

Hydrogen peroxide as sustainable fuel: electrocatalysts for production with a solar cell and decomposition with a fuel cell†

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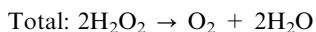
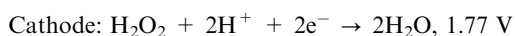
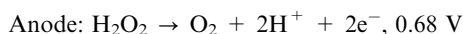
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Hydrogen peroxide was electrochemically produced by reducing oxygen in an aqueous solution with [Co(TCPP)] as a catalyst and photovoltaic solar cell operating at 0.5 V. Hydrogen peroxide thus produced is utilized as a fuel for a one-compartment fuel cell with Ag–Pb alloy nanoparticles as the cathode.

An oil-based society includes insistent problems owing to not only CO₂ but also harmful chemicals such as NO_x, SO_x and particulate matter in the emission gas from an internal-combustion engine. In order to attain really clean air, a hydrogen-based society has been pursued for several decades.¹ A critical problem of hydrogen as an alternative fuel is on its storage and portability.² The hydrogen-based society is really far from real before we develop a new compound, which can store hydrogen in high volumetric density and release it at an ambient condition for portable uses.

Hydrogen peroxide (H₂O₂) has attracted many process chemists, because H₂O₂ can oxidize various chemicals selectively to produce no waste chemicals but water.^{3,4} H₂O₂ can be an energy carrier alternative to oil or hydrogen, because H₂O₂ can be used in a fuel cell, in which the reactions occurring at anode and cathode are given as follows:^{5,6}



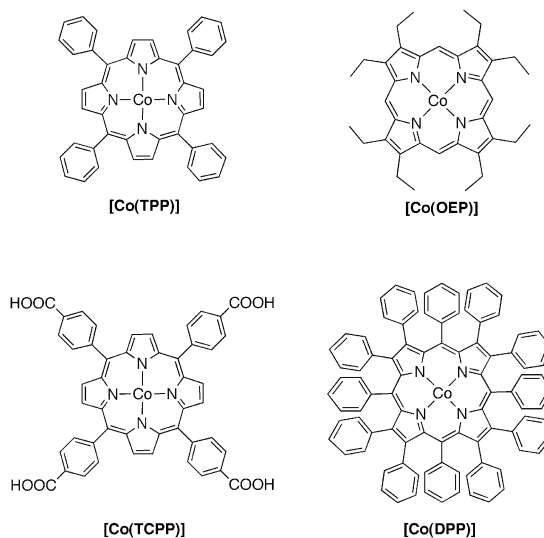
The maximum output potential theoretically achievable is 1.09 V, which is comparable to those of a hydrogen fuel cell (1.23 V) and a direct methanol fuel cell (1.21 V). However, the reported power density has yet to be by far sufficient.⁵

If we can produce H₂O₂ by the electrochemical reduction of O₂ abundant in air with a solar cell, and generate electrical power by an efficient H₂O₂ fuel cell, very ideal recyclable society would be realized because H₂O₂ is liquid at room temperature and the by-product after power generation are

oxygen and water. However, such a combination of production of H₂O₂ with a solar cell and decomposition with a fuel cell has yet to be reported.

We report herein a combination of H₂O₂ production by the electrocatalytic reduction of O₂ in air with electrical power generated by a photovoltaic solar cell and power generation with an H₂O₂ fuel cell. Cobalt porphyrins have been used as electrocatalysts for O₂ reduction to produce H₂O₂.^{7–12} The chemical structures of the Co porphyrins used are depicted in Scheme 1.¹³ In order to improve the performance of an H₂O₂ fuel cell, a cathode composed of Ag and Ag–Pb alloy nanoparticles was employed. Compared with an H₂O₂ fuel cell using an Ag plate as a cathode,⁵ the open circuit potential was improved with comparable current density, resulting in higher power density.

Electrocatalytic O₂ reduction was carried out by using an H-type cell with an agar salt bridge. The thermodynamic potential for the two-electron reduction of O₂ at a given pH is 0.65 V. Cobalt porphyrins in Scheme 1 were mounted on a glassy carbon electrode by a drop-casting method. The prepared electrode catalyst was dipped in hydrosulfuric acid, and Pt wire was put in the other side of the H-type cell. Electrocatalytic O₂ reduction current was recorded against voltage vs. saturated calomel electrode (SCE) as displayed in Fig. 1a. Oxygen reduction current was observed on all catalysts but [Co(DPP)]. Among the Co porphyrins, [Co(TCPP)] showed the highest onset potential of 0.3 V. The onset potential observed on [Co(TPP)] was as same as that of [Co(TCPP)]. [Co(OEP)] showed modest activity, the lower onset potential of 0.1 V, compared to former two Co porphyrins.



