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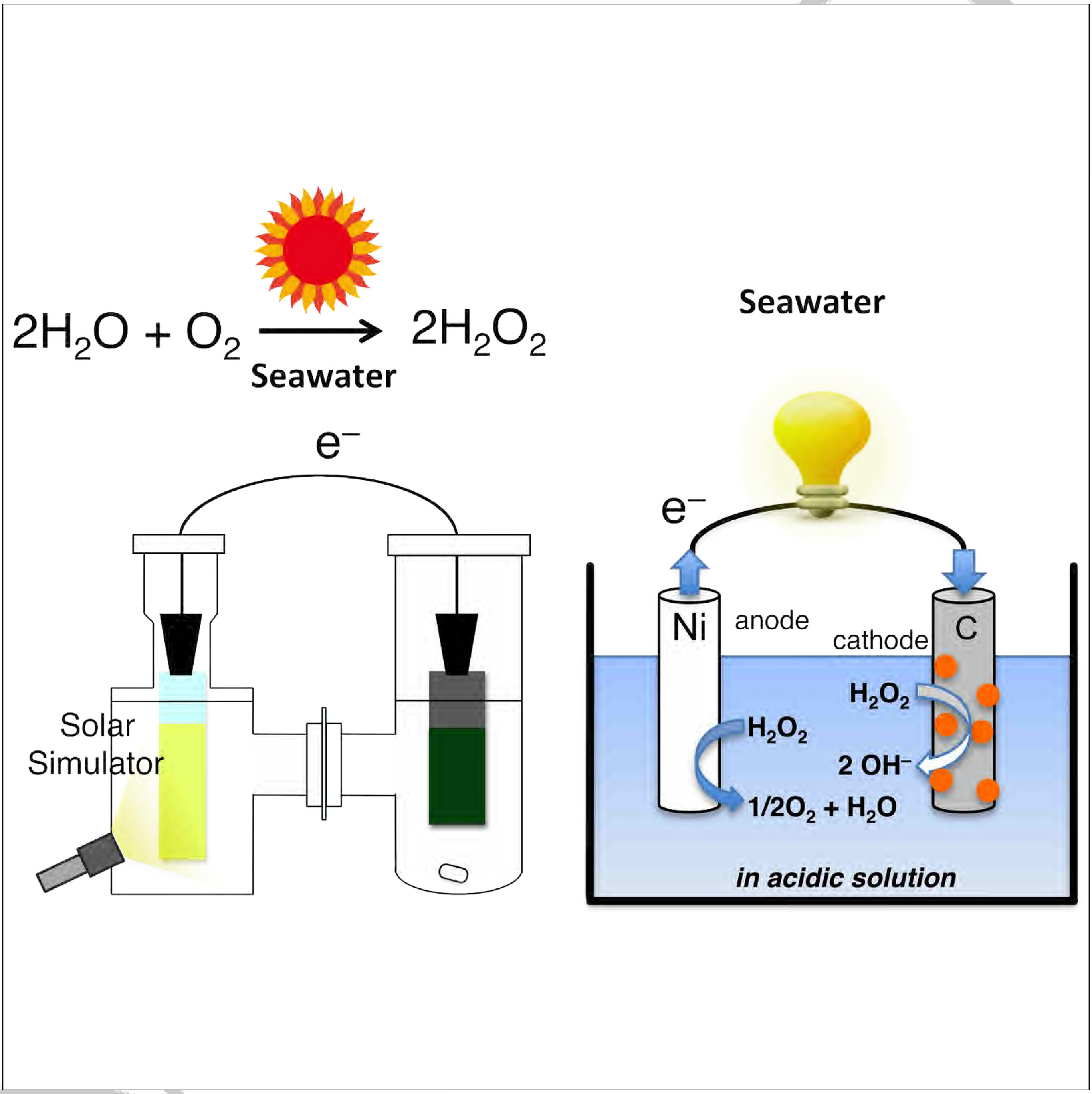
Special Issue

Hydrogen Peroxide used as a Solar Fuel in One-Compartment Fuel Cells

Shunichi Fukuzumi*[a, b] and Yusuke Yamada*[c]

Dedicated to Prof. Cristian Amatore on the occasion of his 65th birthday



Clean and highly efficient production of solar fuels as well as effective methods to store solar fuels have long been sought to solve global energy and environmental issues. Among solar fuels such as gaseous hydrogen and carbon monoxide, aqueous hydrogen peroxide (H_2O_2) is an ideal chemical for energy storage, because endothermic H_2O_2 decomposition produces only water and oxygen. In addition, H_2O_2 can be transported in plastic containers with a high energy density. H_2O_2 can be converted into electricity by using H_2O_2 fuel cells without a membrane and composed of an anode and a cathode, and they can selectively catalyze H_2O_2 oxidation or reduction. The one-compartment structure without a membrane is more promising to develop low-costing fuel cells than a two-compartment structure with expensive membranes. This article provides a focused review of recent developments and future perspectives of H_2O_2 fuel cells without membranes, combined with H_2O_2 production from seawater and dioxygen in the air by utilizing solar energy.

1. Introduction

Global warming caused by the production of greenhouse gases from the combustion of fossil fuels has prompted the development of alternative, renewable energy sources by using solar energy and effective storage.[1–4] Hydrogen can produce electricity by using hydrogen fuel cells, and electricity can produce hydrogen by electrolysis; hydrogen is renewable and harmless to the environment, because hydrogen produces energy by oxidation with dioxygen to yield only water.[5–8] However, high-pressure tanks (35.0–70.0 MPa■■converted into SI unit■■) are necessary to store gaseous hydrogen, whereas cryogenic temperatures are demanded to store hydrogen in liquid form because the boiling point of hydrogen is as low as −252.8 °C at atmospheric pressure.[5–8] Current industrial production processes of hydrogen are expensive and energy consuming, and they often involve the use of fossil fuels. In addition, an effective infrastructure for supplying hydrogen has yet to be established. ■■paragraph ok?■■

In contrast to hydrogen, hydrogen peroxide (H_2O_2), a liquid with high energy density, is a promising energy carrier for portable devices in the next generation, because safety of H_2O_2 is guaranteed not only in aqueous solution but also in solid form through the formation of adducts with urea or carbonate, for which the H_2O_2 concentration can reach higher than about 30 wt %.[9–15] Concentrated hydrogen peroxide is a compound regulated by the Environmental Protection Agency (EPA), because it is hazardous at >52 wt %, which may be an upper concentration limit for practical applications.[9] Nevertheless, this limitation should not prevent its use as a fuel, because concentrated H_2O_2 is a stable liquid as long as it is not exposed to metals that catalyze its decomposition into water and oxygen or organic compounds that pose a combustion threat. H_2O_2 is fairly nontoxic but corrosive even at high concentrations (≈20 M). Thus, H_2O_2 in a plastic container can provide high portability with a high energy density per volume.[9–15] Because the disproportionation of two H_2O_2 molecules to H_2O and O_2 releases a large amount of energy (Figure 1),[15–18] H_2O_2 has been used as an effective fuel and oxidant in rocket propulsion[19–24] and micromotors.[25–30] In industry, H_2O_2 is produced by the anthraquinone catalytic process, in which O_2 is reduced by H_2.[31,32]

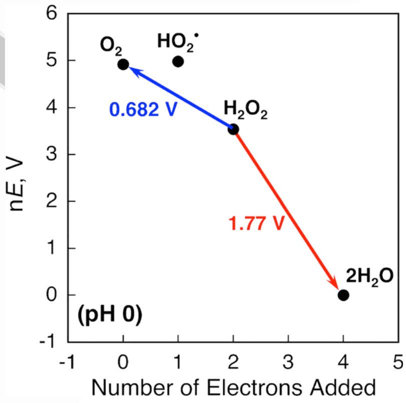


Figure 1. Frost diagrams for O_2 activation.

