First Artificial Energy Conversion from Proton Gradient to Electricity

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The proton gradient is catalytically converted to electricity by ruthenium aqua complex $[Ru(trpy)(3,5\text{-di-tert-butylquinone})(H_2O)]^{2+}$ (trpy = 2,2':6',2"-terpyridine). The first successful energy conversion from proton gradient to electricity is based on the redox reactions of this ruthenium complex coupled with acid-base reaction.

Biological system utilizes proton gradient for synthesis of ATP.[1, 2] In chemiosmotic theory,[3] the proton gradient (Δp) between inside and outside of a cell is depicted as the sum of electric activity ($\Delta\psi$) and chemical activity (ΔpH) components.

$\Delta p = \Delta\psi - Z\Delta pH \quad (Z = 2.303RT/F)$

When we are concerned about chemical activity part, proton gradient is equivalent to the neutralization energy because the reaction, $H^+ + OH^- \rightarrow H_2O$ takes place if the separating membrane is removed. While the biological system converts the neutralization energy into valuable energy source, neutralization energy is just emitted as thermal energy on the disposition of waste acids or bases in industrial process.[4] However, neutralization energy is originated from the binding energy of acid and base, namely is one of the chemical energies, which are able to be converted directly to valuable chemical, electric or mechanical energy in 100% efficiency in principal.[5, 6] In this communication, we describe the first energy conversion from neutralization energy to electronic energy with very simple ruthenium-aqua complex.

Metal-aqua complexes are representative candidates for accumulation of proton gradient energy because they are expected to be converted to the corresponding hydroxy- and oxo-complexes by acid-base equilibria (eq 1),[7] and the redox potentials of complexes change as release of protons.

$$[M(H_2O)] \rightleftharpoons [M(OH)]^- \rightleftharpoons [M(O)]^{2-} \qquad (1)$$

However, hydroxy- and oxo complexes tend to dimerize or polymerize because of its high electron density. To stabilize electron-rich hydroxy and oxo complexes, we prepared the ruthenium-aqua complex having a redox active quinone ligand, $[Ru(trpy)(3,5\text{-di-tert-butylquinone})(H_2O)]^{2+}$ ($[Ru\text{-}H_2O]^{2+}$).[8] This ruthenium aqua complex showed redox reactions coupled with acid-base equilibrium depending on OH^- concentrations.[9] Figure 1a shows the cyclic voltammogram (CV) of $[Ru\text{-}H_2O]^{2+}$ in acetone. $[Ru\text{-}H_2O]^{2+}$ undergoes two reversible redox couples at $E_{1/2} = -0.47$ V and $E_{1/2} = 0.38$V ($E_{1/2} = (E_{pc} + E_{pa})/2$), which are assigned to the $[Ru\text{-}H_2O]^{0/+}$ and $[Ru\text{-}H_2O]^{+/2+}$ couples, respectively, based on the rest potential (V_{rest}) of 0.60 V. When 0.7 equivalent of OH^- was added to the solution, V_{rest} shifted from 0.60 V to 0.30 V across the $E_{1/2}$ of the $[Ru\text{-}H_2O]^{+/2+}$ couple (Figure 1b). At the same time, new redox couples appeared at $E_{1/2} = -0.80$V and 0.00V, which are assigned to the $[Ru\text{-}OH]^{0/+}$ and $[Ru\text{-}OH]^{+/2+}$ couples. Since $E_{1/2}$ of the $[Ru\text{-}OH]^{+/2+}$ couple is more negative than that of the $[Ru\text{-}H_2O]^{+/2+}$ couple, the redox reaction coupled with acid-base reaction took place (eqs 2 and 3), to cause the cathodic shift of V_{rest}.

$$[Ru\text{-}H_2O]^{2+} + OH^- \longrightarrow [Ru\text{-}OH]^+ + H_2O \qquad (2)$$

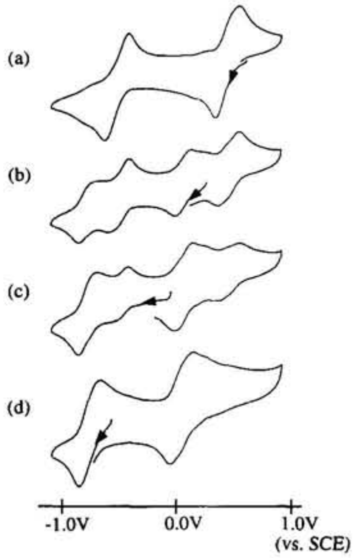

Figure 1. Cyclic voltammogram of $[Ru\text{-}H_2O](ClO_4)_2$ in acetone under N_2 on the addition of various amount of base. Me_4NClO_4 was used as electrolyte: (a) without base, $V_{rest} = 0.60$ V; (b) 0.7 equivalent of OH^-, $V_{rest} = 0.30$V; (c) 1.3 equivalent of OH^-, $V_{rest} = -0.05$V; (d) 2.0 equivalent of OH^-, $V_{rest} = -0.57$V. All CVs started from V_{rest}.

