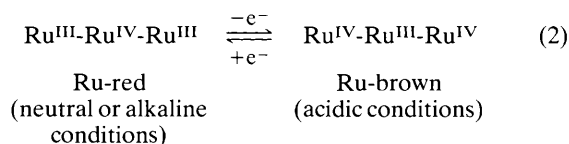
In the oxygen-evolving centre (OEC), more than two Mn ions form a protein complex, which couples the four-electron oxidation of water with photoexcitation. The protein part provides the Mn ions with appropriate redox potentials by complexation. Another important role of the protein is to stabilize the highly oxidized state of the catalyst, which would otherwise oxidize neighbouring organic moieties.

One approach to realize an efficient and stable four-electron water oxidation centre in an artificial system is to design a catalyst in a condensed system such as a polymer membrane.^{3,4} Our intention is to design a model system where the involvement of more than two metal centres leads to the formation of an active multielectron transfer site in a membrane rather than in a homogeneous solution. We have already reported the trinuclear ruthenium complexes, Ru-red [$\{(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5\}^{6+}$, represented as $\text{Ru}^{\text{III}}-\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}$] and Ru-brown [$\{(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5\}^{7+}$, represented as $\text{Ru}^{\text{IV}}-\text{Ru}^{\text{III}}-\text{Ru}^{\text{IV}}$], as four-electron water oxidation catalysts⁵⁻⁷ to evolve dioxygen from water molecules. However, recent studies show that this trimer complex undergoes decomposition in a homogeneous solution during the water oxidation process.^{6,8} We found by an *in situ* spectroscopic voltammogram that the trinuclear ruthenium complexes are highly stabilized when adsorbed into a Nafion membrane. The successful construction of the membrane catalyst system for water oxidation is reported in this paper.

The Ru-red (Wako) was used as received. The Ru-brown was prepared as reported earlier.^{6,9} A 5% Nafion solution

(Aldrich) was diluted into 2.5% using methanol before use. A Nafion coated ITO (indium tin oxide coated glass) electrode was prepared by casting 8 μl of the 2.5% Nafion solution onto an ITO substrate (effective area 1 cm^2). The Nafion-coated ITO was soaked in water for 1 h after evaporating the solvent to improve the film characteristics. The estimated thickness of the film is 0.8 μm . The Nafion coated ITO electrode was dipped in an aqueous solution containing 2 mmol dm^{-3} Ru-red or Ru-brown. After the adsorption of the complex, the electrode (represented as ITO/Nf/Ru-red or Ru-brown) was rinsed with water and kept in water before use. A thin layer ITO cell used for a solution spectroscopic voltammetry was constructed using two ITO-coated quartz plates (both as working electrodes) kept parallel to each other with a thin spacer (175 μm thickness) in between, and a platinum wire and a silver wire were used as counter and reference electrodes, respectively. For the film spectroscopic voltammetry, a conventional three-electrode cell was used with the coated ITO as a working electrode. The *in situ* spectroscopic voltammograms were measured using a Hokuto Denko Potentiostat/Galvanostat HA 301, a function Generator HB 104 and an Otsuka Electronics IMUC 7000 Diode array multichannel detector system assisted by a computer.

A visible absorption spectrum of Ru-red in an aqueous solution showed an intense band at 535 nm.⁹ When Ru-red was dissolved in an aqueous acidic solution, it underwent one-electron oxidation with the formation of Ru-brown which shows an absorption band at 460 nm. A very similar spectral change was observed also for the Ru-red adsorbed into a Nafion film. When Ru-brown was dissolved in neutral water, Ru-red was formed [eqn. (2)]. The reversible formation of Ru-red and Ru-brown has already been well established.^{6,9,10}