To utilize H_2O_2 as a solar fuel, H_2O_2 should be produced by oxidation of H_2O with O_2 by using solar energy and used as a fuel for H_2O_2 fuel cells.[12–15] H_2O_2 is indeed produced by using solar energy in photosynthesis, for which 5–10 % of the total photosynthetic electron flow in C3 plants is consumed to reduce O_2 to H_2O_2 under normal functional conditions, and this can increase to more than 30 % under stress conditions.[15,33–35]

From a thermodynamic point of view, the overall efficiency of the H_2O_2–O_2 system potentially exceeds that of the H_2–H_2O system. For production of H_2O_2 and H_2, the Gibbs energy change for the production of H_2O_2 by O_2 reduction with water is 117 kJ mol^{-1},[36] which is almost half that for H_2O reduction to H_2 (237 kJ mol^{-1}).[36] Also, the thermodynamic efficiency of the fuel cell is given by the ratio of the Gibbs energy change (ΔG°) to the enthalpy change (ΔH°) in the overall cell reaction. The ΔG° and ΔH° values measure the electrical work and the internal energy of the fuel, respectively. Therefore, the efficiency of

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This is an invited contribution for the Christian Amatore Festschrift the ideal H_2 fuel cell is 83 % [$=\Delta G^\circ/\Delta H^\circ$ (-237 kJ mol^{-1})/(-286 kJ mol^{-1})].[36] On the other hand, the efficiency of the ideal H_2O_2 fuel cell is higher than 100 % ($-\Delta G^\circ > -\Delta H^\circ$).[36]

At present, the power density of conventional H_2 fuel cells exceeds more than 1 W cm^{-2}[37] on the other hand, and that of H_2O_2 fuel cells remains lower than 10 mW cm^{-2} on the other hand (Tables 1 and 2).[38–53] Thus, H_2O_2 fuel cells are not yet suitable for large-scale electric devices such as automobiles, but they are used for personal-based small electric items such as cell phones. Although the gravimetric energy density of H_2O_2 is as low as 0.85 kWh kg^{-1}, which is about 40 times lower than that (33 kWh kg^{-1}) of H_2, the volumetric energy density of pure H_2O_2 (1230 Wh L^{-1}) is more than 400 times larger than that of H_2 (2.9 W L^{-1}) under standard ambient temperature and pressure. Thus, the volumetric energy density of an aqueous 30 wt % H_2O_2 solution is equal to that of H_2 compressed under a high pressure of 10 MPa. Whereas a gas tank with high strength is necessary for H_2 transportation, a lightweight plastic bottle is sufficient to store and transport H_2O_2. Thus, at present, H_2O_2 can be regarded as a solar fuel for small personal-based devices.

This minireview focuses on recent developments of one-compartment H_2O_2 fuel cells, which are combined with the production of H_2O_2 from H_2O and O_2 by using solar energy. H_2O_2 fuel cells can generate a theoretical output voltage of 1.09 V by utilizing H_2O_2 as both a fuel at the cathode and an oxidant at the anode with the emission of H_2O and O_2 after power generation (Figure 1). In particular, H_2O_2 is produced from seawater, which is the most earth-abundant resource, and O_2 in the air by using solar energy, and the H_2O_2 thus produced is directly consumed as a fuel in seawater for H_2O_2 fuel cells to generate electrical power on demand.

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Yusuke Yamada earned his Ph.D. degree in macromolecular science from Osaka University in 1998. He worked as a researcher and senior researcher at Osaka National Research Institute (currently AIST) from 1998 to 2009. From 2007 to 2008, he was a visiting scholar at UC Berkeley. He was an Associate Professor of Osaka University from 2009. In 2015, he moved to Osaka City University as a Full Professor.

2. Development of One-Compartment Hydrogen Peroxide Fuel Cells without a Membrane

Proton-exchange membrane (PEM) fuel cells normally require oxygen as the oxidant, and the reductant is separated by the membrane. Aqueous H_2O_2 has been utilized as an alternative oxidant in various types of fuel cells by using borohydride,[54–58] metals,[59–63] methanol,[64–66] ethanol,[67,68] hydrazine,[69] H_2S,[70,71] and biofuels[54,55] as reductants. The fabrication of one-compartment fuel cells without expensive membranes by employing only one chemical as both the fuel and the oxidant seems to be a valuable approach to develop low-costing fuel cells. H_2O_2 can be used not only as an oxidant but also as a reductant, and thereby, one-compartment H_2O_2 fuel cells have recently been developed.[38–45] One-compartment H_2O_2 fuel cells have various advantages over other fuel cells including hydrogen fuel cells. First of all, H_2O_2 is liquid and freely miscible with water and is thereby easy to store and carry in an appropriate container in comparison with hydrogen, which needs a high-pressure tank. Indeed, an aqueous solution of H_2O_2 supplied by a chemical company is kept in a plastic container. Most importantly, no expensive membranes are required for one-compartment H_2O_2 fuel cells, because H_2O_2 can act as both the oxidant and the reductant depending on the catalytic activities of the electrodes using the same H_2O_2 solution. H_2O_2 provides more energy than O_2 for the fuel cell and increases the cell performance, because H_2O_2 has a higher standard reduction potential ($E^\circ = 1.77$ V vs. NHE) than O_2 ($E^\circ = 1.23$ vs. NHE).[15] Furthermore, H_2O_2 does not cause the environmental problems associated with most other chemical reductants and oxidants.

The anodic and cathodic reactions at the electrodes of H_2O_2 fuel cells are given by Equations (1) and (2), respectively.[13–15] The overall reaction [Eq. (3)] indicates that H_2O_2 fuel cells emit only O_2 and H_2O after electrical power generation. The theoretically expected output potential of the H_2O_2 fuel cell is 1.09 V, which is slightly lower but similar to those of a hydrogen fuel cell and a direct methanol fuel cell (1.23 and 1.21 V, respectively). [13–15]

$$\text{Anode: } H_2O_2 \rightarrow O_2 + 2\,H^+ + 2\,e^- \quad 0.68\ \text{V vs. NHE} \tag{1}$$

$$\text{Cathode: } H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O \quad 1.77\ \text{V vs. NHE} \tag{2}$$

$$\text{Total: } 2\,H_2O_2 \rightarrow O_2 + 2\,H_2O \quad 1.09\ \text{V} \tag{3}$$

The first one-compartment H_2O_2 fuel cell employed an Au plate and an Ag plate as the anode and cathode, respectively, in an aqueous solution containing 1 M NaOH and 300 mM H_2O_2 (Figure 2), because these metal plates act as selective oxidation

Table 1. Open-circuit potentials (OCPs) and maximum power densities (MPDs) of one-compartment H_2O_2 fuel cells in literature.

Anode	Cathode	pH	OCP [V]	MPD [mW cm^{-2}]	Ref.
Au	Ag	14	0.095	0.07	[38]
Au	Ag–Pb	14	0.15	0.07	[39]
Ni	$Fe^{III}(Pc)Cl$	3	0.5	0.01	[40]
Ni	Prussian blue	1	0.60	1.55	[41]
Ag	Prussian blue	1	0.52	0.7	[41]
Ni	$Fe^{II}[Co^{III}(CN)_6]$	1	0.80	1.0	[42]
Ni	$Fe^{II}[Co^{III}(CN)_6]$ (heat treated)	1 (Sc^{3+})	0.81	9.9	[43]
Ni	$Fe^{II}[Pt(CN)_4](pyz)$	1	0.7	4	[44]
	$Fe^{II}[Pd(CN)_4](pyz)$[a]	1	0.78	4	[44]
Ni	Fe^{III}(9-hydroxyphenalenone)$_3$	1	0.74	1.43	[45]

[a] ■■pyz = please define■■.

Table 2. Open-circuit potentials (OCPs) and maximum power densities (MPDs) of two-compartment H_2O_2 fuel cells in literature.

