Highly Active Electrocatalytic Water Oxidation System Composed of Trinuclear Ruthenium Complex Supported on Platinum Black

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Trinuclear Ruthenium complex, Ru-red ($[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$) is adsorbed well onto the electrodeposited Pt-black, and the adsorbed Ru-red works as a highly active catalyst for electrochemical water oxidation

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An artificial photosynthesis is attracting much attention as a candidate for solar energy conversion system because of its compatibility with energy cycle in nature.[1] Water oxidation process in an artificial photosynthesis, where four electrons are provided from two water molecules and further transferred to photoexcitation center, is most important since this is a fundamental and first step in the whole electron flow of a photosynthesis.[1]

It has been extensively known that metal oxides such as RuO_2, IrO_2, PtO_2 and MnO_2 possess catalytic activity for water oxidation.[2] However, in order to construct a molecule-based artificial photosynthetic system, the development of an active molecule-based catalyst for water oxidation is a key point. It has been reported that metal complexes function as a molecule-based catalyst for water oxidation in homogeneous aqueous solutions[3,4] and in various heterogeneous systems.[4,5] Trinuclear ruthenium complex, $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$, called Ru-red is one of the most active molecule-based catalysts for water oxidation to evolve oxygen in a chemical water oxidation system with Ce^{IV} oxidant.[4] Ru-red was electrochemically stabilized when incorporated into a Nafion membrane.[6] However, a design of efficient electrocatalytic water oxidation system with this Ru complex has been difficult. This can be ascribed to inefficient charge transfer from the electrode to the complexes. We now found that Ru-red is adsorbed well onto electrodeposited platinum black (Pt-black) and that the adsorbed Ru-red on Pt-black works as a highly active catalyst for electrochemical water oxidation, and will report in the present paper.

Ru-red (Wako) was purchased and used as received. Pt-black was electrodeposited from an aqueous solution containing 1.0×10^{-2} mol dm^{-3} (M) H_2PtCl_6 and 2.0×10^{-4} M $Pb(CH_3COO)_2$ onto the surface of a basal-plane pyrolytic graphite (BPG) electrode by cathodic polarization of the electrode (current density = 20 mA cm^{-2}) to obtain BPG / Pt-black. The amount of the Pt-black deposited on the electrode was estimated from the absorption spectral change of the H_2PtCl_6 solution (ε = 47.3 cm^{-1} M^{-1} at 450 nm) before and after the electrodeposition. An aqueous solution (1 ~ 25 μ dm^3) of 6.2×10^{-4} M Ru-red was cast onto the surface (the area is ca. 0.17 cm^2) of the BPG / Pt-black, and then the electrode was air-dried for ca. 3 hours to obtain BPG / Pt-black [Ru-red]. The electrode was stored in pure water before electrochemical experiments. An electrode coated with a Nafion membrane containing the complex was prepared by absorbing the complex into precoated Nafion membrane. An electrode coated with Kaolin clay adsorbing the complex was prepared by at first coating with clay powders from their aqueous suspension and by following adsorption of the complex into the precoated clay. A conventional single-compartment cell was equipped with the BPG working electrode, a Ag/AgCl reference electrode and a platinum wire counter electrode for electrochemical experiments. An electrolyte solution (pH 6.8) of 0.1 M sodium perchlorate was used and deaerated by bubbling argon gas for about 1 h. Dioxygen (O_2) evolved was analyzed after potentiostatic electrolysis on a gas chromatograph equipped with 5 Å molecular sieve column using argon carrier gas (flow rate is 40 m dm^3 min^{-1}) at 50 °C.

Cyclic voltammograms were measured in the range of 0 V to 1.3 V (vs. Ag/AgCl) using a BPG electrode coated with electrodeposited Pt-black supporting the complex (abbreviated to BPG / Pt-black [Ru-red]) and a BPG electrode coated with deposited Pt-black (BPG / Pt-black). The voltammogram for the BPG / Pt-black [Ru-red]) exhibited a remarkably steep rise of the anodic current ascribed to water oxidation above 1.2 V (vs. Ag/AgCl), and this anodic current was much higher for the BPG / Pt-black [Ru-red] than BPG / Pt-black.

A time-current curve in a potentiostatic electrolysis at 1.3 V (vs. Ag/AgCl) reached a steady state after ca. 10 minute, and the value of the current after 1 h for the BPG / Pt-black [Ru-red] was 7.4 mA cm^{-2}, which is higher than that (0.88 mA cm^{-2}) for the BPG / Pt-black by almost one order of magnitude. As shown in Figure. 1, the amount of the O_2 evolved after potentiostatic electrolysis for 1 h was remarkably higher in the whole potential range for the BPG / Pt-black [Ru-red] than the BPG / Pt-black and a bare BPG electrode, and the potential to start evolving O_2 was significantly lower for the former than the latters. The O_2