Scheme 1 Co porphyrin catalysts for oxygen reduction.¹³

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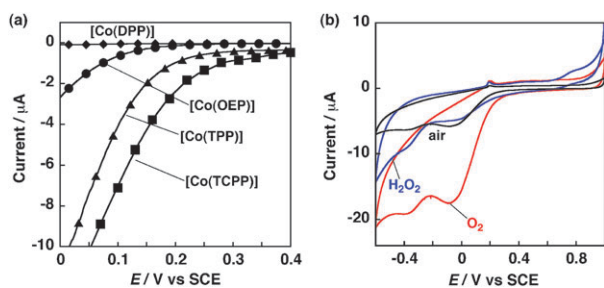


Fig. 1 (a) Electrocatalytic current at oxygen reduction. ♦: [Co(DPP)] ●: [Co(OEP)] ▲: [Co(TPP)] ■: [Co(TCPP)]. (b) CV of [Co(TCPP)] at scan rate = 20 mV s⁻¹ (black; under air, blue; 3 mM H₂O₂, red; with oxygen bubbling). The measurements were performed in 0.1 M hydro-sulfuric acid at 25 °C. To prevent contamination of the coordinating ion or ligands, ultrapure water was used in the experiments.

Fig. 1b compares CV curves of [Co(TCPP)] under three different conditions. When oxygen gas was passed through a solution during the CV measurements, two separated reduction peaks were observed around 0 V and -0.3 V (red). When the solution contained H₂O₂ (3 mM), a reduction peak appeared around -0.3 V predominantly (blue). Although another peak appeared around 0 V, the current level was comparable to that observed at the measurement under air (black). Thus, the first reduction peak that appeared around 0 V corresponds to two electron reduction of O₂. When the applied potential is controlled to around 0 V, H₂O₂ should be formed selectively.

H₂O₂ production by O₂ reduction with the Co porphyrins was performed at 0 V for 1 hour. The concentration of H₂O₂ was determined by the colorimetric titration with oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV).¹⁴ The highest amount of H₂O₂ of 3.4×10^{-8} mol was achieved at [Co(TCPP)]. The current efficiency for H₂O₂ production was nearly 100% under the present conditions.¹⁵

Based on these results, [Co(TCPP)] and Pt wire electrodes were connected to a conventional Si photovoltaic solar cell, which generates electrical power of 0.5 V at 2.5 mA (see ESI†). After 11 hours of running, the amount of H₂O₂ produced reached 1.46×10^{-5} mol. Although the catalytic behavior as well as cell and electrode structures should be improved more for better performance, H₂O₂ was successfully achieved by the reduction of molecular O₂ with a conventional photovoltaic solar cell.

For construction of a one-compartment H₂O₂ fuel cell, Ag–Pb alloy nanoparticles were employed,¹⁶ because higher specific surface area is expected for Ag nanoparticles as compared to an Ag plate,⁵ and also the addition of a foreign element to Ag metal could improve the H₂O₂ reduction activity of Ag. Fig. 2 shows the TEM images of Ag and Ag–Pb alloy nanoparticles. The shape of nanoparticles was nearly spherical independent of their compositions. The average diameter of Ag nanoparticles was 41 nm with the size distributed from 13 nm to 75 nm. Similar average diameters of Ag–Pb alloy were observed, 50 nm (Ag : Pb = 9 : 1), 34 nm (7 : 3) and 39 nm (6 : 4) respectively. The size distributions of alloy particles were 26 nm to 88 nm (9 : 1), 15 to 73 nm (7 : 3) and 14 to 77 nm (6 : 4).

Powder X-ray diffraction analysis of Ag–Pb alloy nanoparticles in Fig. 3 exhibited new peaks assigned to the formation

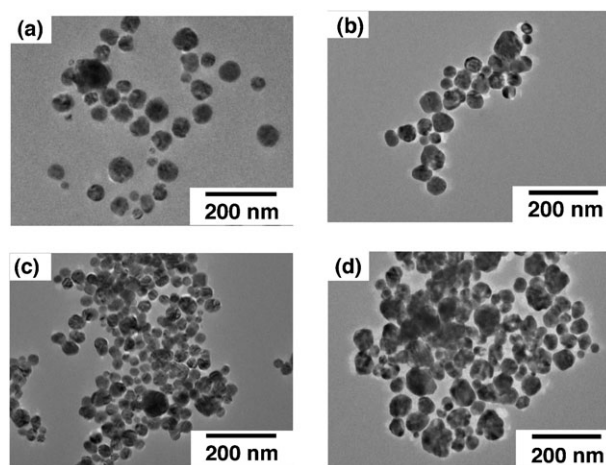


Fig. 2 TEM images of Ag or Ag–Pb alloy nanoparticles. (a) Ag nanoparticles, (b) Ag–Pb alloy (Ag : Pb = 9 : 1), (c) Ag–Pb alloy (7 : 3) and (d) Ag–Pb alloy (Ag : Pb = 6 : 4).

of Ag–Pb alloy with the peaks assigned to Ag which is the core part of the nanoparticles. In the range from 30° to 50° in 2θ, Ag nanoparticles provided two peaks at 38.1° and 44.2° assigned to Ag(111) and Ag(200), respectively (Fig. 3a). Ag–Pb alloy catalysts provided additional two peaks around 41.5° and 35.2° as shown in Fig. 3b and c. The diffraction pattern of Pb metal displayed in Fig. 3d showed no peaks at 41.5° and 35.2°. These diffraction peaks were not assigned to AgO and PbO. Thus, the two peaks appeared were assigned to Ag–Pb alloy. The peaks were almost diminished for the alloy of Ag : Pb = 6 : 4, indicating less alloy formation at high Pb concentration. The Ag–Pb alloy nanoparticles were prepared by the successive reduction process: Ag reduction and Pb reduction in the presence of Ag seeds. Ag–Pb alloy was formed on the surface of nanoparticles.

