Energy Conversion from Proton Gradient to Electricity Based on Characteristic Redox Behavior of an Aqua Ruthenium Complex with a Quinone Ligand

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A ruthenium aqua complex having a quinone ligand, $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ (trpy = 2,2′:6′,2″-terpyridine, dbq = 3,5-di-*t*-butyl-1,2-benzoquinone) ($[Ru(q)(H_2O)](ClO_4)_2$) was prepared. Its electrochemical properties and electronic absorption spectra were measured in the presence of a base in acetone. The detailed analysis of those measurements revealed that the addition of a base caused not only the deprotonation but also the reduction of $[Ru(q)(H_2O)]^{2+}$. The redox reactions coupled with acid–base reactions were demonstrated from the large difference in redox properties of aqua and hydroxo complexes. Taking advantage of unique redox reactions induced by the acid–base equilibrium between aqua and hydroxo complexes, we have succeeded in constructing the first energy transducer which converts the proton gradient to electricity. A similar ruthenium aqua complex with a bipyridine ligand, $[Ru(trpy)(bpy)(H_2O)](ClO_4)_2$, also reversibly dissociates a proton of aqua ligand. However, it has no ability to convert the proton gradient to electricity due to the lack of a suitable molecular orbital which can accommodate electrons on the electron-rich hydroxo ligand.

Biological system uses adenosine triphosphate (ATP) to store, transport and supply energy for maintenance of life.[1] This indispensable chemical material is synthesized from adenosine diphosphate (ADP) and orthophosphate (Pi) on ATPase, utilizing a proton gradient.[2—4] In ingenious chemiosmotic theory,[5,6] the proton gradient (Δp) between the inside and the outside of a cell is depicted as the sum of electric activity ($\Delta\Psi$) and chemical activity (ΔpH) components of Eq. 1.

$$\Delta p = \Delta\Psi - Z\Delta \mathrm{pH}, \tag{1}$$

where

$$Z = 2.303RT/F \tag{2}$$

and R, F, and T are gas constant, Faraday constant, and temperature. When we are concerned about the chemical activity part, the proton gradient is equivalent to the neutralization energy because the reaction, $H^+ + OH^- \rightarrow H_2O$ takes place if the separating membrane is removed. The ΔH for this neutralization reaction is 56.5 $\mathrm{kJ\,mol^{-1}}$,[7,8] which is usually emitted only as thermal energy. However, we can utilize this energy for chemical reactions if we activate compounds chemically with a pH gradient.

Among the compounds sensitive to a pH gradient, metal aqua-complexes are representative candidates for utilization of the pH gradient, since they are expected to be in acid-base equilibria among aqua-, hydroxo- and oxo-complexes (Eq. 3):[9]

$$[M(H_2O)] \rightleftarrows [M(OH)]^- \rightleftarrows [M(O)]^{2-}. \tag{3}$$

The change of the proton concentrations shifts the distribution among aqua, hydroxo and oxo complexes, which is reflected on the redox potentials of the equilibrium system.[10—14] Thus, the redox potentials of this system can be controlled by the pH gradient. Hydroxo and oxo complexes derived from deprotonation of aqua complexes generally have a tendency to polymerize through the bridging of hydroxo or oxo moiety due to their high electron density (or strong basicity).[9] This problem would be overcome if the negative charges produced by deprotonation of the aqua ligand are effectively accommodated in another ligand of those metal complexes. We prepared a ruthenium aqua complex, $[Ru(trpy)(3,5\text{-di-}t\text{-butyl-}1,2\text{-benzoquinone})(H_2O)](ClO_4)_2$ ($[Ru(q)H_2O](ClO_4)_2$), to store electrons generated by dissociation of protons of the aqua ligand. The complex showed a characteristic redox reaction, coupled with acid–base equilibrium, which was utilized for energy conversion from proton gradient to electricity.[15] In this paper we will describe the electrochemical properties and electronic spectra of $[Ru(q)(H_2O)]^{2+}$ under various amounts of *t*-BuOK, and demonstrate the energy conversion from proton gradient to electricity.

Experimental

Materials. $[Ru(trpy)(dbseq)(AcO)]$ (dbseq = 3,5-di-*t*-butylsemiquinone) was prepared as previously reported.[16] $[Ru(trpy)(bpy)(H_2O)](ClO_4)_2$ was synthesized according to the literature procedure.[17] $HClO_4$ (70%) was purchased from Kanto Chemical Co. Inc.. $NaClO_4 \cdot H_2O$ was purchased from Wako Pure Chemicals.

Synthesis of $[Ru(trpy)(3,5\text{-di-}t\text{-butyl-}1,2\text{-benzoquinone})(H_2O)](ClO_4)_2$. $[Ru(trpy)(dbseq)(AcO)]$ (100 mg) was suspended in ca. 3 ml MeOH. Aqueous $HClO_4$ (70%) (1 ml) was added to the purple MeOH suspension. After the suspension became a dark blue solution, an $NaClO_4$ saturated methanol solution (1 ml) was added. Then an addition of H_2O (30 ml) gave small needle-shaped $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ crystals (yield 50%). Elemental analysis. Found: C, 43.65; H, 4.58; N, 5.24%. Calcd for $C_{29}H_{36}N_3O_{12.5}Cl_2Ru$: C, 43.62; H, 4.54; N, 5.26%.

We prepared $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ by the treatment of $[Ru(trpy)(dbq)(AcO)]$ with perchloric acid followed by water. Though the aqua complex, $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$, was synthesized through the treatment of $[Ru(trpy)(dbq)Cl]$ with an equivalent amount of $AgClO_4$,[18] the addition of $AgClO_4$ to $[Ru(trpy)(dbq)Cl]$ produced only the oxidized chloride complex $[Ru(trpy)(dbq)Cl]^+$.

Measurements and Instruments. Methanol solutions of *t*-BuOK and CF_3SO_3H ($1\ M$, $1\ M = 1\ mol\,dm^{-3}$) were used as base and as acid, respectively. Electronic absorption spectra were recorded on a Shimadzu UV-vis-NIR scanning spectrophotometer UV-3100PC. Cyclic voltammetric experiments were carried out in a one-compartment cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/Ag^+ reference electrode. A Hokuto Denko HA-151 potentiostat/function generator and Riken Denshi Co. F-35 X–Y recorder were used to collect cyclic voltammetric data. All solutions were deoxygenated by passing a stream of nitrogen gas into the solution prior to recording the data. To avoid the unstability of Ag/Ag^+ electrode, all potentials are quoted vs. SCE electrode. Spectroelectrochemistry was performed with a thin-layer electrode cell with a platinum mini grid working electrode sandwiched between two glass sides of an optical cell (the path length; 0.5 mm), where an Ag/Ag^+ reference electrode were separated from the working compartment by a luggin capillary. For the energy conversion from proton gradient to electricity, the glass cells separated by anion exchange membrane were used. Platinum plates washed with dilute aqueous HNO_3 and water were employed as electrodes. The amount of electricity was measured by a Hokuto Denko HF-201 Coulomb/Amperehour Meter.