$$[Ru\text{-}H_2O]^{2+} + [Ru\text{-}OH]^+ \longrightarrow [Ru\text{-}H_2O]^+ + [Ru\text{-}OH]^{2+} \qquad (3)$$

The addition of 1.3 equivalent of OH^- caused slight decrease and increase of the peak current of the $[Ru\text{-}H_2O]^{0/+/2+}$ and $[Ru\text{-}OH]^{0/+/2+}$ couples, respectively (Figure 1c). In the course of Figure 1b to 1c, V_{rest} shifted from 0.30V to -0.05V across the $E_{1/2}$ of the $[Ru\text{-}OH]^{+/2+}$ couple, which showed that redox reaction coupled with acid-base reaction also occurred. When the pK_a value of $[Ru\text{-}H_2O]^+$ was larger than that of $[Ru\text{-}OH]^{2+}$, $[Ru\text{-}H_2O]^+$ released the proton first and V_{rest} must shift more negative with the disappearance of the redox couples of the aqua complex. The survival of the $[Ru\text{-}H_2O]^{0/+/2+}$ couples indicates that not the $[Ru\text{-}H_2O]^+$, but the deprotonation of $[Ru\text{-}OH]^{2+}$ proceeds (eq. 4). The resulting $[Ru\text{-}O]^+$ should be oxidized by $[Ru\text{-}OH]^{2+}$ to produce $[Ru\text{-}O]^{2+}$ and $[Ru\text{-}OH]^+$ (eq 5), because the $E_{1/2}$ of the $[Ru\text{-}O]^{+/2+}$ couple is inferred more negative than that of the $[Ru\text{-}OH]^{+/2+}$ couple from the analogy of the relation between $E_{1/2}$ of the $[Ru\text{-}OH]^{+/2+}$ couple (0.00 V) and the $[Ru\text{-}H_2O]^{+/2+}$ couple (0.38 V). The resultant $[Ru\text{-}O]^{2+}$ probably reproduces $[Ru\text{-}OH]^{2+}$ by abstraction of H•

$$[Ru\text{-}OH]^{2+} + OH^- \longrightarrow [Ru\text{-}O]^+ + H_2O \qquad (4)$$

$$[Ru\text{-}OH]^{2+} + [Ru\text{-}O]^+ \longrightarrow [Ru\text{-}OH]^+ + [Ru\text{-}O]^{2+} \qquad (5)$$

from the solvent, since the redox couples of oxo species did not appear and the shape of redox couples of hydroxy complexes did not decrease.[10] Indeed, analogous $[Ru(bpy)(trpy)O]^{2+}$ derived from $[Ru(bpy)(trpy)(H_2O)]^{2+}$ by electrochemical oxidation, shows high oxidation reactivity toward alcohols, aldehydes and unsaturated hydrocarbons.[11]

The redox reaction coupled with the acid-base reaction also

Table 1. Main components in two cells and the amount of electricity obtained[a]

	main components in cell (I)	main components in cell (II)	main redox reactions		electricity
(a)	$[Ru\text{-}H_2O]^{2+}$	$[Ru\text{-}H_2O]^{2+}$			
	$\downarrow$ OH^- (1.6 eq)		$[Ru\text{-}OH]^+ \longrightarrow [Ru\text{-}OH]^{2+} + e^-$	(8)	
	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^+$		$[Ru\text{-}H_2O]^{2+} + e^- \longrightarrow [Ru\text{-}H_2O]^+$	(9)	0.50C (0.71 eq)
(b)	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^{2+}$	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^{2+}$			
	$\downarrow$ OH^- (1.6 eq)		$[Ru\text{-}H_2O]^0 \longrightarrow [Ru\text{-}H_2O]^+ + e^-$	(10)	
	$[Ru\text{-}H_2O]^0$, $[Ru\text{-}OH]^+$		$[Ru\text{-}OH]^{2+} + e^- \longrightarrow [Ru\text{-}OH]^+$	(11)	0.50C (0.71 eq)
(c)	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^+$	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^+$			
	$\downarrow$ H^+ (1.5 eq)		$[Ru\text{-}H_2O]^{2+} + e^- \longrightarrow [Ru\text{-}H_2O]^+$	(12)	
	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}H_2O]^{2+}$		$[Ru\text{-}OH]^+ \longrightarrow [Ru\text{-}OH]^{2+} + e^-$	(13)	0.27C (0.39 eq)
(d)	$[Ru\text{-}H_2O]^+$	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^{2+}$			
	$\downarrow$ OH^- (1.6 eq)		$[Ru\text{-}H_2O]^0 \longrightarrow [Ru\text{-}H_2O]^+ + e^-$	(14)	
	$[Ru\text{-}H_2O]^0$, $[Ru\text{-}OH]^+$		$[Ru\text{-}OH]^{2+} + e^- \longrightarrow [Ru\text{-}OH]^+$	(15)	0.35C (0.50 eq)
(e)	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^+$	$[Ru\text{-}H_2O]^+$, $[Ru\text{-}OH]^+$			