The electrochemical study^{5,6} in an aqueous solution revealed

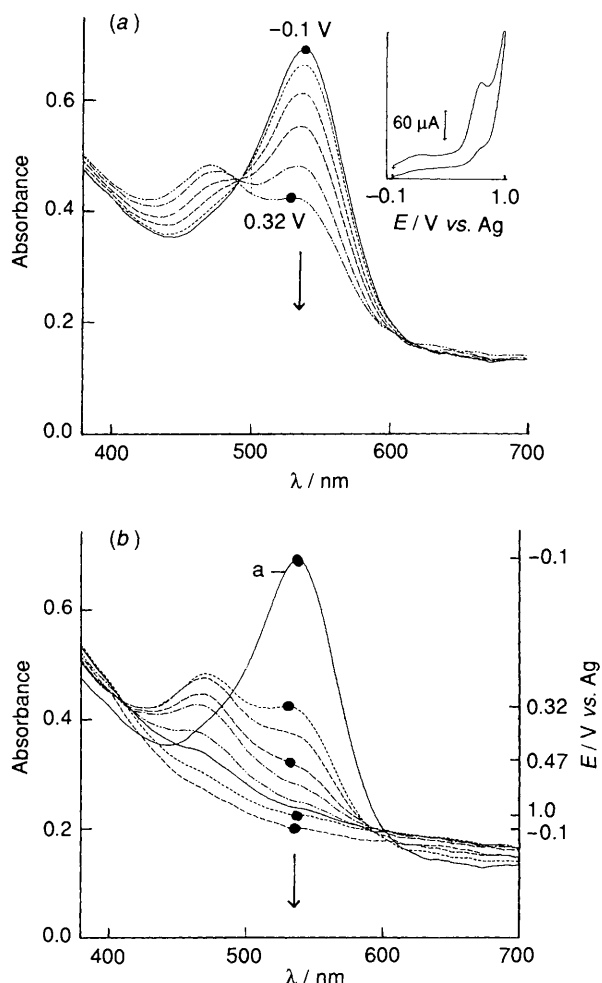


Fig. 1 *In situ* absorption spectra of Ru-red in an aqueous solution (pH 7.4 phosphate buffer) measured during a voltammetric scan at 5 mV s^{-1} using a thin layer ITO cell. The direction of the absorbance change and the potential range are indicated. (a). Absorption spectra recorded during the oxidative scan from -0.1 to 0.32 V vs. Ag . Inset: cyclic voltammogram recorded during the *in situ* absorption spectral measurements at 5 mV s^{-1} . (b). Absorption spectra recorded during the oxidative scan from 0.32 to 1.0 V vs. Ag and during the reductive scan from 1.0 to -0.1 V vs. Ag . Spectrum a: Absorption spectrum recorded in the beginning of the scan.

that the Ru-red undergoes five-step oxidations to form the higher oxidation state $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}\text{-Ru}^{\text{V}}$ complex.

The cyclic voltammogram recorded for a Ru-red aqueous solution at pH 7.4 (phosphate buffer) with a scan rate of 5 mV s^{-1} using a thin layer ITO cell is shown in Fig. 1(a). Besides the oxidation peak at around 0.8 V vs. Ag , it shows a large anodic current at higher positive potentials due to catalysed water oxidation.^{5,6} In the reverse scan, the cyclic voltammogram does not show any distinguishable reduction peak, which is due to the reduction of the higher oxidation state complex by water molecules.⁷ The *in situ* absorption spectra recorded during the scan from -0.1 to 1.0 V vs. Ag at 5 mV s^{-1} scan rate are shown in Fig. 1(a) and 1(b). The absorption spectra recorded in the potential range from -0.1 to 0.32 V vs. Ag [Fig. 1(a)] show a decrease in the absorbance at 535 nm peak with a concomitant increase in the absorbance at 470 nm with an isosbestic point at 490 nm . The decrease in the absorbance at 535 nm is assigned to the oxidation of Ru-red ($\text{Ru}^{\text{III}}\text{-Ru}^{\text{IV}}\text{-Ru}^{\text{III}}$) and the increase in the absorbance at 470 nm to the formation of Ru-brown ($\text{Ru}^{\text{IV}}\text{-Ru}^{\text{III}}\text{-Ru}^{\text{IV}}$).^{6,9} When the applied potential was increased above 0.32 V vs. Ag , both the absorbances at 470 and 535 nm start decreasing [Fig. 1(b)], and when the potential reached 1.0 V vs. Ag , the

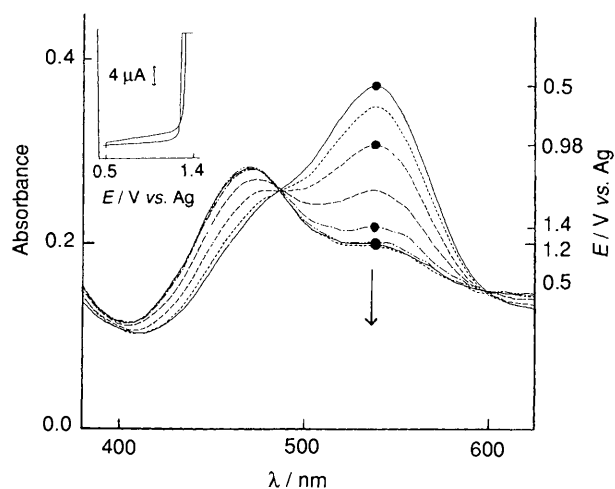


Fig. 2 *In situ* absorption spectra of ITO/Nf/Ru-red dipped in water (pH 7.4 phosphate buffer) at 0.5 mV s^{-1} scan rate. The direction of the absorption and the potential range are indicated. Inset: Cyclic voltammogram recorded during the *in situ* absorption spectral measurements.