Results

Electrochemical Behavior and Vis-NIR spectra of $[Ru(trpy)(dbq)(H_2O)]^{2+}$. The ruthenium aqua complex $[Ru(trpy)(dbq)(H_2O)]^{2+}$ ($[Ru(q)(H_2O)]^{2+}$) shows two reversible redox waves at $E_{1/2} = -0.47$ and 0.38 V, an anodic wave at 1.4 V, and a cathodic wave at 1.0 V in acetone (Fig. 1). The former two are tentatively assigned to the ligand-localized redox reactions of the $[Ru(q)(H_2O)]^{2+}/[Ru(seq)(H_2O)]^+$ and $[Ru(seq)(H_2O)]^+/[Ru(cat)(H_2O)]^0$ (seq = 3,5-di-*t*-butylsemiquinone, cat = 3,5-di-*t*-butylcatechol) couples, respectively, on the basis of the rest potential (V_{rest}) of 0.60 V of the solution. The anodic and cathodic waves at 1.4 and 1.0 V are associated with the redox reaction of the central metal of the $[Ru^{II}(q)(H_2O)]^{2+}/[Ru^{III}(q)(H_2O)]^{3+}$ couple, but a large peak separation between the anodic peak and the cathodic one ($\Delta V = 0.4$ V) indicates the lability of $[Ru^{III}(q)(H_2O)]^{3+}$ in acetone.

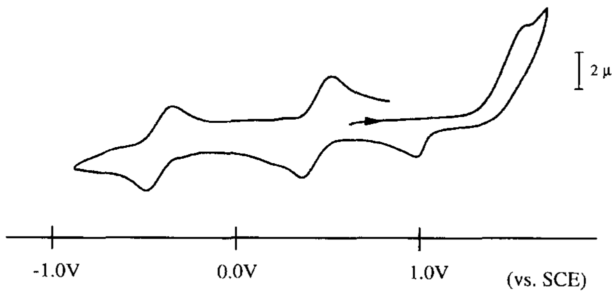


Fig. 1. Cyclic voltammogram of $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ in acetone under N_2. Me_4NClO_4 was employed as electrolyte. The rest potential is 0.60 V.

The aqua complex shows characteristic electronic spectra in Vis-NIR region depending on the oxidation states (Fig. 2). The dicationic species, $[Ru(q)(H_2O)]^{2+}$ has a strong absorption band at 600 nm ($\varepsilon = 1.5 \times 10^4$ L·mol^{-1}·cm^{-1}). Controlled potential electrolysis of the solution at 0.0 V results in disappearance of the band at 600 nm, and a new band emerges at 850 nm assignable to $[Ru(seq)(H_2O)]^+$ (Fig. 2). Reoxidation of the solution at +0.6 V completely recovered the electronic absorption spectrum of $[Ru(q)(H_2O)]^{2+}$. A series of $[Ru(bpy)_2(quinone)]^{2+}$ and $[Ru(trpy)(quinone)X]^+$ (quinone = 3,5-di-*t*-butyl-1,2-benzoquinone, 1,2-benzoquinone, 3,4,5,6-tetrachloro-1,2-benzoquinone; X = Cl^-, acetate) display also a strong band around 600 nm; a band shift is found around 850 nm upon one-electron reduction of those Ru^{II}–quinone complexes to Ru^{II}-semiquinone complexes.[16,19] The characteristic bands around 600 and 850 nm of the present complexes, therefore, are also attributed to the MLCT (metal-to-ligand charge transfer) band of Ru^{II}-quinone and that of Ru^{II}-semiquinone complexes, respectively. It is helpful to note that Ru^{II}-catechol complexes have no characteristic MLCT band in the visible region.[16,19] Based on the CV (Fig. 1), $[Ru(cat)(H_2O)]^0$ is also expected to be generated by the two-electron reduction of $[Ru(q)(H_2O)]^{2+}$. Electrochemical reduction of the $[Ru(seq)(H_2O)]^+$ solution at -0.6 V resulted in a decrease of the absorbance of the 850 nm band, but the electronic spectrum of $[Ru(seq)(H_2O)]^+$ was

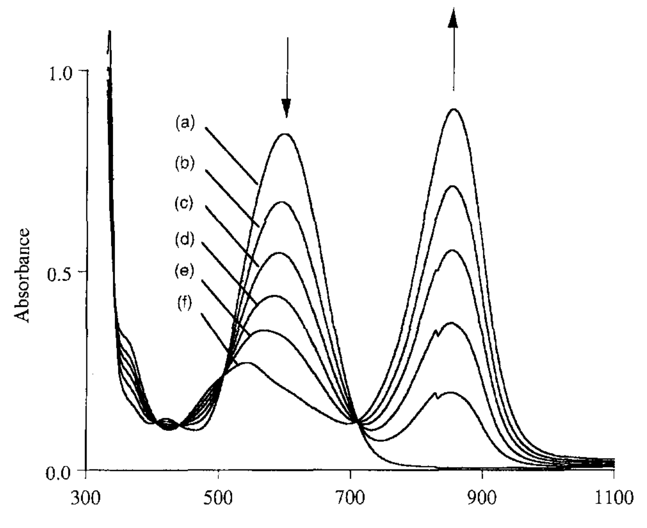


Fig. 2. The electronic spectra of $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ under electrolysis at 0.0 V in acetone solution. Initially, $[Ru(trpy)(dbq)(H_2O)]^{2+}$ showed the spectrum (a), and spectrum changes gradually to (f) as electrolysis proceeded. Each spectrum measured at every 5 minutes.

not completely recovered by the re-oxidation of the resultant solution at 0.0 V. Thus, $[Ru(cat)(H_2O)]^0$ is not so stable in prolonged electrolysis in acetone as $[Ru(seq)(H_2O)]^+$ and $[Ru(q)(H_2O)]^{2+}$.