Cathode	Catholite	Anode	Anolite	OCP [V]	MPD [mW cm^{-2}]	Ref.
Pt	1.5 M H_2SO_4	Ni	6 M KOH	0.90	3.9	[46]
				0.90	58.4 (60 °C)	[47]
Au@Pd	2 M H_2SO_4	Au@Pd	4 M KOH	0.90	20.7	[48]
Pt	1.5 M H_2SO_4	$PbSO_4$	3 M KOH	≈1	10	[49]
Au	2 M H_2SO_4	Au	4 M KOH	0.8	14	[50]
Pd	2 M H_2SO_4	Ni	4 M KOH	0.9	21.6 (20 °C)	[51]
					53.8 (50 °C)	[51]
Pd	2 M H_2SO_4	Ni	4 M KOH	0.9	48.7 (20 °C)	[52]

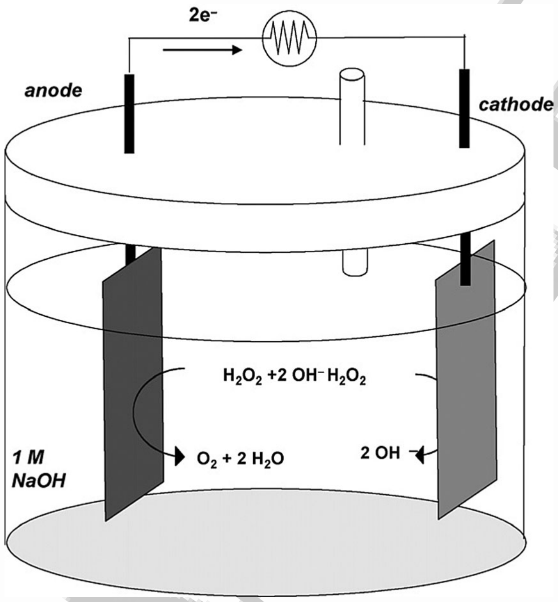


Figure 2. One-compartment H_2O_2 fuel cell under basic conditions (pH 14).[38]

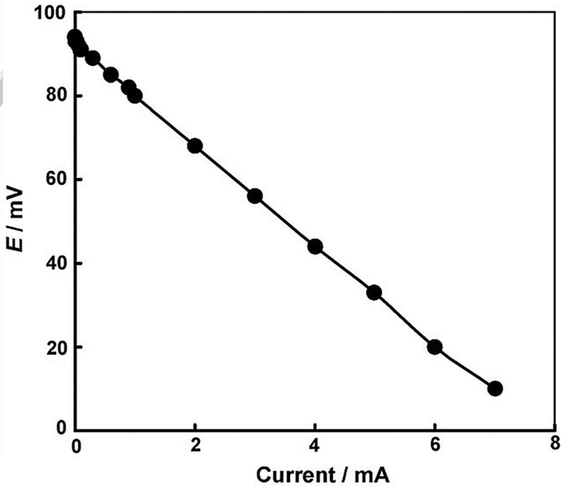


Figure 3. *I*–*V* curve of a one-compartment H_2O_2 fuel cell with a Au anode and a Ag cathode. Performance tests were conducted in aqueous solution containing 1 M NaOH and 300 mM H_2O_2. The electrode surface areas were fixed at 2.4 cm^2.[38]

and reduction electrocatalysts toward H_2O_2, respectively.[38] However, the open-circuit potential (OCP) was as low as 0.095 V (Figure 3), which is much lower than the theoretically expected output voltage of 1.09 V.[38] The low OCP value results from a large overpotential at the Ag cathode.[38]

The performance of the H_2O_2 fuel cell in Figure 2 was improved by using Ag–Pb alloy nanoparticles as the cathode, because Ag nanoparticles possess a higher specific surface area than the Ag plate and also the catalytic activity of the Ag nanoparticles cathode was enhanced by the addition of a foreign element to Ag metal.[39] The higher power density, open-

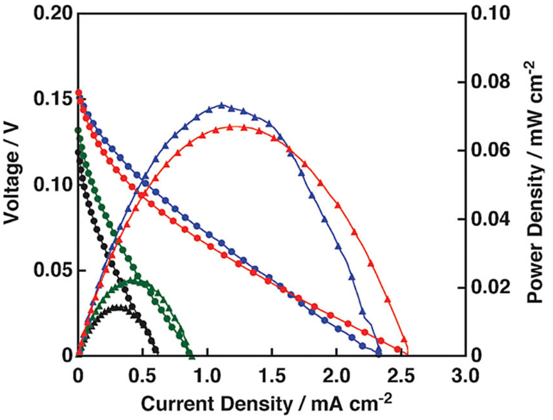


Figure 4. *I–V* and *I–P* curves of a one-compartment H_2O_2 fuel cell with a Ag or Ag–Pb alloy cathode. Au anode: 1 M NaOH, 300 mM H_2O_2. Black: Ag, green: Ag/Pb = 6:4, red: Ag/Pb = 7:3, blue: Ag/Pb = 9:1.[39]

circuit potential (0.16 V), and short-circuit current were obtained by employing Ag–Pb alloys as cathodes (Ag/Pb = 9:1, 7:3, 6:4 in Figure 4).[39] Such highly active cathode materials for H_2O_2 reduction would be beneficial not only for other types of fuel cells using H_2O_2 as the oxidant but also those using O_2, because the four-electron reduction of O_2 is sometimes accompanied by two-electron reduction of O_2 to produce peroxide species.

A two-compartment H_2O_2 fuel cell composed of a Pt/C cathode and a carbon paper (CP) anode deposited with nanonickel metal (Ni/CP), separated by a Nafion-117 membrane, was reported by using an acidic H_2O_2 solution (1.5 M H_2SO_4 + 2.0 M H_2O_2) as the catholite and a basic H_2O_2 solution (6.0 M NaOH + 1.0 M H_2O_2) as the anolite; this cell afforded an OCP of 0.90 V and a power density of 3.9 mW cm^{-2}.[46] The peak power density was as high as 58.4 mW cm^{-2} at 60 °C upon using 4.0 M KOH + 1.0 M H_2O_2 as the fuel and 2.0 M H_2SO_4 + 2.0 M H_2O_2 as the oxidant.[46] However, it is highly desired to develop a one-compartment H_2O_2 cell by using the same H_2O_2 solution under acidic conditions to combine the production of H_2O_2 through the two-electron reduction of O_2, which is more efficient under acidic conditions. The key issue is the enhancement in the catalytic reactivity for H_2O_2 reduction.

The low output potentials of H_2O_2 fuel cells result from a large overpotential for H_2O_2 reduction at the cathode.[38] Basic solutions impose thermodynamically unfavorable conditions for H_2O_2 reduction, for which a large overpotential is necessary. Thus, neutral to acidic solutions should be employed to improve the open-circuit potentials of H_2O_2 fuel cells.

In natural systems, iron porphyrin complexes are used as active sites of hydroperoxidases, which can efficiently catalyze the reduction of H_2O_2 under neutral pH conditions.[72–75] Thus, the iron porphyrin and iron phthalocyanine complexes shown in Figure 5, which mimic the active sites of hydroperoxidases, were have been employed as cathode catalysts to improve the H_2O_2 reduction activity under acidic conditions.[40]

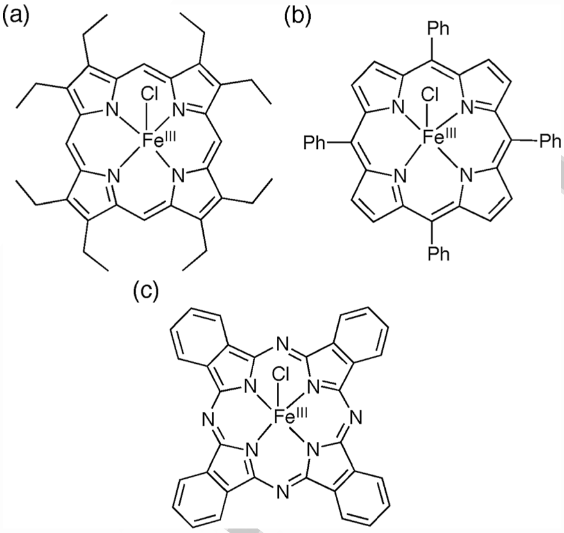


Figure 5. Chemical structures of porphyrin and phthalocyanine iron(III) complexes similar to the active-site structures of hydroperoxidases as candidates of cathodes of a H_2O_2 fuel cell. a) [Fe^{III}(OEP)Cl], b) [Fe^{III}(TPP)Cl], and c) [Fe^{III}(Pc)Cl].[40]

