

Synthesis of Metal Complexes Aiming at Storage and Release of Chemical Energy

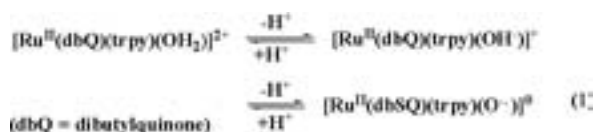
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Metal complexes that have an ability to oxidize H_2 and alcohols at potentials more negative than reduction of dioxygen are feasible electrode catalysts in H_2/O_2 and alcohol/ O_2 fuel cells. Electrochemical oxidation of $\text{Ru}^{\text{II}}(\text{polypyridyl})(\text{OH}_2)$ is accompanied by deprotonation to produce the correspondent $\text{Ru}^{\text{IV}}=\text{O}$ and $\text{Ru}^{\text{V}}=\text{O}$ complexes. Those high valent $\text{Ru}=\text{O}$ complexes are expected for an application to electrode catalysts in fuel cells, since they have an ability to oxidize of some of organic molecules. However, intrinsic highly positive redox potentials for the generation of the active species does not meet a requirement to convert chemical energy of H_2 and alcohols to electricity. On the other hand, introduction of dioxolene ligands into Ru-aqua complexes results in spontaneous deprotonation of the aqua ligand, and unusual Ru-oxyl radical complexes are formed due to intra-molecular charge transfer from the resultant O^{2-} ligand to dioxolene (eq. 1). Oxyl radical complexes formed in eq. 1 are expected to have an ability of not only abstraction of hydrogen atom of C–H bonds of alcohols but also formation of oxygen–oxygen bond

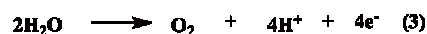
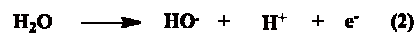


in the four-electron oxidation of water. Oxidations of alcohols and water under mild conditions would play the key role in the energy conversion to construct a sustainable society.

1. Substituents Dependent Capability of Bis(ruthenium-dioxoleneterpyridine) Complexes toward Water Oxidation

Water splitting to H_2 and O_2 driven by visible light is an

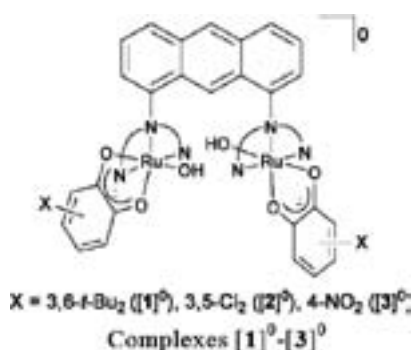
ultimate energy conversion from sunlight to a storable chemical energy. Water splitting using semiconductors under visible light irradiation has been well documented so far. Relatively low quantum efficiencies (~5%) in those reactions are ascribed to a reaction path through highly energetic one electron water oxidation that takes place at quite positive potentials (+2.31 V vs. NHE, pH 7, eq. 2). Accordingly, developments of efficient catalysts that have an ability to catalyze four-electron oxidation of water opens a door leading to an energetically sustainable society because four-electron water oxidation thermodynamically occurs at much more modest potentials (+0.815 V, eq. 3).



Recently, water oxidation using transition metal complexes has been intensively studied, though the reaction mechanism, especially the step of O–O bond formation from two water molecules, still remains unclear. Furthermore, Ce(IV) was used as an oxidant in most of water oxidation reactions. Taking into account that Ce(IV) is available as an oxidant only in very strong acidic aqueous solutions, electrochemical oxidation of water has various advantages not only to regulate the reaction conditions such as pH, applied potentials, and solvents but also to keep track of efficiencies and durability of catalysts by a change of catalytic currents during the reactions.

Dioxolenes coordinated on metals take three redox states; quinone (q), semiquinone (sq), and catechol (cat). Among various metal-dioxolene complexes, ruthenium complexes in particular show strong interactions between Ru and dioxolene because of close energy levels of the $d\pi$ orbital of Ru to π and π^* orbitals of dioxolene. Furthermore, three oxidation states of dioxolene are able to coordinate on Ru^{II} , Ru^{III} and Ru^{IV} , but

strict classification of those nine redox isomers (3×3) is practically impossible due to close energy levels of HOMO and LUMO energy levels of the metal and ligand. For example, the actual electronic structure of $[\text{Ru}(\text{OAc})(\text{dioxolene})(\text{trpy})]^0$ ($\text{trpy} = 2,2':4',2''\text{-terpyridine}$) gradually changes from the canonical $\text{Ru}^{\text{II}}(\text{sq})$ configuration to the $\text{Ru}^{\text{III}}(\text{cat})$ one with increasing electron withdrawing ability of dioxolene substituents. We have reported that a dinuclear ruthenium complex $[\text{Ru}_2(\text{OH})_2(3,6\text{-}t\text{-Bu}_2\text{q})_2(\text{btpyan})](\text{SbF}_6)_2$ ($[1]^{2+}$, $3,6\text{-}t\text{-Bu}_2\text{q} = 3,6\text{-di-}t\text{-butyl-1,2-benzoquinone}$, $\text{btpyan} = 1,8\text{-bis}(2,2':6',2''\text{-terpyrid-4'-yl)anthracene}$) work as an excellent catalyst in the four-electron oxidation of water, since the electrochemical oxidation of water using an ITO electrode modified with $[1](\text{SbF}_6)_2$ evolved large amounts of O_2 (33,500 turn-overs) at pH 4 (buffered) in H_2O . In the electrochemical oxidation of water catalyzed by $[1]^{2+}$, redox reactions of dioxolene ligands play the central roles in not only the store of the electrons generated by proton dissociation of the hydroxyl group but also release of them to ITO electrode. However, the actual oxidation state of the Ru atom and dioxolene ligands in the catalytic cycle, and the process of the oxygen-oxygen bond formation prior to O_2 evolution still remain unclear. We, therefore, prepared bis(ruthenium-hydroxo) complexes having dichloro ($[2]^0$) and NO_2 ($[3]^0$) substituted dioxolene, and compared the redox behavior among $[1]^0$, $[2]^0$, and $[3]^0$ to elucidate the role of dioxolene ligand in water oxidation.