Electrochemical Behavior and Vis-NIR Spectra in the Presence of Base. It was reported that a ruthenium terpyridine aqua complex $[Ru(trpy)(bpy)(H_2O)]^{2+}$ reacts with bases to give $[Ru(trpy)(bpy)(OH)]^+$.[17] These aqua and hydroxo complexes exhibit their MLCT bands at 476 nm and 508 nm in acetone. The present aqua complex, $[Ru(q)(H_2O)]^{2+}$, also releases a proton on the treatment with bases.[15] Figure 3 shows the electronic absorption spectra of $[Ru(q)(H_2O)]^{2+}$ in the presence of various amounts of *t*-BuOK. A gradual addition of *t*-BuOK to the $[Ru(q)(H_2O)]^{2+}$ solution caused a small bathochromic shift of the band at λ_{max} 600 to 585 nm with decreasing the absorbances (Fig. 3). At the same time, a band at 850 nm assignable to $[Ru(seq)(H_2O)]^+$ appears in the presence of small amounts of *t*-BuOK; then the λ_{max} moves to 890 nm with an increment of the absorbances. An addition of 2.1 equivalent amounts of *t*-BuOK to the $[Ru(q)(H_2O)]^{2+}$ solution gave the electronic absorption spectrum (g) of Fig. 3, which was not influenced by further addition of *t*-BuOK. Thus, $[Ru(q)(H_2O)]^{2+}$ showed a bathochromic shift as large as 290 nm on the addition of a base, in contrast to a small shift of the λ_{max} ($\Delta\lambda_{max} = 32$ nm) of the MLCT band between $[Ru(trpy)(bpy)(H_2O)]^{2+}$ (476 nm) and $[Ru(trpy)(bpy)(OH)]^+$ (508 nm). On the other hand, the electronic spectra of Fig. 3 show that the addition of *t*-BuOK causes the formation of $[Ru(seq)(H_2O)]^+$. Therefore, the addition of *t*-BuOK to $[Ru(q)(H_2O)]^{2+}$ causes not only deprotonation but also the redox reaction of the aqua complex. Because λ_{max} at 600 nm shifted to 585 nm, and λ_{max} at 850 nm of $[Ru(seq)(H_2O)]^+$ moves to 890 nm upon an addition of *t*-BuOK to the $[Ru(q)(H_2O)]^{2+}$ solution, at least two complexes besides $[Ru(seq)(H_2O)]^+$ and $[Ru(q)(H_2O)]^{2+}$ are formed on the deprotonation of $[Ru(q)(H_2O)]^{2+}$ (one is a Ru^{II}–quinone complex and the other is a Ru^{II}–semiquinone complex, judging from their λ_{max} values). The most plausible species for these new bands are the hydroxo species: $Ru^{II}(L)(OH)$ (L = q and seq). To clarify the redox reactions and the complexes which appeared in electronic absorption spectra, we examined electrochemical properties of $[Ru(q)(H_2O)]^{2+}$ under basic conditions.

Figure 4 shows the CVs of $[Ru(q)(H_2O)]^{2+}$ on the addition of *t*-BuOK. As mentioned above, $[Ru(q)(H_2O)]^{2+}$ undergoes two reversible redox reactions at $E_{1/2} = 0.38$ and -0.47 V. When ca. 0.7 equivalent amount of *t*-BuOK was added to the solution, the peak currents of the redox reactions of the $Ru(L)(H_2O)$ species (L = q, seq, cat) decrease and new redox waves appeared at $E_{1/2} = 0.00$ and -0.80 V. The acidification of the solution by an addition of CF_3SO_3H recovered the CV of $[Ru(q)(H_2O)]^{2+}$. Therefore, we assigned these newly appearing redox waves to the $[Ru(q)(OH)]^{2+}/[Ru(seq)(OH)]^+$ and the $[Ru(seq)(OH)]^+/[Ru(cat)(OH)]^0$ couples.[20] As the amount of *t*-BuOK increases, the peak current of the $[Ru(q)(H_2O)]^{2+}/[Ru(seq)(H_2O)]^+/[Ru(cat)(H_2O)]^0$ couples continuously decreased and those of the $[Ru(q)(OH)]^{2+}/[Ru(seq)(OH)]^+/[Ru(cat)(OH)]^0$ ones increased (Figs. 4(c) and 4(d)). The final CV was obtained after an addition of 2.0 equivalent amounts of *t*-BuOK (Fig. 4(d)); further addition of the base did not cause any change of the CV. Acidification of the solution of Fig. 4(d)

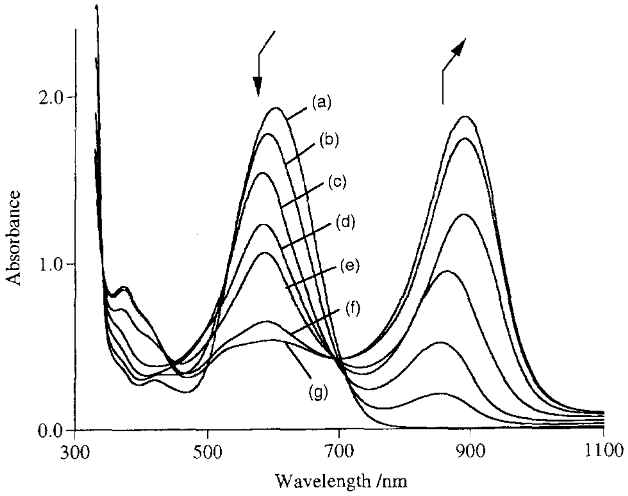


Fig. 3. The electronic spectra of $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ on the addition of *t*-BuOK in acetone. Each line shows the spectrum on the addition of every 0.35 equivalent amount of base.

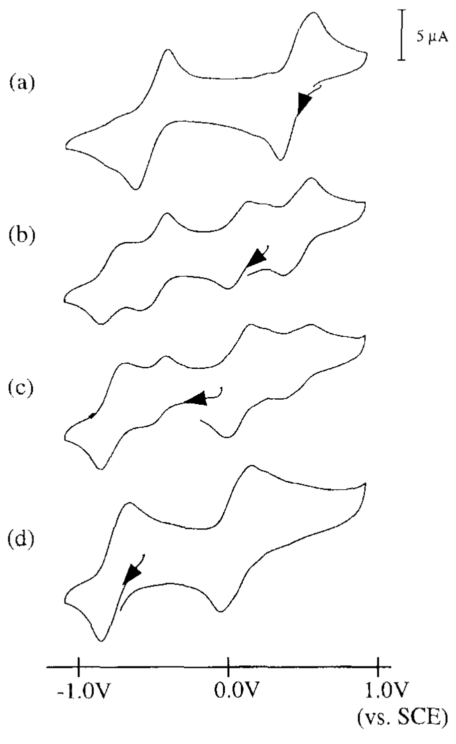


Fig. 4. Cyclic voltammogram of $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ in acetone under N_2 on the addition of various amount of base. Me_4NClO_4 was used as electrolyte. (a) without base, $V_{rest} = 0.60$ V; (b) 0.7 equivalent of *t*-BuOK, $V_{rest} = 0.30$ V; (c) 1.3 equivalent of *t*-BuOK, $V_{rest} = -0.05$ V; (d) 2.0 equivalent of *t*-BuOK, $V_{rest} = -0.57$ V. All CVs started from V_{rest}.