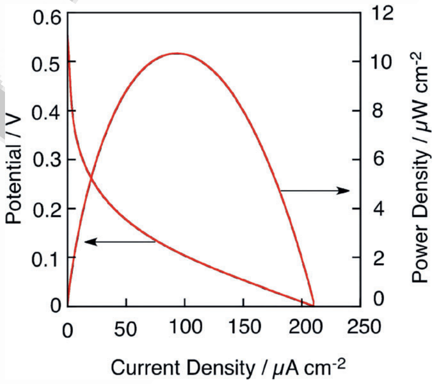


Figure 6. *I–V* and *I–P* curves of a one-compartment H_2O_2 fuel cell with a Ni anode and a [Fe^{III}(Pc)Cl] cathode. Performance tests were conducted in an acetate buffer containing 300 mM H_2O_2 at pH 3.0[40]

The OCP was improved to 0.55 V by using iron(III) phthalocyanine (Pc)■■ok?■■ chloride supported on a glassy carbon as the cathode of a H_2O_2 fuel cell working at pH 3 (Figure 6).[40] The catalytic activities of the iron complexes for H_2O_2 reduction were evaluated by cyclic voltammetry (CV) measurements of H_2O_2. The iron complexes were mounted on glassy carbon electrodes to be used as the working electrodes in aqueous acetate buffer containing H_2O_2 (pH 4, 3 mM).[40] In the presence of H_2O_2, catalytic currents with the Fe complexes in cathodic sweeps were observed, which indicated that they could act as catalysts for H_2O_2 reduction in acidic media.[40] The onset potential for H_2O_2 reduction on electrodes with [Fe^{III}(Pc)Cl] was 0.5 V, which is more positive than that observed with either [Fe^{III}(OEP)Cl] (■■OEP = please define■■) or [Fe^{III}(TPP)Cl] (0.2 V) (■■TPP = please define■■), which suggests that [Fe^{III}(Pc)Cl] is the most promising cathode material for a H_2O_2 fuel cell operating under acidic solutions.[40]

Prussian blue [ferric ferrocyanide: (Fe$_4^{III}$[Fe^{II}(CN)$_6$]$_3$)] has been used for the cathode in a one-compartment H_2O_2 fuel cell under acidic conditions by using 0.10 M HCl and 0.50 M H_2O_2.[41]

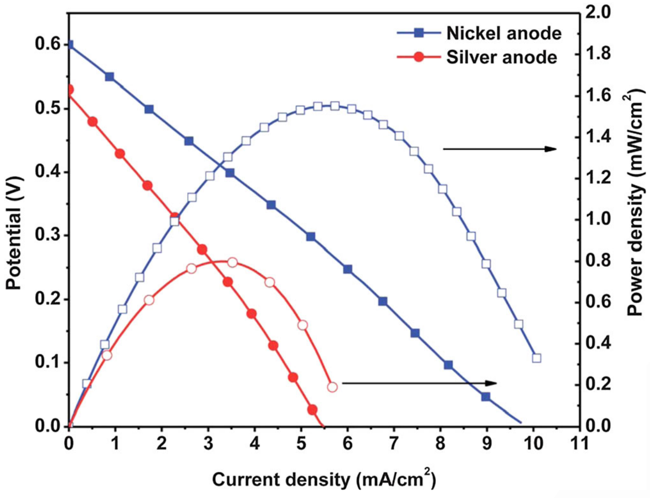


Figure 7. *I–V* and *I–P* curves of a one-compartment H_2O_2 fuel cell with nickel and silver anodes and unsupported Prussian blue coated on carbon paper as the cathode. Performance tests were performed under acidic conditions by using 0.10 м HCl and 0.50 м H_2O_2.[41]

An OCP of 0.60 V and a maximum power density of 1.55 mW cm^{-2} were obtained to maintain stable long-term operation in acidic media (Figure 7).[41]

A higher OCP of 0.8 V for a H_2O_2 fuel cell with the one-compartment structure was obtained by using the polynuclear cyanide complex $Fe^{III}_3[Co^{III}(CN)_6]_2$ and Ni mesh as the cathode and anode, respectively, under acidic conditions at pH 1 (Figure 8).[42] The maximum power density of the fuel cell was 1.0 mW cm^{-2}.[42] The presence of nitrogen-bound Fe^{2+} ions in the cathode was found to be important for the higher performance of the one-compartment H_2O_2 fuel cell.[66] The stability of the H_2O_2 fuel cell was improved by replacing the carbon cloth electrode with a carbon-paste electrode containing 25 wt % $Fe^{III}_3[Co^{III}(CN)_6]_2$. Severe deactivation of the cell performance resulting from detachment of $Fe^{III}_3[Co^{III}(CN)_6]_2$ from the carbon cloth was suppressed.[42] After 50 cycles, only a subtle change was observed in the OCP, and more than 80 % of the initial maximum power density was maintained ■■ok? ■■(Figure 8 b).[42]

The maximum power density of a H_2O_2 fuel cell was improved by employing a pyrazine-bridged $Fe[M^C(CN)_4]$ complex ($M^C = Pt^{2+}$ and Pd^{2+}) with a 3D porous structure as the as the cathode and a nickel mesh as the anode operating in 0.30 м H_2O_2 at pH 1.0 (Figure 9).[44] The power density of the H_2O_2 fuel cell with pyrazine-bridged $Fe[Pt(CN)_4]$ exceeded 4 mW cm^{-2}.[44] In contrast, H_2O_2 fuel cells with pyrazine-bridged $M^N[Pt(CN)_4]$ ($M^N = Co^{2+}$ and Mn^{2+}) as the cathodes showed power densities lower than 0.01 mW cm^{-2}, which suggests that Fe^{2+} ions play a crucial role and that the Pt^{2+} ions are not important for achieving a high power density.[44]

The OCP and power density of the H_2O_2 fuel cell with heat-treated $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ at 60 °C were much improved by adding Sc^{3+} ions into the aqueous H_2O_2 fuel at concentrations of 50 mм or higher. The OCP value increased in proportion to the concentration of Sc^{3+} to reach a constant value of (0.81 ± 0.01) V (Figure 10).[43] Additionally, the maximum power density exceeded (9.9 ± 0.13) mW cm^{-2} by increasing the concentration of Sc^{3+} ions to 120 mм (Figure 10). This value is larger than the value [(7.5 ± 0.05) mW cm^{-2}] obtained with nitric acid (pH 1.0).[43]

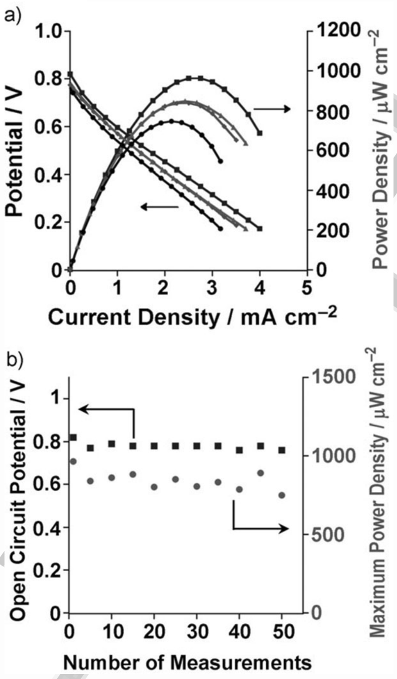


Figure 8. a) *I–V* and *I–P* curves of a one-compartment H_2O_2 fuel cell with a Ni anode and a carbon-paste electrode that was modified with $Fe_3[Co^{III}(CN)_6]_2$ after the 1st (■), 5th (◆), 25th (▲), and 50th cycles (●). Performance tests were performed in an aqueous solution of $HClO_4$ (pH 1) that contained H_2O_2 (0.30 м) and NaCl (1.0 м). Currents and powers were normalized by the geometric surface area of the electrode. b) Changes in the open-circuit potential (■) and power density (●) after repeated measurements of the H_2O_2 fuel cell.[42]