The electronic structure of $[1]^0$ is expressed by $[(\text{sq})\text{Ru}^{\text{II}}(\text{OH})(\text{HO})\text{Ru}^{\text{II}}(\text{sq})]^0$. The catalytic cycle of water oxidation by $[1]^0$ is explained by the following stepwise reactions (i) two-electron oxidation of $[1]^0$ produces $[(\text{q})\text{Ru}^{\text{II}}(\text{OH})(\text{HO})\text{Ru}^{\text{II}}(\text{q})]^{2+}$ ($[1]^{2+}$), (ii) dissociation of protons coupled with electron transfer to q generates $[(\text{sq})\text{Ru}^{\text{II}}(\text{O}^{\bullet-})(^{\bullet-}\text{O})\text{Ru}^{\text{II}}(\text{sq})]^0$, (iii) coulomb repulsion between two $\text{O}^{\bullet-}$ ligands are removed by oxidation of sq, which facilitates to form O–O bond by a radical coupling reaction, (iv) an attack of water to a Ru atom is induced by oxidation of the complex, which cleaves one of the resultant Ru–O–O–Ru bond, (v) the second attack of water to another Ru atom release O_2 with regeneration of $[1]^{2+}$. On the other hand, the electronic structures of $[2]^0$ and $[3]^0$ are

approximated by $[(\text{cat})\text{Ru}^{\text{III}}(\text{OH})(\text{HO})\text{Ru}^{\text{III}}(\text{cat})]^0$. Two-electron oxidation of the latter takes place on metal center to give $[(\text{cat})\text{Ru}^{\text{IV}}=\text{O} \text{ O}=\text{Ru}^{\text{IV}}(\text{cat})]^0$ rather than ligand centered oxidation affording $[(\text{sq})\text{Ru}^{\text{III}}(\text{OH})(\text{HO})\text{Ru}^{\text{III}}(\text{sq})]^{2+}$. It is considered that the O–O bond formation in $[(\text{cat})\text{Ru}^{\text{IV}}=\text{O} \text{ O}=\text{Ru}^{\text{IV}}(\text{cat})]^0$ is very hard due to the stability of the $(\text{cat})\text{Ru}^{\text{IV}}=\text{O}$ moiety. Indeed, the complexes $[2]^0$ and $[3]^0$ practically did not evolve O_2 under the electrolysis up to +2.20 V (vs. SCE) in H_2O .

2. A New Type of Electrochemical Oxidation of Alcohols Mediated with a Ruthenium-Dioxolene-Amine Complex in Neutral Water

The present society is maintained by combustion of tremendous amounts of fossil fuels and consumption of natural resources without regeneration of them. Global industrialization since 19 century inevitably has caused serious depletion of natural resources and environmental damages. As a result, energy conversion from natural energy to chemical one is believed as the top research area to build a sustainable society. Both H_2/O_2 and direct methanol (CH_3OH) fuel cells have the great feasibility as future energy sources. A key issue in practical uses of fuel cells is that only platinum or platinum-based alloys have been used as H_2 and CH_3OH oxidation electrodes. It is, therefore, highly desired to develop metal complexes that have an ability to oxidize H_2 and CH_3OH under mild conditions in place of platinum metal.

Aminyl radicals (NR_2^{\bullet}) that are known as reactive reaction intermediates abstract hydrogen atoms of various organic molecules. Some of those radicals are stabilized on metal complexes and successfully isolated. Recently, we have demonstrated that deprotonation of amino group of $\text{Ru}(\text{dioxolene})$ (amine) (dioxolene = 3,5-di-*tert*-butyl-1,2-benzoquinone (q), -semiquinonate (sq), and -catecholate (cat)) reversibly produces the correspondent aminyl radical complex due to an intra-molecular electron transfer between deprotonated amino group and dioxolene ligand. Although aminyl radical metal complexes hardly showed a catalytic activity for oxidation of organic molecules, two-electron oxidation of those complexes creates catalytic ability to oxidize alcohols. This fact has driven us to examine a potential application for electrocatalysts of oxidation of CH_3OH in aqueous conditions by considering smooth conversion between aminyl radical and amino groups on Ru. So, we examined the redox behavior of the $[\text{Ru}^{\text{II}}(\text{terpy})(\text{sq})(\text{NH}_3)]^+ / [\text{Ru}^{\text{II}}(\text{terpy})(\text{q})(\text{NH}_3)]^{2+}$ ($\text{terpy} = 2,2':6',2''\text{-terpyridine}$) couple (abbreviated as $[\text{Ru}^{\text{II}}(\text{sq})(\text{NH}_3)]^+ / [\text{Ru}^{\text{II}}(\text{q})(\text{NH}_3)]^{2+}$) in the absence and presence of a base in CH_3OH and in H_2O , and found an unprecedented two-electron oxidant character created by proton and electron loss of $[\text{Ru}^{\text{II}}(\text{q})(\text{NH}_3)]^{2+}$ in the oxidation of alcohols in neutral water.