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Spectroelectrochemical investigation of electrocatalytic water oxidation by a mononuclear ruthenium complex in a homogeneous solution

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ABSTRACT

Electrochemical water oxidation by $[Ru(EtOtpy)(bpy)OH_2]^{2+}$ (**1**) (EtOtpy = 4′-ethoxy-2,2′:6′2″-terpyridine, bpy = 2,2′-bipydidine) was investigated in a homogeneous solution under weakly acidic conditions (pH 5.3). The cyclic voltammogram of a **1** aqueous solution showed that successive proton-coupled electron transfer reactions of $Ru^{II}—OH_2$ / $Ru^{III}—OH$ and $Ru^{III}—OH/Ru^{IV}{=}O$ redox pairs and high anodic current above 1.1 V *vs* SCE. Electrocatalytic water oxidation was corroborated by the bulk electrolysis at 1.5 V; the significant amount of O_2 was evolved compared with the blank during the electrolysis. Potential-step chronocoulospectrometry (PSCCS) from 0.0 V to 1.52 V *vs* SCE was conducted to observe the change of **1** in solution during the electrocatalysis. The *in situ* UV visible spectral change showed oxidation of **1** ($Ru^{II}—OH_2$) to $Ru^{III}—OH$ and to further oxidation of $Ru^{III}—OH$ to $Ru^{IV}{=}O$, and that the $Ru^{IV}{=}O$ species mainly exists in a steady state after 200 s in the electrocatalysis. The *in situ* UV–vis spectral change in a reverse potential step from 1.52 V to 0.22 V *vs* SCE exhibited that $Ru^{II}—OH_2$ completely recovers by two electron re-reduction process from the steady state in the electrocatalysis. The observation of $Ru^{IV}{=}O$ in a steady state suggests that a rate determining step in the catalytic cycle is oxidation of $Ru^{IV}{=}O$ to $Ru^{V}{=}O$ rather than the O—O bonding formation by nucleophilic attack of water to $Ru^{V}{=}O$ in the electrocatalysis in a homogeneous solution.

1. Introduction

Much attention has recently been paid to clean alternative energy sources due to recent problems on energy and environment. Artificial photosynthesis is one of the potential clean energy-providing systems in future [1–3]. Although water oxidation catalyst is necessary to extract electrons from water (as an electron source) for producing high energy compounds in artificial photosynthesis, development of an efficient and robust water oxidation catalyst is a bottleneck and very important task to bring a breakthrough in the field. In a recent decade, a variety of metal complexes based on manganese, [4–8] ruthenium [9–28] and iridium [29–32], iron [33,34], cupper [35–37] and cobalt [38–41] have been reported as active catalysts for water oxidation. The catalyses by ruthenium complexes are studied most extensively. Meyer reported a one-site catalytic mechanism by $Ru(tpy)(bpz)OH_2]^{2+}$ (bpz = 2,2′-bipyrazine) and $[Ru(tpy)(bpm)(OH_2)]^{2+}$ (bpm = 2,2′-bipyrimidine) for chemical water oxidation using a Ce(IV) oxidant [10]. In this mechanism the complex is oxidized to a $Ru^{V}{=}O$ state by proton-coupled electron transfer, and then an O—O bond is formed by nucleophilic attack of water to $Ru^{V}{=}{—}O$ bond formation process is supposed to be a rate-determining step in most case using a large excess of a Ce(IV) oxidant. Sakai reported the detailed mechanism of the chemical water oxidation by $[Ru(tpy)(bpy)OH_2]^{2+}$ and spectroscopic identification of all the intermediate in homogenous solution using a stopped-flow technique with global fitting kinetic analysis and density functional theory calculations. We reported that the turnover frequency of $[Ru(EtOtpy)(bpy)OH_2]^{2+}$ (EtOtpy = 4′-ethoxy-2,2′:6′2″-terpyridine) for the chemical water oxidation is higher than that of $[Ru(tpy)(bpy)OH_2]^{2+}$ in a homogeneous solution by one order of magnitude due to loading of an electron-donating ethoxy group [24]. The chemical water oxidation experiments using a Ce(IV) oxidant are limed under only acidic conditions less than pH 3.5 due to stability of Ce(IV) ions ($Ce(OH)_4$ is formed above the pH). Moreover, the catalytic mechanism could be complicated because Ce(IV) was pointed out to work not only as a simple electron oxidant but also for inducing a radical character of coordinated hydro oxide [42].