The effect of other Lewis acids upon the performance of H_2O_2 fuel cells was also examined. The performance was improved by the addition of trivalent Yb^{3+} and Y^{3+} ions (100 mм); however, the obtained OCPs and power densities remained at low levels, < 0.5 V and < 1.1 mW cm^{-2}.[43] The most effective divalent ion was Ca^{2+}; however, the OCP and power density for the H_2O_2 fuel cell with the use of an aqueous H_2O_2 fuel containing Ca^{2+} ions were as low as (0.47 ± 0.02) V and (0.47 ± 0.05) mW cm^{-2}, respectively. Thus, the strongest Lewis acid among the metal ions, that is, Sc^{3+} ions,[76–78] acted as the most effective additive for improving the performance of the H_2O_2 fuel cell in terms of both OCP and power density.[43] In addition, H_2O_2 decomposition in the reaction solution was efficiently avoided by the addition of Sc^{3+} ions, which led to high power densities and durability,[43] because Sc^{3+} ions have been reported to bind with H_2O_2 to stabilize it.[79] Only a small decrease in the output potential (40 mV) was observed under operation for 90 min by using aqueous H_2O_2 containing 100 mм Sc^{3+} ions as the fuel, whereas the output potential decreased to 0 V within 5 min without the Sc^{3+} ions.[43]

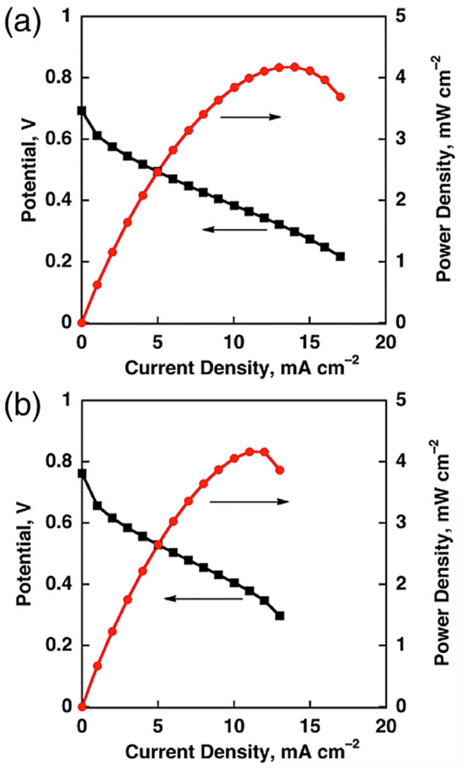


Figure 9. a) *I–V* (■) and *I–P* (●) curves of a one-compartment H_2O_2 fuel cell with a nickel anode and a carbon-cloth electrode modified with a pyrazine-bridged Fe[M^C(CN)$_4$] complex [M^C = Pt^{2+} (a) and Pd^{2+} (b)]. Performance tests were conducted in an aqueous solution of $HClO_4$ (pH 1) that contained H_2O_2 (0.30 M) and NaCl (1.0 M). Currents and powers were normalized by the geometric surface area of the electrode.[44]

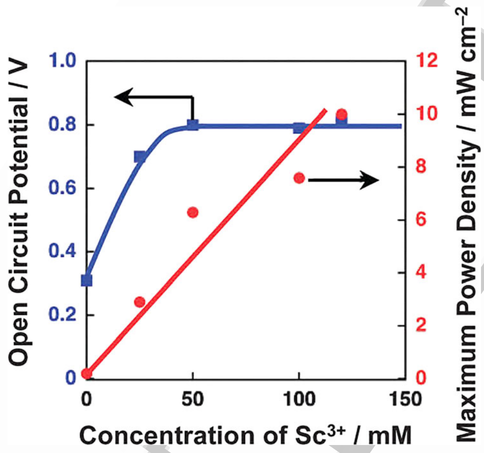


Figure 10. Plots of the open-circuit potentials and maximum power densities versus concentrations of Sc(NO$_3$)$_3$ for a one-compartment H_2O_2 fuel cell with a Ni anode and a carbon cloth electrode modified with [Fe^{II}(H$_2$O)$_2$]$_3$[Co^{III}(CN)$_6$]$_2$ in an aqueous solution containing 0.30 M H_2O_2 and Sc(NO$_3$)$_3$.[43]

3. Production of Hydrogen Peroxide from Water and Oxygen as a Solar Fuel

The generation of H_2O_2 by the photoreduction of O_2 is an interesting approach, because photoreduction of O_2 requires less energy than H_2 generation. On the one hand, the redox potential of $2H^+ + 2e^- = H_2$ is 0 V versus NHE; on the other hand, that of $O_2 + 2H^+ + 2e^- = H_2O_2$ is 0.68 V versus NHE, which suggests that a wide variety of materials can be used as an electron source. For example, oxalate is used as an electron source for efficient photocatalytic H_2O_2 production. However, utilization of water as an electron source is still a challenge.

H_2O_2 was produced by electrocatalytic O_2 reduction by employing a two-compartment cell connected to an agar salt bridge.[39] Glassy carbon electrodes modified with the cobalt porphyrins shown in Figure 11 were used as electrocatalysts, because cobalt porphyrins are well known to act as selective catalysts for the two-electron reduction of O_2 to produce H_2O_2.[79–89] Among the Co porphyrins evaluated, [Co(TCPP)] (■■TCPP = please define■■) showed the highest onset potential of 0.3 V for catalytic O_2 reduction. On the basis of these results, [Co(TCPP)] and Pt wire electrodes were connected to a conventional Si photovoltaic solar cell that generated electrical power of 0.5 V at 2.5 mA.[39] After running for 11 h, the amount of H_2O_2 produced reached 1.46×10^{-5} mol.[39] H_2O_2 generation was observed by the reduction of O_2 by using a conventional photovoltaic solar cell,[39] although it is still necessary to improve the electrocatalytic behavior and the structures of the cell and electrode for better performance.

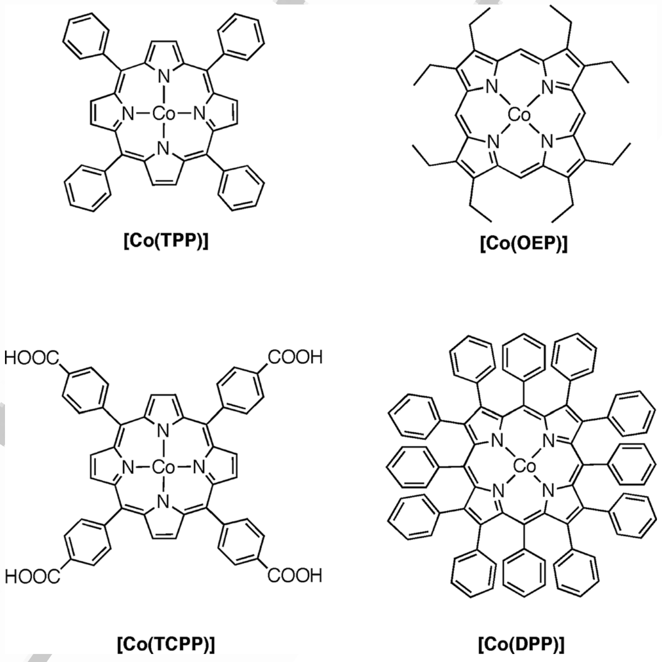
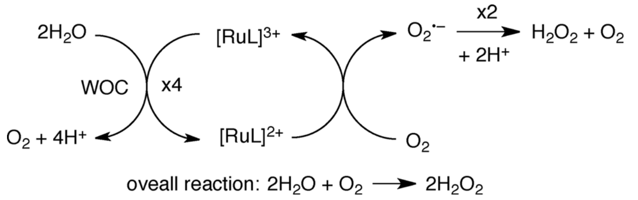


Figure 11. Structures of Co porphyrin catalysts for two-electron reduction of O_2.[39]

It has been shown that H_2O_2 can be produced by combining photoinduced electron transfer from Ru^{II} complexes ([Ru^{II}L]$^{2+}$) to O_2 and catalytic water oxidation by [Ru^{III}L]$^{3+}$ with a water oxidation catalyst (WOC), as shown in Scheme 1.[90]

Photoinduced electron transfer from the excited state of [Ru^{II}L]$^{2+}$ to O_2 produces [Ru^{III}L]$^{3+}$ and $O_2^{\cdot -}$, the latter of which is protonated in the presence of acids to produce $HO_2^{\cdot}$, and



Scheme 1.