by an addition of 2 equivalent amounts of a methanol solution of CF_3SO_3H almost completely recovered the CV of the $[Ru(q)(H_2O)]^{2+}$/$[Ru(seq)(H_2O)]^+$/$[Ru(cat)(H_2O)]^0$ redox couples of Fig. 4(a). Thus, the aqua complexes are reversibly converted to the hydroxo ones by the change of proton concentrations. It is worthy to note that the rest potential of the solution (V_{rest}) shifts to a very negative value on the addition of *t*-BuOK. An addition of ca. 0.7 equivalent amount of *t*-BuOK to the $[Ru(q)(H_2O)]^{2+}$ solution results in the shift of V_{rest} from 0.60 to 0.30 V (Figs. 4(a) and 4(b)). Further addition of the base also induces the negative shift of V_{rest}, which finally reached −0.57 V upon the addition of 2.0 equivalent amounts of the base (Fig. 3(d)).

An addition of a small amount of *t*-BuOK to the $[Ru(q)(H_2O)]^{2+}$ solution gives rise to deprotonation of a part of the aqua complex to produce $[Ru(seq)(OH)]^+$.[21] The redox potential ($E_{1/2}$) of the $[Ru(q)(OH)]^{2+}$/$[Ru(seq)(OH)]^+$ couple (0.0 V) is more negative than that of the $[Ru(q)(H_2O)]^{2+}$/$[Ru(seq)(H_2O)]^+$ one (0.38 V). Therefore, $[Ru(q)(H_2O)]^{2+}$ is reduced to $[Ru(seq)(H_2O)]^+$ by $[Ru(seq)(OH)]^+$ generated by the addition of the base (Eqs. 4 and 5). Thus, V_{rest} of the solution of 0.30 V (Fig. 4(b)) reflects the consumption of $[Ru(q)(H_2O)]^{2+}$ and the formation of $[Ru(seq)(H_2O)]^+$ and $[Ru(q)(OH)]^{2+}$ by Eqs. 4 and 5.

$$[Ru(q)(H_2O)]^{2+} + t\text{-}BuO^- \rightarrow [Ru(seq)(OH)]^+ + t\text{-}BuOH, \qquad (4)$$

$$[Ru(q)(H_2O)]^{2+} + [Ru(seq)(OH)]^+ \rightarrow [Ru(seq)(H_2O)]^+ + [Ru(q)(OH)]^{2+}. \qquad (5)$$

According to Eqs. 4 and 5, $[Ru(q)(H_2O)]^{2+}$ should be converted to $[Ru(seq)(H_2O)]^+$ and $[Ru(q)(OH)]^{2+}$ in the presence of 0.5 equivalent amount of *t*-BuOK (Eq. 6). Under such conditions, V_{rest} must be settled at the middle point between the redox waves of the $[Ru(q)(OH)]^{2+}$/$[Ru(seq)(OH)]^+$ and $[Ru(q)(H_2O)]^{2+}$/$[Ru(seq)(H_2O)]^+$ couples. Although Fig. 4(b) is obtained in the presence of 0.7 equivalent amount of *t*-BuOK, the distribution of the aqua and hydroxo complexes is close to the reaction conditions of Eq. 6.[22]

$$[Ru(q)(H_2O)]^{2+} + 1/2t\text{-}BuO^- \rightarrow 1/2[Ru(seq)(H_2O)]^+ + 1/2[Ru(q)(OH)]^{2+} + 1/2t\text{-}BuOH \qquad (6)$$

Further addition of the base to the solution causes the deprotonation of $[Ru(seq)(H_2O)]^+$ or $[Ru(q)(OH)]^{2+}$ depending on the relative acidity of both complexes. Treatment of $[Ru(q)(H_2O)]^{2+}$, with 1.3 equivalent amounts of *t*-BuOK still exhibits the redox couples of both aqua and hydroxo complexes (Fig. 4(c)). The existence of the aqua complexes indicates the deprotonation of $[Ru(q)(OH)]^{2+}$ rather than $[Ru(seq)(H_2O)]^+$. The difference in the redox potentials of the $[Ru(q)(OH)]^{2+}$/$[Ru(seq)(OH)]^+$ couple (0.0 V) and $[Ru(seq)(H_2O)]^+$/$[Ru(cat)(H_2O)]^0$ couples (−0.47 V) also support the higher acidity of $[Ru(q)(OH)]^{2+}$ than that of $[Ru(seq)(H_2O)]^+$. Deprotonation of $[Ru(q)(OH)]^{2+}$ would produce the corresponding $[Ru(seq)(O)]^+$ (Eq. 7),[23] which is probably oxidized by $[Ru(q)(OH)]^{2+}$ (Eq. 8), as in the case of the redox reaction of Eq. 6. Although we could not get a direct evidence for the formation of $[Ru(seq)(O)]^+$ and $[Ru(q)(O)]^{2+}$ (Eqs. 7 and 8), high valent ruthenium polypyridyl oxo complexes $[Ru(polypyridyl)_n(O)]^{2+}$ are known to oxidize various organic compounds (e.g. alcohols, phenols, hydroquinone) to generate the hydroxo complex via a hydride transfer or a simultaneous electron/proton transfer (Eq. 9).[24—30] Accordingly, if the high valent $[Ru(q)(O)]^{2+}$ in Eq. 8 also has an ability to oxidize acetone, the absence of the redox couples of Ru(L)(O) (L = q, seq) species in the CV of Fig. 4(c) is explained by smooth regeneration of the Ru(L)(OH) species (Eq. 9).[31] These assumptions (Eqs. 7, 8, and 9) reasonably explain the complete reduction of $[Ru(q)(OH)]^{2+}$ to $[Ru(seq)(OH)]^+$ in the presence of *t*-BuOK (Eq. 10).