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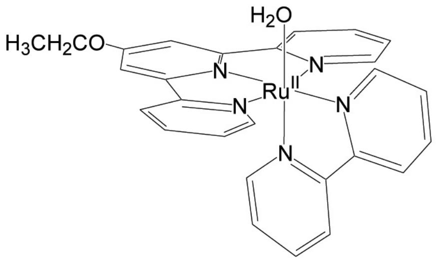
The electrochemical technique is a useful method to study water oxidation reactions under weakly acidic or neutral conditions. It is important to directly observe the real change of the redox centers in addition to electrochemical data of current or charge on the electrode for monitoring electrocatalytic reactions by molecular catalysts [43–47]. Herein we first report electrocatalytic water oxidation by $[Ru(EtOtpy)(bpy)OH_2]^{2+}$ in a homogeneous solution under weakly acidic conditions (pH 5.3) using a spectroelectrochemical technique. The mechanism of electrocatalytic water oxidation by $[Ru(EtOtpy)(bpy)OH_2]^{2+}$ will be discussed.

2. Experimental

2.1. Materials

$[Ru(EtOtpy)(bpy)OH_2]^{2+}$ (**1**) was prepared according to the literature [24]. An indium tin oxide (ITO)-coated glass substrate was obtained from Asahi Glass Co. Millipore water was used for all the experiments. All other chemicals of analytical grade were used as received unless mentioned otherwise.



$[Ru(EtOtpy)(bpy)OH_2]^{2+}$ (**1**)

2.2. Measurement

All the electrochemical experiments were implemented under argon atmosphere at 25 °C using an electrochemical analyzer (Hokuto Denko, HZ-3000). The cyclic voltammograms (CV) were measured in a **1** aqueous solution (0.5 mM, pH 5.3) using a one-compartment electrochemical cell equipped with a glassy carbon rod working electrode, a saturated calomel (SCE) reference electrode and a Pt wire counter electrode. The pH of the solutions was buffered at an ionic strength of 0.1 M by Na_2HPO_4 and KH_2PO_4. Bulk electrolysis was carried out in a **1** aqueous solution (0.5 mM, 4.0 ml) at 1.54 V *vs* Ag/AgCl (−42 mV *vs* SCE) for 2 h using a two-compartment electrochemical cell equipped with a Pt plate working electrode. For spectroelectrochemical measurement, a thin-layer spectroelectrochemical cell was constructed by an ITO electrode (9 mm × 19 mm) and a quartz glass equipped with an Ag wire reference electrode and a Pt wire counter electrode (0.3 mm of a light pass length). The concentration of the **1** aqueous solution is 0.5 mM, and the amount of **1** in a thin-layer spectroelectrochemical cell is 2.6×10^{-8} mol. The spectroelectrochemical measurement was set up by combining the elecltrochemical analyzer with a photodiode array spectrophotometer (Shimadzu, Multispec-1500) at 1.3 V *vs* Ag (222 mV *vs* SCE) for 1 h. The potentials are expressed as values *vs* SCE unless otherwise noted.