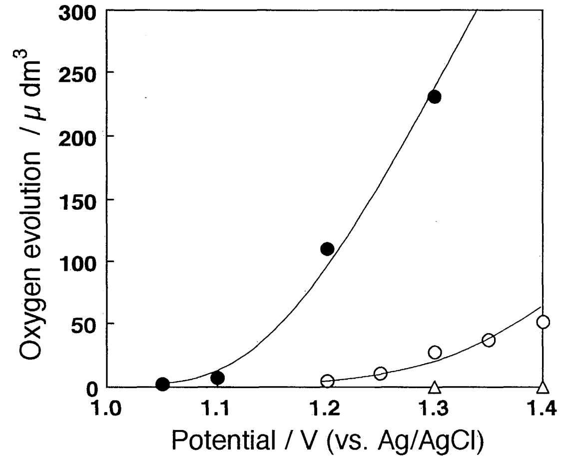

Figure 1. Relationship between oxygen evolution and applied potential in potentiostatic electrolysis for 1 h using various electrodes. (●) BPG / Pt-black [Ru-red]; (○) BPG / Pt-black; (△) bare BPG; The amount of Ru-red and Pt-black on the electrode is 9.3×10^{-9} mol and 6.0×10^{-6} mol, respectively.

(231 μ dm^3) evolved for the BPG / Pt-black [Ru-red] at 1.3 V (vs. Ag/AgCl) was 8.3 times as high as that (28.0 μ dm^3) for the BPG / Pt-black. Turnover numbers of the complex was 900 h^{-1} for the BPG / Pt-black [Ru-red]. It should be noted that the catalytic activity of the complex supported on the Pt-black is strikingly high when considering the turnover number (55 h^{-1}) of the complex for O_2 evolution in a homogeneous aqueous solution (at 2 x 10^{-4} M) with Ce^{IV} oxidant.[4] It should also be noted that only low amount of O_2 was evolved even at 1.6 V (vs. Ag/AgCl) for the electrode coated either with a Nafion membrane incorporating the complex or with Kaolin clay adsorbing the complex under the present conditions.

High catalytic activity was also obtained by incorporating other molecule-based water oxidation catalysts (e.g., $[Ru(NH_3)_5Cl]^{2+}$ (**1**), $[(H_2O)(bpy)_2Ru\text{-}O\text{-}Ru(bpy)_2(H_2O)]^{4+}$ (**2**) and $[(bpy)_2Mn(\mu\text{-}O)_2Mn(bpy)_2]^{3+}$ (**3**) ; bpy = 2,2'-bipyridine) onto the deposited Pt-black. The order of the activity of the BPG / Pt-black [complex] was, Ru-red (900 h^{-1}) > (**1**) (470 h^{-1}) > (**2**) (120 h^{-1}) > (**3**) (< 1 h^{-1}), which is parallel to the activity order,[7] Ru-red (158 h^{-1}) > (**1**) (12.4 h^{-1}) > (**2**) (3.0 h^{-1}) > (**3**) (< 2 h^{-1}), of the chemical water oxidation system composed of Kaolin clay adsorbing one of the complexes using Ce^{IV} oxidant in an aqueous solution. The high activity of the Ru-red is ascribed to the capability of 4-electron oxidation of water by one Ru-red molecule. Other complexes can be only 2-electron oxidant except (**2**) which can be a 4-electron oxidant but decomposes during catalysis to lose its activity. The complex must function as a molecule-based catalyst for water oxidation even when supported on the Pt-black. The possibility that an oxidatively and unimolecularly transformed species of the complex works as catalyst was undeniable from another experiment. However, the catalytic activity of the complex remarkably depended on its structure, showing that the original complex or decomposed species which maintain the trinuclear structure of the complex catalyzes water oxidation.

The complex was supported stably on the Pt-black without dissolution during water oxidation. The catalytic activity of the BPG / Pt-black [Ru-red] greatly depended on the amount of the complex. It is interesting that too much loading of the complex onto the Pt-black lowered the activity, and optimum loading ratio of Ru-red / Pt-black was found. The amount of O_2 evolved exhibited maximum value when the amount of the complex on the 6.0 x 10^{-6} mol Pt-black is 9.3 x 10^{-3} mol.

It is important to diminish the overpotential required for evolving O_2 in an electrochemical water oxidation system. The O_2 evolution could be observed at the BPG / Pt-black [Ru-red] even at 1.05 V (vs. Ag/AgCl)(see Figure 1), but it could be observed at the BPG / Pt-black only at the potentials higher than 1.2 V (vs. Ag/AgCl). Namely, the potential at which O_2 starts to evolve shifts to lower potential by 150 mV for the Ru-red modified electrode.

Electrocatalytic activity for water oxidation would be determined both by the intrinsic activity of a catalyst and by charge transport from the electrode surface to the catalyst. In our chemical water oxidation system composed of Ce^{IV} oxidant and Ru-red adsorbed on a matrix such as Pt-black, kaolin clay, or Nafion membrane, the catalytic activity of the complex was not affected much by the matrix which supports the complex. In the present electrocatalytic water oxidation, however, the catalytic activity of Ru-red was remarkably affected by the matrix. The complex is adsorbed on the surface of Pt-black, so that charge is directly injected from the Pt-black to the complex. This efficient charge transport from the electrode surface to the complex would be of importance for the BPG / Pt-black [Ru-red]. This would be the important reason for the high activity of the present water oxidation catalyst. The Pt-black in this system would work as a matrix not only to support the complex but also to facilitate charge transport from the base electrode to the complex.

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7 Calculated from the 30 min activity data.