$$[Ru(q)(OH)]^{2+} + t\text{-}BuO^- \rightarrow [Ru(seq)(O)]^+ + t\text{-}BuOH \qquad (7)$$

$$[Ru(q)(OH)]^{2+} + [Ru(seq)(O)]^+ \rightarrow [Ru(seq)(OH)]^+ + [Ru(q)(O)]^{2+} \qquad (8)$$

$$[Ru(q)(O)]^{2+} \xrightarrow[\text{solvent}]{} [Ru(seq)(OH)]^+ \text{ or } [Ru(q)(OH)]^{2+} \qquad (9)$$

$$[Ru(q)(OH)]^{2+} + t\text{-}BuO^- \xrightarrow[\text{solvent}]{} [Ru(seq)(OH)]^+ + t\text{-}BuOH \qquad (10)$$

As expected from Eqs. 6 and 10, when $[Ru(q)(OH)]^{2+}$ is completely reduced to $[Ru(seq)(OH)]^+$, the solution contains $1/2[Ru(seq)(H_2O)]^+$ and $1/2[Ru(seq)(OH)]^+$ (Fig. 4(c), $V_{rest} = -0.05$ V). Consequent addition of *t*-BuOK to the solution must cause the deprotonation of $[Ru(seq)(H_2O)]^+$, which will lead to the formation of $[Ru(cat)(OH)]^0$ (Eq. 11). The V_{rest} of the solution reached −0.57 V when $[Ru(seq)(H_2O)]^{2+}$ was treated with two equivalent amount of *t*-BuOK. Taking into account the results that the $E_{1/2}$ values of the $[Ru(seq)(H_2O)]^+$/$[Ru(cat)(H_2O)]^0$ and $[Ru(seq)(OH)]^+$/$[Ru(cat)(OH)]^0$ redox couples are −0.47 and −0.80 V, respectively, the shift of V_{rest} to −0.57 V is ascribed to the occurrence of the inter-molecular redox reaction between $[Ru(cat)(OH)]^0$ and $[Ru(seq)(H_2O)]^+$ affording $[Ru(seq)(OH)]^+$ and $[Ru(cat)(H_2O)]^0$ (Eq. 12).

$$[Ru(seq)(H_2O)]^+ + t\text{-}BuO^- \rightarrow [Ru(cat)(OH)]^0 + t\text{-}BuOH \qquad (11)$$

$$[Ru(cat)(OH)]^0 + [Ru(seq)(H_2O)]^+ \rightarrow [Ru(seq)(OH)]^+ + [Ru(cat)(H_2O)]^0 \qquad (12)$$

The basicity of both $[Ru(seq)(OH)]^+$ and $[Ru(cat)(H_2O)]^0$ is too high to undergo deprotonation in acetone because the CV of Fig. 4(d) did not change any more on further addition of an excess amount of *t*-BuOK to the solution. Consequently, $[Ru(q)(H_2O)]^{2+}$ is converted into $[Ru(seq)(OH)]^+$ and $[Ru(cat)(H_2O)]^0$ via $[Ru(seq)(H_2O)]^+$ and $[Ru(q)(OH)]^{2+}$ along the Eqs. 4, 5, 6, 7, 8, 9, 10, 11, and 12. As already depicted, two new species are found in electronic absorption spectra on the addition of *t*-BuOK (Fig. 3). From the detailed analyses of CVs, therefore, these new species are reasonably assigned to hydroxo complexes. To confirm the absorption band of $[Ru(q)(OH)]^{2+}$ and $[Ru(seq)(OH)]^+$, we performed controlled potential electrolysis of $[Ru(q)(H_2O)]^{2+}$ in the presence of *t*-BuOK.

Figure 5(a) shows the electronic absorption spectra of $[Ru(q)(H_2O)]^{2+}$ in the presence of 1.5 equivalent amounts of *t*-BuOK in acetone. As discussed above, $[Ru(q)(H_2O)]^{2+}$ is reduced to $[Ru(seq)(H_2O)]^+$ and $[Ru(seq)(OH)]^+$ on this condition and the λ_{max} are at 578 and 876 nm. Based on the redox potential of the $[Ru(q)(OH)]^{2+}/[Ru(seq)(OH)]^+$ couple (0.0 V) and $[Ru(q)(H_2O)]^{2+}/[Ru(seq)(H_2O)]^+$ couple (0.38 V), selective oxidation of $[Ru(seq)(OH)]^+$ to $[Ru(q)(OH)]^{2+}$ was performed under the controlled potential electrolysis at +0.3 V. The λ_{max} shifts from 876 to 850 nm with decreasing the absorbance, and the absorption at the 585 nm band increased under the electrolysis conditions ((a) to (d) in Fig. 5). Thus, the strong absorption band at 585 nm is reasonably assigned to $[Ru(q)(OH)]^{2+}$. Similar reductive controlled potential electrolysis at −0.6 V revealed that the band at 890 nm is assigned to $[Ru(seq)(OH)]^+$. The redox potential and λ_{max} of Vis-NIR spectra of complexes are shown in Scheme 1. Because the four bands which appeared in Fig. 2 are assigned to aqua and hydroxo complexes, the conversion of $[Ru(q)(OH)]^{2+}$ on the addition of *t*-BuOK is confirmed from electronic absorption spectra as well as from cyclic voltammograms. Namely, the shift of λ_{max} from 600 to 585 nm and the appearance of the band at 850 nm (Fig. 2(c)) indicates the formation of $[Ru(q)(OH)]^{2+}$ and $[Ru(seq)(OH)]^+$ from $[Ru(q)(H_2O)]^{2+}$ on the addition of 0.7 equivalent amount of *t*-BuOK. The shift of λ_{max} from 850 to 890 nm (Figs. 2(c), 2(d), 2(e), 2(f), and 2(g)) shows the formation of $[Ru(seq)(OH)]^+$ on the successive addition of *t*-BuOK.

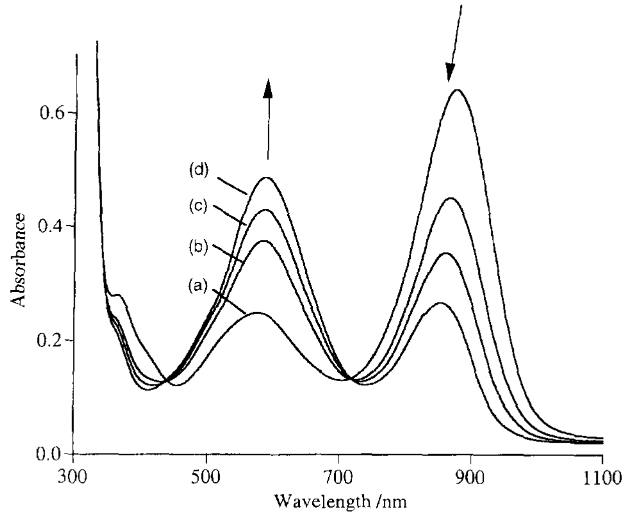


Fig. 5. The electronic spectra of $[Ru(trpy)(dbq)(H_2O)]^{2+}$ on the controlled potential electrolysis under the presence of base. The addition of 1.5 equivalent amount of *t*-BuOK gave spectrum (a). Spectrum changes from (a) to (d) on the electrolysis at 0.3 V. As the electrolysis proceeded, the intensity of the band at 585 nm increased, which corresponded to the formation of $[Ru(q)(OH)]^{2+}$ by the oxidation of $[Ru(seq)(OH)]^+$.