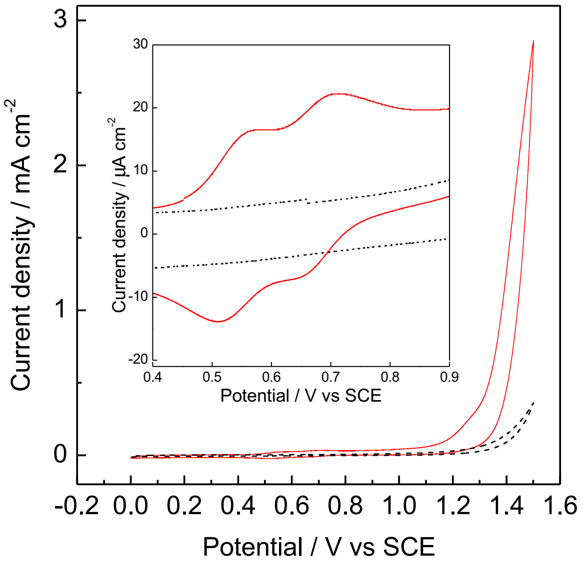


Fig. 1. Cyclic voltammogram (CV) of 0.5 mM **1** in an aqueous solutions at pH 5.3 from 0.0 to 1.5 V *vs* SCE as measured at 2 mV s^{-1} of a scan rate and 25 °C. The dashed line is blank CV without **1**. The inset shows magnified CV from 0.4 to 0.9 V.

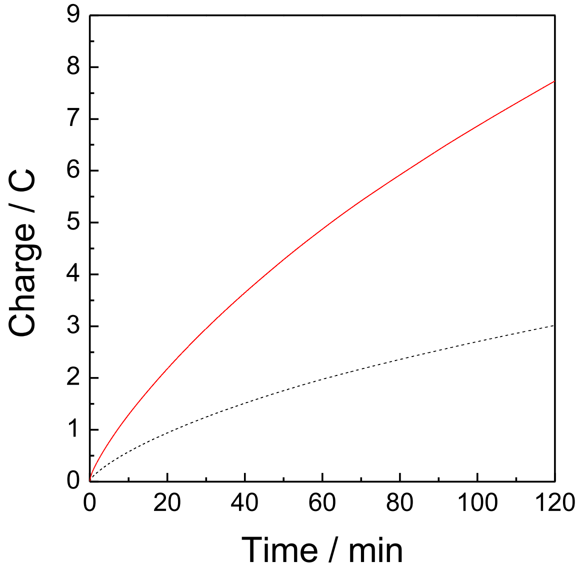


Fig. 2. Time course of the charge amount passed during bulk electrolysis of 0.5 mM **1** at 1.5 V *vs* SCE at pH 5.3 (solid line). The dashed line is blank data without **1**.

3. Results and discussion

CV of a **1** aqueous solution provided two redox waves at $E_{1/2}$ = 0.54 and 0.66 V [48] at pH 5.3 in a potential range from 0.4 to 0.9 V (Fig. 1), both of which are pH-dependent in a range of pH 2.0–10.5. The both redox waves are assigned to the proton-coupled redox reactions of $Ru^{II}—OH_2$ / $Ru^{III}—OH$ and $Ru^{III}—OH$ / $Ru^{IV}=O$ according to Pourbaix Diagram of **1** reported earlier, respectively [24]. The anodic current density rose at 1.1 V due to water oxidation (theoretical potential for water oxidation at pH 5.3, 0.68 V *vs* SCE), and the current density reached 2.8 mA cm^{-2} at 1.5 V, which was 8 times higher than that (0.36 mA cm^{-2}) of the blank (without complex). Bulk electrolysis was conducted in the **1** solution at 1.5 V (Fig. 2). The charge amount was 2.6 times higher than that for the blank, and the significant amount (13.2 μmol, Faraday efficiency: 66%) of O_2 was evolved compared with that (4.5 μmol, 58%) for the blank during the 2 h electrolysis [49]. These results corroborate that **1** works for electrocatalytic water oxidation in homogeneous solution at pH 5.3. The amount (8.7 μmol) of O_2 evolved in the electrocatalysis by **1** for 2 h corresponds to 4.4 equivalent of the