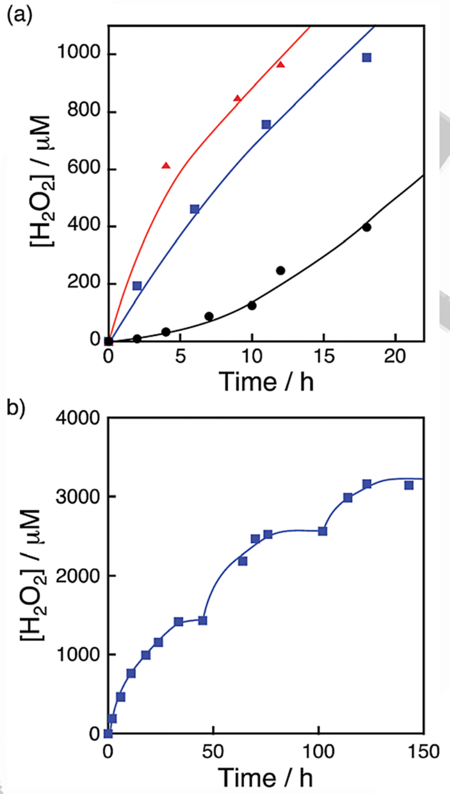


Figure 12. a) Time course of H_2O_2 production under visible-light irradiation ($\lambda > 420$ nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (200 μM) in the presence of $Sc(NO_3)_3$ (100 mM) and $NiFe_2O_4$ (0.17 $g\,L^{-1}$) with diameters of 1300 nm (●), 120 nm (■), and 91 nm (▲) in O_2-saturated H_2O (3.0 mL, $[O_2] = 1.2$ mM). b) Time course of H_2O_2 production in the presence of $NiFe_2O_4$ (0.17 $g\,L^{-1}$) and $Sc(NO_3)_3$ (100 mM) under visible-light irradiation ($\lambda > 420$ nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (200 μM) in O_2-saturated H_2O (3.0 mL, $[O_2] = 1.2$ mM). $[Ru^{II}(Me_2phen)_3]^{2+}$ was added twice to the reaction suspension after 50 and 100 h of photoirradiation. The amount of $[Ru^{II}(Me_2phen)_3]^{2+}$ added each time at 50 and 100 h to the reaction suspension was calculated in terms of the concentration increase of 200 μM.[106]

the disproportionation of $HO_2^{\cdot}$ yields H_2O_2 and O_2.[90,91] Various metal complexes and metal nanoparticles are known to catalyze water oxidation by $[Ru^{III}L]^{3+}$ to produce O_2.[92–103] Thus, the overall reaction is the photocatalytic oxidation of H_2O by O_2 to produce H_2O_2, in which photocatalytic two-electron reduction of O_2 and the catalytic four-electron oxidation of H_2O proceed.[83] Upon using $[Ru^{II}(Me_2phen)_3]^{2+}$ ($Me_2phen = $ 4,7-dimethyl-1,10-phenanthroline) and $[Co^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl; bpy = 2,2′-bipyridine) as the photocatalyst and WOC, respectively, in the presence of $Sc(NO_3)_3$ in water, the optimized quantum yield of the photocatalytic production of H_2O_2 at $\lambda = 450$ nm was determined to be 37%.[90] The conversion efficiency from solar energy to chemical energy was determined to be 0.25%.[90] Photocatalytic H_2O_2 production proceeded through electron transfer from photoexcited $[Ru^{II}(Me_2phen)_3]^{2+}$ to O_2 to produce $[Ru^{III}(Me_2phen)_3]^{3+}$ and $O_2^{\cdot-}$ binding to Sc^{3+}.[90] The disproportionation of $O_2^{\cdot-}$–Sc^{3+} in water yielded H_2O_2, whereas 4 equivalents of $[Ru^{III}(Me_2phen)_3]^{3+}$ oxidized H_2O to O_2 in the presence of the WOC.[90]

Graphitic carbon nitride with electron-deficient aromatic diimide units (g-C_3N_4/PDI; PDI = pyromellitic diimide) was reported to work as a photocatalyst for H_2O_2 production from H_2O and O_2.[104] However, the amount of H_2O_2 formed by photoirradiation for 48 h was only 30 μmol.[104]

The production of H_2O_2 from H_2O and O_2 as a solar fuel was also performed by using $NiFe_2O_4$ nanoparticles composed of earth-abundant metals as a WOC[105] in the presence of $[Ru^{II}(Me_2phen)_3]^{2+}$ and $Sc(NO_3)_3$ under visible-light irradiation ($\lambda > 420$ nm).[106] The $NiFe_2O_4$ catalyst was reused after H_2O_2 production ceased due to the decomposition of the photocatalyst by repeated addition of an aqueous solution of $[Ru^{II}(Me_2phen)_3]^{2+}$ to the reaction suspension. The concentration of H_2O_2 after repeated reactions reached as high as 3.3 mM, which is indicative of the high stability of the nanoparticles as a WOC (Figure 12b).[106] The initial rates of H_2O_2 production were increased 22- and 33-fold by employing smaller $NiFe_2O_4$ nanoparticles with diameters of 120 and 91 nm, respectively, relative to the initial rate of H_2O_2 production by using large $NiFe_2O_4$, with a diameter of 1300 nm (Figure 12a).[106] This enhanced reactivity resulted from the high specific surface area of the smaller catalyst.[106]

Various heteropolynuclear cyanide metal complexes containing different metal ions, $Co_3[Fe(CN)_6]_2$, $Co_3[Co(CN)_6]_2$, $Cu_3[Co(CN)_6]_2$, $Co[Ni(CN)_4]$, $Fe_3[Cr(CN)_6]_2$, $Mn_3[Fe(CN)_6]_2$, $Co_3[Mn(CN)_6]_2$, $Co_3[Fe(CN)_6]_2$, $Co[Pd(CN)_4]$, and $Co[Pt(CN)_4]$, were also used for water oxidation in the photocatalytic production of H_2O_2 from H_2O and O_2 in an aqueous solution containing $\{[Ru^{II}(Me_2phen)]_3\}^{2+}$ and $Sc(NO_3)_3$ under visible-light irradiation with a xenon lamp by using a UV light cut filter ($\lambda > 420$ nm).[107] Among the various heteropolynuclear cyanide complexes, the highest catalytic reactivity was obtained with $Fe_3[Co(CN)_6]_2$.[107] The catalytic reactivity was further enhanced by using the heteropolynuclear cyanide complexes $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ ($x = 0$, 0.10, 0.50, 0.75, 0.90, and 1) shown in Figure 13.