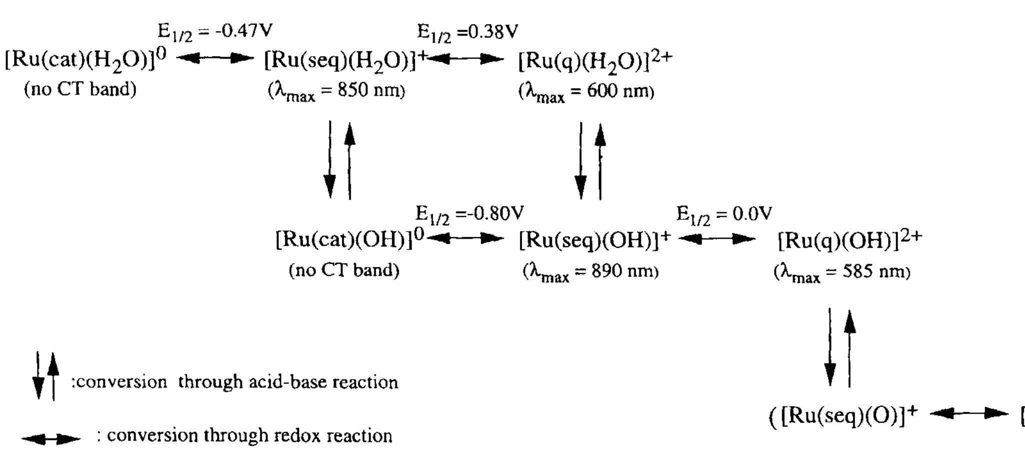
Energy Conversion from Proton Gradient to Electricity. The CV and Vis-NIR spectra reveal that $[Ru(q)(H_2O)]^{2+}$ is reversibly converted to $[Ru(seq)(OH)]^+$ or $[Ru(cat)(H_2O)]^0$ depending on the amount of base. From the viewpoints of the redox potentials of these complexes, the former is expected to work as an oxidant and the latter two as reductants, respectively. We, therefore, applied this system for an energy transducer from proton gradient to electricity.

An acetone solution of $[Ru(q)(H_2O)](ClO_4)_2$ (7.0 µmol/15 ml in each cell) was filled in two glass cells: cell(I) and cell(II), which were separated by an anion exchange membrane (Scheme 2). An addition of 1.6 equivalent amounts of methanol solution of *t*-BuOK in the cell(I) resulted in the shift of V_{rest} of the solution from +0.60 to −0.13 V due to the formation of $[Ru(seq)(H_2O)]^+$ and $[Ru(seq)(OH)]^+$ in cell(I). Connection of cell(I) and cell(II) through an electric wire induced the outer-sphere electron transfer from $[Ru(seq)(OH)]^+$ to $[Ru(q)(H_2O)]^{2+}$ (Eqs. 13 and 14), and 0.5 C of electricity was generated in the inter-molecular redox reaction.

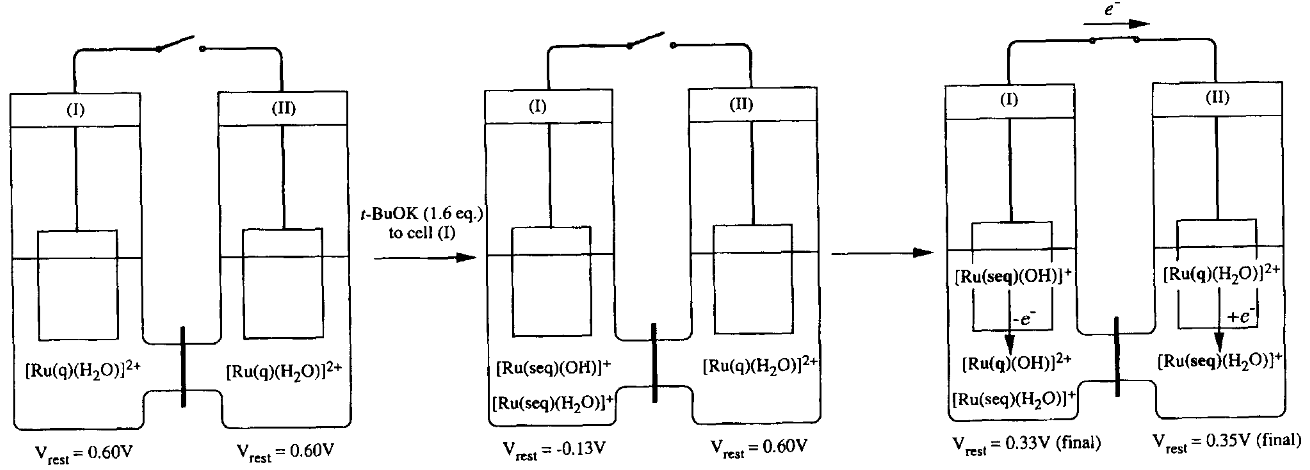
$$\text{cell(I)}: \; [Ru(seq)(OH)]^+ \rightarrow [Ru(q)(OH)]^{2+} + e^- \qquad (13)$$

$$\text{cell(II)}: \; [Ru(q)(H_2O)]^{2+} + e^- \rightarrow [Ru(seq)(H_2O)]^+ \qquad (14)$$

As the reaction proceeded, V_{rest} of two cells shifted positive and negative directions, respectively. As the difference of



Scheme 1.



Scheme 2.

