Hydrogen Peroxide as Solar Fuel

Shunichi Fukuzumi[a,b]

[a] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency, Suita, Osaka 565-0871, Japan*
[b] *Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea*

fukuzumi@chem.eng.osaka-u.ac.jp

Sustainable and clean energy resources are highly required in order to solve global energy and environmental issues. Extensive efforts have so far been devoted to develop an artificial version of photosynthesis for sustainable fuel production such as hydrogen from water [1,2]. The important advantage of hydrogen is that carbon dioxide is not produced when hydrogen is burned to produce only water. However, the storage of hydrogen has been a difficult issue, because hydrogen is a gas having a low volumetric energy density. On the other hand, hydrogen peroxide has merited significant attention, because hydrogen peroxide can oxidize various chemicals selectively to produce no waste chemicals but water [3,4]. Hydrogen peroxide can be an ideal energy carrier alternative to oil or hydrogen, because it can be used in a fuel cell leading to the generation of electricity [3-5]. Thus, a combination of hydrogen peroxide production by the electrocatalytic reduction of dioxygen in air with electrical power generated by a photovoltaic solar cell and power generation with a hydrogen peroxide fuel cell provides a sustainable solar fuel [5-7]. We report herein photocatalytic reduction of dioxygen to hydrogen peroxide as well as the electrocatalytic production together with hydrogen peroxide fuel cells in which hydrogen peroxide (H_2O_2) is used as a fuel.

In order to utilize H_2O_2 as an energy carrier, hydrogen peroxide should be produced by a convenient method without any special equipment. One such method is electroreduction of O_2 with a solar cell in an acidic aqueous solution under air [6]. The solar cell is a convenient power source usable anywhere during the sun-shiny days. H_2O_2 can be produced anywhere by plugging electrodes with an O_2 reduction catalyst into solar cells in an acidic solution. H_2O_2 production by the electrocatalytic reduction of O_2 under air with electrical power generated by a photovoltaic solar cell has been performed using Co-porphyrin compound, [6] because cobalt porphyrins act as efficient selective two-electron reduction of O_2.

Direct H_2O_2 fuel cells have number of merits as compared with other fuel cells: (1) H_2O_2 is liquid and soluble in water and thereby easy to store and carry: (2) H_2O_2 has higher standard reduction potential than O_2 (e.g., 1.776 V vs. SHE for H_2O_2 and 1.229 V vs. SHE for O_2 in acidic medium; (3) there is no need to use membranes, because H_2O_2 can act both oxidant and reductant [4]. Thus, fuel cells with H_2O_2 used as both oxidant and reductant can have much simpler cell structure (i.e., one compartment cell without membrane), theoretically providing higher power output than those with oxygen used as an oxidant. H_2O_2 fuel cells emit only oxygen after electrical power generation. The theoretical maximum of the output potential of the H_2O_2 fuel cell is 1.09, which is comparable to those of a hydrogen fuel cells (1.23 V) and a direct methanol fuel cell (1.21 V) [4].

A one-compartment H_2O_2 fuel cell using an iron phthalocyaninato complex can be operated under acidic conditions [7]. The choice of iron porphyrin and analogous compounds for H_2O_2 reduction is quite reasonable because in natural systems, the reduction of hydrogen peroxide is owing to hydroperoxidases, which contain iron(III)-porphyrins in their active sites. A one-compartment H_2O_2 fuel cell working in an acidic media was constructed with a glassy carbon electrode mounting iron phthalocyanine [Fe^{III}(Pc)Cl] as a cathode and Ni metal as an anode [7]. The cell performance was evaluated by dipping the anode and cathode in a buffer solution containing 300 mM H_2O_2. The open-circuit potential was 0.5 V, which is similar in level to that (0.6–0.9 V) of a H_2O_2 fuel cell operated with an acidic solution for a cathode and a basic solution for an anode and more than three times higher than that (0.15 V) of the one-compartment H_2O_2 fuel cell operated under basic conditions [7].

Prussian Blue, ferric ferrocyanide ($Fe_4^{III}[Fe^{II}(CN)_6]_3$)), has recently been employed for cathode side in a single-chamber membraneless H_2O_2 fuel cell to achieve an open circuit potential of 0.6 V with the maximum power density was 1.55 mW/cm^2 in acidic media (pH 1) [8]. We have employed metal substituted analogs of Prussian Blue ($Fe_3^{II}[M^{III}(CN)_6]_2$: M = Mn, Co) as a cathode of a one-compartment membraneless H_2O_2 fuel cell to achieve a higher open circuit potential (0.65 V) than Prussian Blue at pH 3.

The photocatalytic production of H_2O_2 from H_2O and O_2 will also be reported using a Ru complex as a photocatalyst and $Ir(OH)_3$ nanoparticles as a water oxidation catalyst. Thus, the combination of the photocatalytic H_2O_2 production from H_2O and O_2 using solar energy with the one-compartment H_2O_2 fuel cell provides on-site production of a solar fuel and the usage.

References

[1] (a) Fukuzumi, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2283. (b) Fukuzumi, S.; Ohkubo, K. *J. Mater. Chem.* **2012**, *22*, 4575.
[2] Fukuzumi, S.; Yamada, Y. *J. Mater. Chem*. **2012**, *22*, 24284.
[3] Disselkamp, R. S. *Int. J. Hydrogen Energy*, **2010**, *35*, 1049.
[4] Fukuzumi, S.; Yamada, Y.; Karlin, K. D. *Electrochim. Acta* **2012**, *82*, 493.
[5] Sanli, A. E.; Aytac, A. *Int. J. Hydrogen Energy* **2011**, *36*, 869.
[6] Yamada, Y.; Fukunishi, Y.; Yamazaki, S.; Fukuzumi, S. *Chem. Commun*. **2010**, 46, 7334.
[7] Yamada, Y.; Yoshida, S.; Honda, T.; Fukuzumi, S. *Energy Environ. Sci*. **2011**, *4*, 2822.
[8] Shaegh, A. A. M.; Nguyen, N.-T.; Ehteshami, S. M. M.; Chan, S. H. *Energy Environ. Sci*. **2012**, *5*, 8225.