The catalytic activity was maximized if the Fe/Co ratio in the (Fe_xCo_{1-x}) moiety of $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ was 0.75.[107] WOCs with a larger Fe ratio would have more active sites for water oxidation, whereas a complex with a smaller Fe ratio would stabilize the high-valent metal ions generated during the photocatalytic reaction.[107] The optimized ratio of Fe in $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ ($x = 0.75$) was obtained by the balance of the two opposite effects of Fe on the water oxidation reaction.[107]

If water oxidation and O_2 reduction were performed in a one-compartment cell as described above, the oxidation of H_2O_2 inevitably competed with water oxidation in the presence

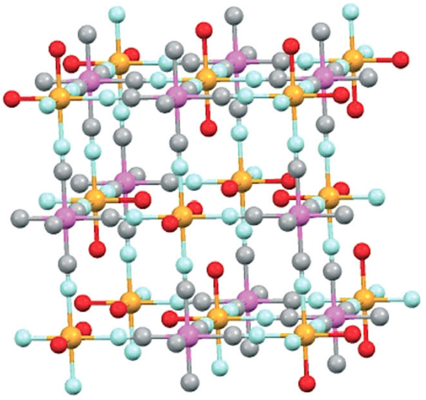


Figure 13. A schematic drawing of $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$, for which $x = 0$, 0.10, 0.50, 0.75, 0.90, and 1. Ions are color coded: N-bound Co^{II} and Fe^{II} (orange), C-bound Co^{III} (pink), C (gray), N (blue), and O (red).[107]

of a WOC to prevent the production of H_2O_2 at higher concentrations. Thus, the photocatalytic production of H_2O_2 from H_2O and O_2 was performed by using a two-compartment cell by employing a semiconductor photocatalyst anode in one cell and a carbon mesh cathode in an O_2-saturated aqueous solution containing Ru complexes and $Sc(NO_3)_3$ in the other cell to achieve higher concentrations of H_2O_2 than that obtained with a one-compartment cell.[108] A schematic drawing of the two-compartment cell is depicted in Figure 14, for which WO_3 or $BiVO_4$ was used as the anode[109,110] for the photooxidation of water and a carbon mesh cathode was employed for photoreduction of O_2 by Ru complexes.[108] The two compartments were separated by a Nafion membrane.[108] Upon using $[Ru^{II}\{(MeO)_2bpy\}_3]^{2+}$ [$(MeO)_2bpy = 4,4'$-dimethoxy-2,2′-bipyridine] as the catalyst for the two-electron photoreduction of O_2 in the presence of $Sc(NO_3)_3$ (100 mм) in an O_2-saturated aqueous solution at the carbon mesh cathode and the $BiVO_4$ photoanode, the best performance was obtained in terms of the H_2O_2 yield and reaction rate, as shown in Figure 15.[108]

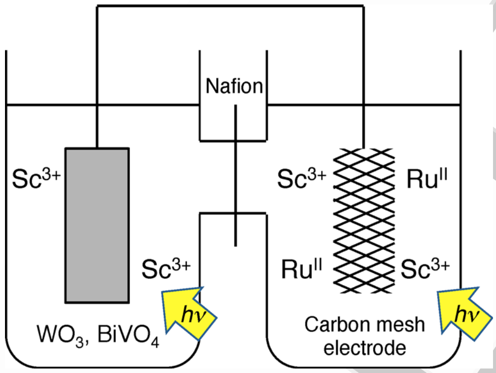


Figure 14. Schematic drawing of a two-compartment cell for the photocatalytic production of H_2O_2 from H_2O and O_2 under visible-light irradiation.[108]

The photocatalytic production of H_2O_2 from H_2O and O_2 in a two-compartment cell is shown in Scheme 2.[108] Electron transfer from photogenerated $[Ru^{II}\{(MeO)_2bpy\}_3]^{2+*}$ to O_2 occurs to produce $[Ru^{III}\{(MeO)_2bpy\}_3]^{3+}$ and $O_2^{\cdot-}$. Strong binding of Sc^{3+} to $O_2^{\cdot-}$ to give a $O_2^{\cdot-}$–Sc^{3+} complex prohibits back electron transfer from the $O_2^{\cdot-}$–Sc^{3+} complex to $[Ru^{III}\{(MeO)_2bpy\}_3]^{3+}$.[111,112] Disproportionation of the $O_2^{\cdot-}$–Sc^{3+} complex provides H_2O_2 in the presence of H^+. On the other hand, $BiVO_4$ catalyzes the photooxidation of water to O_2 by using the strong oxidation ability of the photogenerated holes. Reduction of $[Ru^{III}\{(MeO)_2bpy\}_3]^{3+}$ to regenerate $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ proceeds by using the photoexcited electrons in the conduction band of $BiVO_4$.

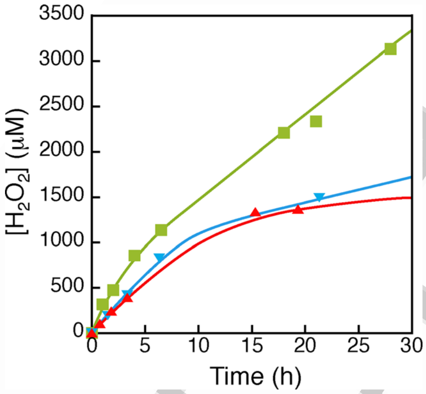
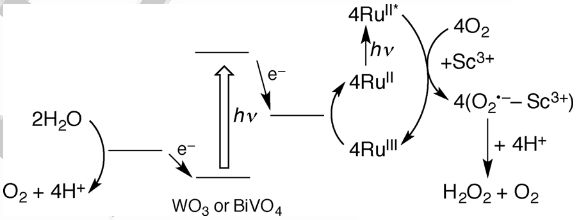


Figure 15. Production of H_2O_2 under photoirradiation of a two-compartment cell composed of a semiconductor photocatalyst anode [$BiVO_4$ (green and blue lines) or WO_3 (red line)] in one cell and a carbon cloth cathode in the presence of $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (160 μм, black line) or $[Ru^{II}(Me_2phen)_3]^{2+}$ (160 μм, blue and green lines) in the other cell. Both cells were filled with aqueous solution of $Sc(NO_3)_3$ (100 mм, 8.0 mL for each cell). A Xe lamp ($\lambda > 420$ nm) and a solar simulator were used to irradiate the Ru complex and semiconductor photocatalyst, respectively.[108]



Scheme 2.

4. Production and use of Hydrogen Peroxide as a Solar Fuel in Seawater

Pure water is a limited resource; thus, utilization of earth-abundant seawater instead of pure water is desirable for any practical applications of H_2O_2 as a solar fuel. Efficient photocatalytic production of H_2O_2 from seawater and O_2 in the air was performed in a two-compartment photoelectrochemical cell. The cell used mesoporous WO_3 supported on a fluorine-doped tin oxide glass substrate (m-WO_3/FTO) as a photocatalyst for water oxidation and a cobalt chlorin complex supported on a carbon paper [Co^{II}(Ch)/CP] for the selective two-electron reduction of O_2, as shown in Figure 16.[112] Photoirradiation of m-WO_3/FTO with a solar simulator (1 sun, AM1.5G) in the anode cell result-

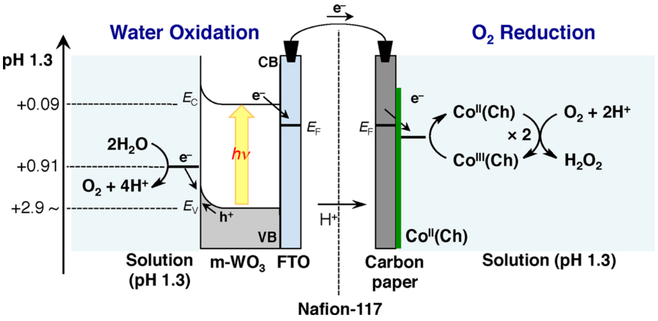


Figure 16. Photocatalytic production of H_2O_2 from water and O_2 by using a m-WO_3/FTO photoanode and a Co^{II}(Ch)/CP cathode in water or seawater under simulated 1 sun (AM1.5G) illumination.[112]

ed in efficient generation of H_2O_2 in the cathode cell of the two-compartment photoelectrochemical configuration without any external bias potential. The time course of the concentration of H_2O_2 produced by the photocatalytic reaction is shown in Figure 17.[112] A negligible amount of H_2O_2 was formed in the absence of Co^{II}(Ch) on the carbon paper electrode, which suggested that Co^{II}(Ch) efficiently catalyzed the selective two-electron reduction of O_2 to yield H_2O_2[83,112] before charge recombination of the photoexcited electrons in the conduction band and the holes■■ok?■■ generated in the valence band of WO_3. After illumination for 24 h, the amount of H_2O_2 produced in seawater reached about 48 mM, which was high enough to operate a H_2O_2 fuel cell (see below).[112] However, an extreme deceleration in the production of H_2O_2 was observed if pure water was used instead of seawater for the photocatalytic H_2O_2 production system.