V_{rest} of two cells became smaller, the current obtained gradually reduced, and finally V_{rest} of cell(I) and cell(II) became +0.33 and +0.35 V. The main components and V_{rest} in the cell(I) and cell(II), the redox reactions in both cells, and the electricity generated are summarized in Table 1. A further addition of *t*-BuOK (Table 1(b)) to the solution in the cell(I) brought about the formation of $[Ru(cat)(H_2O)]^0$ as the reductant, and V_{rest} of the solution in the cell(I) shifted from 0.33 to −0.65 V. The connection of the two cells again produced 0.50 C of electricity, and V_{rest} of cell(I) and cell(II) became 0.02 V. An addition of CF_3SO_3H to the resulting solution in cell(I) (Table 1(c)) produced $[Ru(q)(H_2O)]^{2+}$ as the oxidant and V_{rest} shifted from 0.02 to 0.41 V. The inter-molecular electron transfer between the two cells further generated 0.27 C of electricity before V_{rest} in cell(I) and cell(II) reached 0.20 and 0.18 V. Moreover, V_{rest} of the cell(I) still moved from 0.20 to −0.53 V by an addition of *t*-BuOK due to the formation of $[Ru(cat)(H_2O)]^0$ and $[Ru(seq)(OH)]^+$ in the cell(I) (Table 1(d)). The redox reactions between the cells generated 0.35 C. The current stopped when V_{rest} of the two cells became −0.08 V. Thus, an addition of base or acid to cell(I) effectively generates reductant and oxidants, and the inter-molecular electron transfer through the electric wire generates electricity. It should be noticed that the start-

Table 1. Main Components in Two Cells and the Amount of Electricity Obtained[a]

	Main components in cell (I) (V_{rest})	Main components in cell (II) (V_{rest})	Electricity[b]
	Redox reaction	Redox reaction	
(a)	$[Ru(q)(H_2O)]^{2+}$(0.60 V) ↓ OH^- (1.6 equiv) $[Ru(seq)(H_2O)]^+$, $[Ru(seq)(OH)]^+$ (−0.13 V)	$[Ru(q)(H_2O)]^{2+}$ (0.60 V)	
	$[Ru(seq)(OH)]^+ \rightarrow [Ru(q)(OH)]^{2+} + e^-$	$[Ru(q)(H_2O)]^{2+} + e^- \rightarrow [Ru(seq)(H_2O)]^+$	0.50 C (71%)
(b)	$[Ru(seq)(H_2O)]^+$, $[Ru(q)(OH)]^{2+}$ (0.33 V) ↓OH^- (1.6 equiv) $[Ru(cat)(H_2O)]^0$, $[Ru(seq)(OH)]^+$ (−0.65 V)	$[Ru(seq)(H_2O)]^+$, $[Ru(q)(OH)]^{2+}$ (0.35 V)	
	$[Ru(cat)(H_2O)]^0 \rightarrow [Ru(seq)(H_2O)]^+ + e^-$	$[Ru(q)(OH)]^{2+} + e^- \rightarrow [Ru(seq)(OH)]^+$	0.50 C (71%)
(c)	$[Ru(seq)(H_2O)]^+$, $[Ru(seq)(OH)]^+$ (0.02 V) ↓ H^+ (1.5 equiv) $[Ru(seq)(H_2O)]^+$, $[Ru(q)(H_2O)]^{2+}$ (0.41 V)	$[Ru(seq)(H_2O)]^+$, $[Ru(seq)(OH)]^+$ (0.02 V)	
	$[Ru(q)(H_2O)]^{2+} + e^- \rightarrow [Ru(seq)(H_2O)]^+$	$[Ru(seq)(OH)]^+ \rightarrow [Ru(q)(OH)]^{2+} + e^-$	0.27 C (39%)
(d)	$[Ru(seq)(H_2O)]^+$ (0.20 V) ↓ OH^- (1.6 equiv) $[Ru(cat)(H_2O)]^0$, $[Ru(seq)(OH)]^+$ (−0.53 V)	$[Ru(seq)(H_2O)]^+$, $[Ru(q)(OH)]^{2+}$ (0.18 V)	
	$[Ru(cat)(H_2O)]^0 \rightarrow [Ru(seq)(H_2O)]^+ + e^-$	$[Ru(q)(OH)]^{2+} + e^- \rightarrow [Ru(seq)(OH)]^+$	0.35 C (50%)
(e)	$[Ru(seq)(H_2O)]^+$, $[Ru(seq)(OH)]^+$ (−0.08 V)	$[Ru(seq)(H_2O)]^+$, $[Ru(seq)(OH)]^+$ (−0.05 V)	

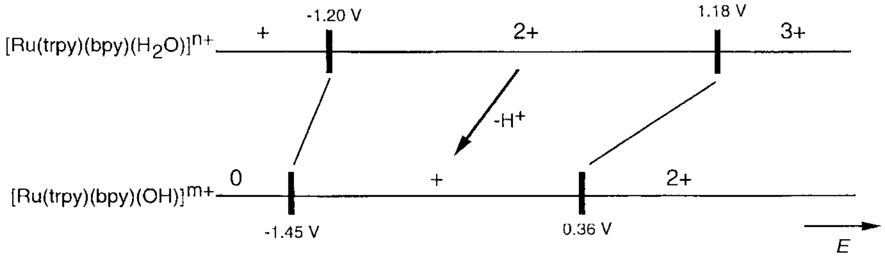
a) The amounts of acid and base are against the amount of complexes in cell (I). b) The value of current efficiency (%) is against the amount of complexes in cell (I).

ing solutions in the cell(I) and cell(II) are identical and the difference between the two cells is only the proton concentrations. Thus, this system converts the proton gradient into electricity catalytically.