[a] The amounts of acid, base and electricity are against the amount of complex in cell(I).

took place on the addition of more OH^-. V_{rest} moved up to -0.57 V by the addition of 2.0 equivalent of OH^- to the solution (Figure 1d) and further addition of excess OH^- did not change the CV. A distinct decrease in the peak currents of the $[Ru\text{-}H_2O]^{0/+/2+}$ couples results from deprotonation of $[Ru\text{-}H_2O]^+$ producing $[Ru\text{-}OH]^0$ (eq 6). Once $[Ru\text{-}OH]^0$ is produced, it reduces $[Ru\text{-}H_2O]^+$, since $E_{1/2}$ of the $[Ru\text{-}OH]^{0/+}$ couple (-0.80V) is more negative than that of the $[Ru\text{-}H_2O]^{0/+}$ one (-0.47V) (eq. 7).

$$[Ru\text{-}H_2O]^+ + OH^- \longrightarrow [Ru\text{-}OH]^0 \qquad (6)$$

$$[Ru\text{-}OH]^0 + [Ru\text{-}H_2O]^+ \longrightarrow [Ru\text{-}OH]^+ + [Ru\text{-}H_2O]^0 \qquad (7)$$

These redox reactions of this ruthenium aqua complex coupled with acid-base reactions enable the energy conversion from proton gradient to electricity. The energy conversion was conducted with two compartment cells (I and II) separated by an anion exchange membrane filled with an acetone solution of $[Ru\text{-}H_2O]^{2+}$ (7.0 μmol/15 ml in each cell). The results of the energy conversion are summarized in Table 1. Upon an addition of 1.6 equivalent of OH^- to cell(I), $[Ru\text{-}H_2O]^+$ and $[Ru\text{-}OH]^+$ formed and V_{rest} shifted from 0.60V to -0.13 V (eqs 2-5). The connection of two cells induced current flow from the cell(II) to cell(I) through the redox reaction of eqs 8 and 9 in Table 1. At the end of the discharge (12 hr later), V_{rest} of two cells were 0.33 ± 0.02 V, and 0.50 C of electricity was obtained.[12] Because the only difference between two cells is the amount of OH^-, pH gradient produces electric energy with this complex.

Further addition of 1.6 equivalent of OH^- to the cell(I) caused the formation of $[Ru\text{-}H_2O]^0$ and $[Ru\text{-}OH]^+$ and the shift of V_{rest} from 0.33 V to -0.65 V (eqs 6 and 7). The connection of two cells generated 0.5 C of electricity (eqs 10 and 11 in Table 1) and V_{rest} of two cells were 0.02 ± 0.02 V at the end of the discharge. Successively, by the addition of 1.5 equivalent of H^+ and 1.6 equivalent of OH^-, acid-base and redox reactions took place and V_{rest} shifted positive to 0.41 V and negative to -0.53V, respectively. Connection of two cells generated 0.27 C of electricity in the procedure of (c) and 0.35C in (d) through the redox reactions shown in Table 1.

As already described above, the current flows are induced from the difference of OH^- concentration or H^+ concentration between two cells, namely the proton gradient are transformed to electronic energy with this ruthenium complex. Moreover, the neutralization energy are catalytically transformed to electric energy since the solution in two cells return the same composition from (c) to (e) in Table 1. This electronic cell is the first system which converts the neutralization energy to electric energy. The large difference of redox potentials between aqua and corresponding hydroxy complexes, both of which are reversibly converted with each other by the acid base equilibrium, is utilized for the energy conversion in this system. The reactions used in this electronic cell is reversible redox and acid-base reactions, therefore, this system enables itself to work as a proton pump. When this system runs reversely, pH gradient should be induced as well as biological system.

References and Notes

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8 $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ was prepared as follows. Aqueous $HClO_4$ solution (60%) was added to $[Ru(trpy)(dbq)(AcO)]$[13] MeOH solution. After the solution became dark blue, saturated Me_4NClO_4 MeOH solution was added. The addition of H_2O gave small needle shape $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2$ crystals (yield 50%). Elemental analysis. Found: C, 43.65 %; H, 4.58%; N, 5.24%. Calcd for $[Ru(trpy)(dbq)(H_2O)](ClO_4)_2 \cdot 1.5H_2O$: C, 43.62 %; H, 4.54 %; N: 5.26 %.

9 The methanol solution of CF_3SO_3H was used as acid. The methanol solution of Me_4NOH or ^{t}BuOK were used as base.

10 The identification of oxo species and the detailed mechanism of oxidation are now under investigation.

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12 Only V_{rest} shifted positive in the cell(I) during the discharge, though the peak currents of the $[Ru\text{-}OH]^{0/+/2+}$ couples increased and those of $[Ru\text{-}H_2O]^{0/+/2+}$ ones decreased in the cell(II) (Table 1 (b)). It is ascribed to partial penetration of OH^- from the cell(I) to the cell(II) through an anion exchange membrane during the experimental time.

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