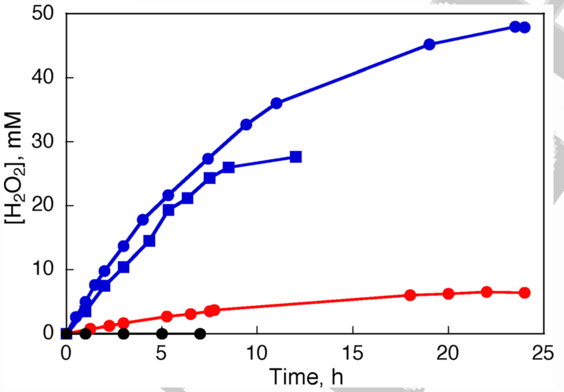


Figure 17. Time course of H_2O_2 production with a m-WO_3/FTO photoanode and Co^{II}(Ch)/CP cathode in pH 1.3 water (●), in pH 1.3 seawater (●), and in an NaCl aqueous solution (pH 1.3) (■) under simulated 1 sun (AM1.5G) illumination. Time course of H_2O_2 production in the absence of Co^{II}(Ch) from carbon paper under simulated 1 sun (AM1.5G) illumination in pH 1.3 water is also shown (●).[112]

An enhancement in the photocatalytic activity was observed in an NaCl solution for the reaction system in which seawater was used, and the concentration of NaCl was the same as that in seawater■■ok?■■. The enhanced photocatalytic activity for water oxidation in the presence of NaCl was elucidated by the following Cl$^-$-mediated mechanism.[113–117] Upon photoexcitation of WO_3, Cl$^-$ oxidation by photogenerated holes resulted in the formation of chlorine (Cl_2), which occurred prior to the oxidation of water [Eq. (4)].[114] Cl_2 thus formed reacted with water to form HClO depending on the pH of the reaction solution [Eq. (5)].[115] Decomposition of HClO provided O_2 and Cl$^-$ under photoirradiation [Eq. (6)].[115] Thus, the water oxidation efficiently proceeded by using Cl$^-$ as a mediator [Eq. (7)]. The formation of HClO/Cl_2 was confirmed during the photocatalytic water oxidation in the presence of Cl$^-$.[112]

$$2\,Cl^- + 2\,h^+ \xrightarrow{h\nu} Cl_2 \tag{4}$$

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^- \tag{5}$$

$$2\,HClO \xrightarrow{h\nu} O_2 + 2\,H^+ + 2\,Cl^- \tag{6}$$

$$2\,H_2O + 4\,h^+ \xrightarrow{h\nu} O_2 + 4\,H^+ \tag{7}$$

The amount of O_2 evolved after photoirradiation for 1 h (12.7 μmol) in the anode cell containing seawater was more than three times larger than that in pure water (3.7 μmol). Thus, the enhancement in the photocatalytic production of H_2O_2 in seawater (Figure 17) resulted from the Cl$^-$-catalyzed photooxidation of water.[112]

A high solar energy conversion efficiency of 0.55 % was achieved in the photocatalytic production of H_2O_2 in seawater under photoirradiation with a solar simulator (1 sun, 1.5AM).[112] A higher solar energy conversion efficiency of 0.94 % was achieved if the illumination intensity was reduced to 0.1 sun. This efficiency exceeds that of swichgrass (0.2 %), which is regarded as a promising biomass crop for the production of biofuel,[117] and also exceeds the value for photocatalytic H_2O_2 production in a one-compartment cell (0.25 %).[90]

The chemical energy of H_2O_2 produced by the photocatalytic oxidation of seawater by the O_2 in the air was converted into electricity by using a one-compartment H_2O_2 fuel cell by employing a Fe$^{II}_3$[Co^{III}(CN)$_6$]$_2$-modified carbon cloth and a nickel mesh as the cathode and anode, respectively.[112] The reaction solution (seawater, pH 1.3) containing about 48 mM of H_2O_2 produced by the photocatalytic reaction was transferred into the H_2O_2 fuel cell. The cell exhibited an OCP of 0.78 V and a maximum power density of 1.6 mW cm^{-2} (Figure 18).[112] The energy conversion efficiency of the H_2O_2 fuel cell was determined to be around 50 % by measuring the output energy as electrical energy versus consumed chemical energy of H_2O_2; this value is comparable to the efficiency of a H_2 fuel cell.[112]

5. Conclusions

The most serious problem accompanied with the use of H_2 as an energy carrier has been solved by using a high-pressure tank with an extremely high strength, which was developed only recently. However, the tank cannot be incorporated into personal-based small electric devices such as cell phones. For this purpose, liquid or solid energy carriers storable in lightweight containers are necessary. These days, the capacity and

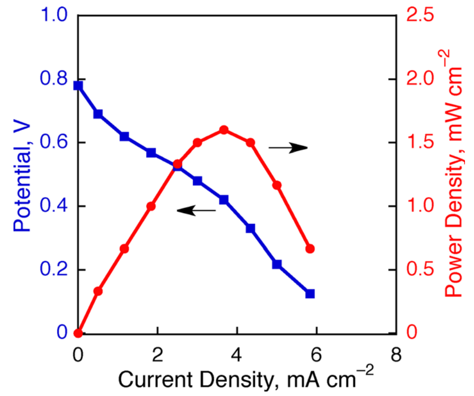


Figure 18. I–V (■) and I–P (●) curves of the one-compartment H_2O_2 fuel cell with a Ni mesh anode and $Fe^{II}_3[Co^{III}(CN)_6]_2$/carbon cloth cathode in the reaction solution containing H_2O_2 (47.9 mM) produced by photocatalytic reaction in seawater as shown in Figure 17 (●).[112]

durability of lithium-ion batteries have been much improved; however, high costs and limited resources remain critical issues. H_2O_2 can be an alternative sustainable and green fuel for personal-based electric items, because abundant oxygen, water, and sunlight are resources, and power generation is possible with a fuel cell with a simple one-compartment structure.■■paragraph ok?■■

As described above, the proof of concept has been demonstrated for the production of H_2O_2 from sweater and the O_2 in the air by using solar energy and its direct use on demand as a fuel in one-compartment H_2O_2 fuel cells. There are still many things left to improve the performance of one-compartment H_2O_2 fuel cells, including the development of better cathode and anode materials. One-compartment cells without any membranes and the use of seawater containing H_2O_2 are more advantageous than the production of gaseous H_2 and its use in H_2 fuel cells, because seawater is the most earth-abundant resource. The production of fuels by utilizing solar energy and the generation of electricity with the fuels in seawater are beneficial for practical applications. Further improvement in the photocatalytic activity for the production of H_2O_2 from seawater and O_2 together with more efficient one-compartment H_2O_2 fuel cells without membranes for use in personal-based sustainable energy-conversion systems are targets for the future.■■ok?■■

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Keywords: energy conversion · fuel cells · hydrogen peroxides · photocatalysis · solar fuels

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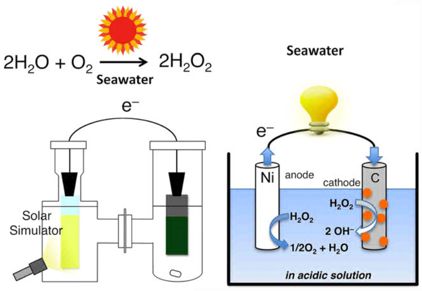
So much to sea: Hydrogen peroxide can be produced from seawater and dioxygen by using solar energy. This article provides a focused review of recent developments and future perspectives of H_2O_2 fuel cells without membranes, combined with H_2O_2 production from seawater and dioxygen in the air by utilizing solar energy.■■ok?■■



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