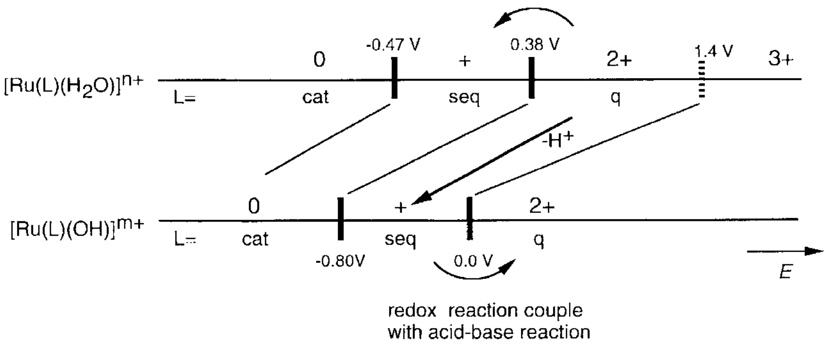
Discussion

Redox Reaction Coupled with Acid Base Reaction. The CVs and Vis-NIR spectra reveal that deprotonation of $[Ru(q)(H_2O)]^{2+}$ induces the ligand localized redox reaction (Eqs. 4, 5, 6, 7, 8, 9, 10, 11, and 12). A hydroxo moiety formed by dissociation of proton of metal–aqua complexes usually works as a strong electron donating group to the central metal atoms. As a result, reduction of metal-hydroxo complexes takes place at more negative potentials than that of corresponding aqua-complexes.[10—14] However, no example has been reported in which a metal-aqua complex is reduced by the metal–hydroxo complexes derived from the aqua-complex by deprotonation. Indeed, $[Ru(trpy)(bpy)(H_2O)]^{2+}$ undergoes two reversible redox reactions in acetone at $E_{1/2} = -1.20$ and 1.18 V resulting from the trpy/trpy$^{\bullet -}$ and $Ru^{II/III}$ couples, respectively. When $[Ru(trpy)(bpy)(H_2O)]^{2+}$ is converted into $[Ru(trpy)(bpy)(OH)]^{+}$ upon the deprotonation at the treatment with base, these redox potentials shift to $E_{1/2} = -1.45$ and 0.36 V, respectively. Thus, the redox potential of the Ru^{II}/Ru^{III} couple shifts from 1.18 to 0.36 V upon the deprotonation. However, the reduction potential of $[Ru(trpy)(bpy)(H_2O)]^{2+}$ is as negative as -1.20 V. Thus, electron transfer from $[Ru(trpy)(bpy)(OH)]^{+}$ to $[Ru(trpy)(bpy)(H_2O)]^{2+}$ thermodynamically an unfavorable process, as depicted in Fig. 6(a). In contrast to deprotonation of $[Ru(trpy)(bpy)(H_2O)]^{2+}$ affording $[Ru(trpy)(bpy)(OH)]^{+}$, dissociation of proton from $[Ru(q)(H_2O)]^{2+}$ is accompanied by the reduction of the dbq ligand via the intra-molecular electron transfer to produce $[Ru(seq)(OH)]^{+}$. The aqua complex, $[Ru(q)(H_2O)]^{2+}$, undergoes two reversible redox reactions at $E_{1/2} = -0.47$ and +0.38 V due to the cat/seq and seq/q couples, respectively, which shifted to -0.80 and 0.00 V upon deprotonation of $[Ru(q)(H_2O)]^{2+}$. Thus, the reduction of $[Ru(q)(H_2O)]^{2+}$ by $[Ru(seq)(OH)]^{+}$ is a thermodynamically favorable process (Fig. 6(b)). The successful conversion from proton gradients to electricity in the present study is ascribed to the characteristic redox behavior of the aqua and hydroxo complexes; $E_{1/2}$ of the $[Ru(q)(OH)]^{2+}/[Ru(seq)(OH)]^{+}$ couple is more negative than that of the $[Ru(q)(H_2O)]^{2+}/[Ru(seq)(H_2O)]^{+}$ one. The redox property of quinone ligand was suitable for the construction of such a redox system.

Energy Conversion. Taking advantage of characteristic redox behavior of $[Ru(L)(H_2O)]^{n+}$ and $[Ru(L)(OH)]^{n+}$ (L = q, seq, cat; $n = 0, 1, 2$), the proton gradient is successfully converted to electricity as depicted in Table 1. The solutions in the cell(I) and cell(II) involve only $[Ru(q)(H_2O)]^{2+}$ in the initial stage. The addition of an base converts $[Ru(q)(H_2O)]^{2+}$ to $[Ru(seq)(OH)]^{+}$ which works as the reductant for $[Ru(q)(H_2O)]^{2+}$. The connection of the two cells generates electricity, and the complexes involved in the two cells become the reductive form. Subsequent addition of CF_3SO_3H makes the reductant to oxidant conversely. Accordingly, the addition of base and acid directly converts the electrochemical property of the solution between oxidative and reductive states. The difference of the potential between the two cells is taken out as electricity. The hydrogen electrode can also con-



(a): $[Ru(trpy)(bpy)(H_2O)]^{n+}$



(b): $[Ru(trpy)(dbq)(H_2O)]^{n+}$

Fig. 6. The mechanism of redox reaction coupled with acid–base reaction. (a) the redox behavior of aqua- and hydroxo-trpy-bpy-ruthenium complexes; (b) the redox behavior of the aqua- and hydroxo-trpy-dbq-ruthenium complexes.

vert proton gradient catalytically to electricity utilizing the equilibrium $H_2 \rightleftarrows 2H^+ + 2e^-$ on Pt electrode, when two hydrogen electrodes in different pH conditions are connected.[32] Coexistence of H^+, H_2, and Pt electrode, therefore, are the essential components to construct the system. On the other hand, the characteristic redox behavior of $[Ru(q)(H_2O)]^{2+}$ can convert the proton gradient to electrochemical energy. The present study is the first example of the direct energy conversion from proton gradient to electricity using a homogeneous catalyst.

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20 When the redox waves at 0.0 V corresponded to $[Ru(seq)(OH)]^+/[Ru(cat)(OH)]^0$ couple, rest potential should not be more negative than $E_{1/2}$ of $[Ru(q)(H_2O)]^{2+}/[Ru(seq)(H_2O)]^+$ (0.38 V) when $[Ru(q)(H_2O)]^{2+}$ and $[Ru(seq)(OH)]^+$ exists simultaneously on the addition of base.

21 The electronic absorption spectra indicates that the oxidation state of Ru-dioxolene moiety is Ru^{II}–semiquinone in this hydroxo complex. The intra-molecular electron transfer from electron-rich hydroxo ligand to quinone ligand should cause such modification of oxidation state. The detailed mechanism of intra-molecular electron transfer is now under investigation.

22 It may have an possibility that an excess of *t*-BuOK (0.2 equiv) to $[Ru(q)(H_2O)]^{2+}$ is consumed in a reaction with acetone due to lability of the solvent toward the base.

23 The deprotonation of hydroxo ligand leaves a lone pair on oxo ligands. We supposed the intra-molecular electron transfer from the lone pair of oxo ligand to quinone ligand as in the case on the conversion of aqua ligand to hydroxo ligand.

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30 In case of the oxidation with $[Ru\ (polypyridyl)_n(O)]^{2+}$, the hydroxo compounds were also reactive and the aqua complex formed. In the case of quinone complex the hydroxo complexes are stable judged from Vis-NIR spectra and CVs.

31 Since acetone is not very stable in basic condition, the unstable species derived from acetone is regarded to be oxidized. Oxidation with this complex is now under investigation.

32 In one acidic cell, the reaction, $H^+ + e^- \rightarrow 1/2H_2$, proceeds, and in the other basic cell, the reaction, $1/2H_2 + OH^- \rightarrow H_2O + e^-$, proceeds. Since the total reaction is $H^+ + OH^- \rightarrow H_2O$, the pH gradient can be catalytically converted into electricity with two hydrogen electrodes.