two peaks almost completely disappeared. In the reverse scan from 1.0 to -0.1 V vs. Ag , there was no recovery of the absorbances at 470 and 535 nm . These results show that the trimer Ru-red has decomposed probably to form monomeric ruthenium complexes upon oxidation to $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}\text{-Ru}^{\text{V}}$ in a homogeneous solution at higher positive potentials. It has been reported⁸ that Ru-red undergoes decomposition during chemical oxidation by Ce^{IV} ions in a homogeneous solution. Even though the trinuclear complex decomposed to monomeric complex, it would retain catalytic activity. It has clearly been established that the monomeric ammine complexes of ruthenium are active catalysts for water oxidation in a homogeneous solution.^{11,12} Analogous spectral changes were also observed for the Ru-brown dissolved in an aqueous solution at pH 1 (HNO_3) in the *in situ* spectrocyclic voltammetry studies.

The cyclic voltammogram recorded for the ITO/Nf/Ru-red dipped in water at pH 7.4 is shown in the inset of Fig. 2. The oxidation peak is not clear because of the large anodic current at higher positive potentials due to water oxidation. Electro-catalytic oxygen evolution by water oxidation with this complex/polymer coated system has already been reported by us.⁷ A slower scan rate of 0.5 mV s^{-1} was employed in the case of the Nafion coated ITO electrodes. The trimer complexes in a homogeneous solution underwent rapid decomposition at both the scan rates of 5 and 0.5 mV s^{-1} . However, the complexes incorporated into a Nafion film (ITO/Nf/Ru-red or Ru-brown) were found to be very stable. The *in situ* absorption spectra of the ITO/Nf/Ru-red recorded during the scan from 0.5 to 1.4 V vs. SCE at the scan rate of 0.5 mV s^{-1} (pH 7.4) are shown in Fig. 2. They show a decrease in the absorbance at 540 nm with a simultaneous absorbance increase at 470 nm and with an isosbestic point at 487 nm . The absorbance decrease at 540 nm is assigned to the oxidation of the Ru-red ($\text{Ru}^{\text{III}}\text{-Ru}^{\text{IV}}\text{-Ru}^{\text{III}}$) and the increase in the absorbance at 470 nm to the formation of the Ru-brown.^{5,6,9,10} During the reverse scan in the potential range from 1.4 to 1.2 V vs. SCE , Ru-red still underwent oxidation to a little extent as noticed in the absorbance increase at 470 nm . In the potential scan from 1.2 to 0.5 V vs. SCE , the absorption spectra do not show any change demonstrating the stability of the Ru-brown in the Nafion film during the catalytic water oxidation. The absorption spectra did not show any further change in repeated cyclic scans. When the applied potential was increased above 1.2 V vs. SCE , the Ru-red and Ru-brown should undergo oxidation to produce $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}\text{-Ru}^{\text{V}}$ complex,⁶ but this $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}\text{-Ru}^{\text{V}}$ complex must be rapidly

reduced by water molecules to produce Ru-brown ($\text{Ru}^{\text{IV}}\text{-Ru}^{\text{III}}\text{-Ru}^{\text{IV}}$) by four-electron process. The cyclic reaction between $\text{Ru}^{\text{IV}}\text{-Ru}^{\text{III}}\text{-Ru}^{\text{IV}}$ and $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}\text{-Ru}^{\text{V}}$ showed only the spectrum of the Ru-brown independent of the pH. When the ITO/Nf/Ru-brown electrode was dipped in neutral or alkaline water after the voltammetric studies, the Ru-brown was reduced to Ru-red. All the experiments were repeated at least three times to confirm the data.

The metal complex adsorbed into the Nafion membrane would be located in a microheterogeneous environment imposed by the hydrophobic fluorocarbon moiety, and the cationic complex ion would be held electrostatically by the sulfonate ions. In this polymer membrane, the complexes are isolated with each other and the microheterogeneous environment would alter the interaction between the complex ion and the solvent. Such effects have been well studied for macromolecular metal complexes.^{3,4} These water oxidation catalysts are powerful oxidants in their higher oxidation state and in a homogeneous aqueous solution a highly oxidized complex may oxidize organic ligands of another complex molecule assisted by solvation with water molecules. However, such oxidative degradation would be hindered in a polymer membrane by the microheterogeneous environment imposed on the isolated metal complex entities.

These results are of great importance in relation to the water oxidation site in the photosynthetic membrane system. The oxidation of water molecules in OEC is understood to be realized by an enzymatic organization of a special Mn cluster in a protein architecture.^{1,2} The present work not only demonstrates the construction of an efficient water oxidation system utilizing a polymer membrane, but also shows remark-

able stabilization of the water oxidation catalyst against decomposition in a heterogeneous environment.

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