Fig. 4 shows the *I*–*V* and *I*–*P* curves of the constructed fuel cells with a cathode of a glassy carbon electrode mounting Ag nanoparticles or Ag–Pb alloy nanoparticles and an anode of Au electrode. The current density was normalized by the

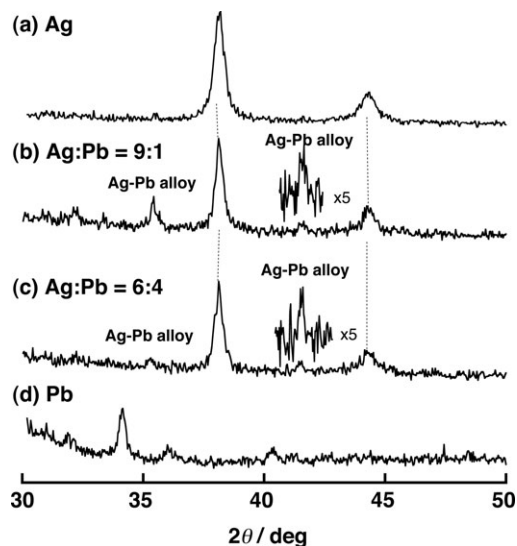


Fig. 3 X-Ray diffraction patterns of nanoparticles composed of (a) Ag, (b) Ag–Pb alloy (9 : 1), (c) Ag–Pb alloy (6 : 4) and (d) Pb.

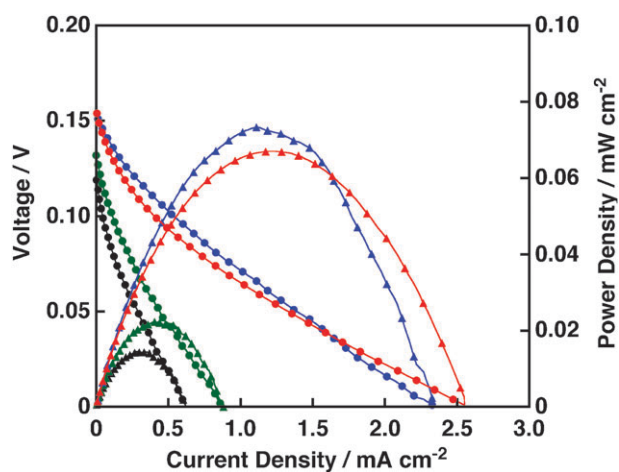


Fig. 4 I - V and I - P curves of a one-compartment H_2O_2 fuel cell with Ag or Ag-Pb alloy cathode. (Au anode, 1N NaOH, 300 mM H_2O_2 . Black: Ag, green: Ag : Pb = 6 : 4, red: Ag : Pb = 7 : 3 and blue: Ag : Pb = 9 : 1).

geometric surface area of the glassy carbon electrode. The plot in black is the results obtained by Ag nanoparticles without Pb addition. The higher power density, open circuit voltage and short-circuit current were obtained when Ag-Pb alloys were used as cathodes (Ag : Pb = 9 : 1 (blue), 7 : 3 (red), 6 : 4 (green) in Fig. 4). The higher values were achieved on Ag-Pb alloys with the ratios of 9 : 1 and 7 : 3. The open-circuit potential of ca. 150 mV far from the theoretical potential (1.09 V) is ascribed to the overpotentials observed at the anode and the cathode. The CV of H_2O_2 over the Ag-Pb alloy exhibited the onset potential (ca. -0.08 V vs. SCE) for the H_2O_2 reduction far from the thermodynamic value (0.70 V) at the given pH (Fig. S1 in ESI†).

In the present approach, H_2O_2 is produced in acidic media and power generation by the direct H_2O_2 fuel cell in basic media. In order to achieve a more efficient system, the media conditions should be the same or similar for H_2O_2 production and power generation. For H_2O_2 production in neutral to basic conditions, O_2 reduction over a Pd-loaded catalyst under mild conditions has been reported.¹⁷ For H_2O_2 reduction in acidic conditions, some metal complexes such as Prussian Blue have been reported to show a certain activity although their activity is not sufficient.¹⁸ In the next step it is required to improve either or both the catalysts for realizing a H_2O_2 -based society.¹⁹

In conclusion, we have demonstrated the potential use of H_2O_2 as an energy carrier alternative to oil or hydrogen. H_2O_2 was produced by the electrocatalytic reduction of O_2 in air using a [Co(TCPP)]-modified electrode with the electric power generated by a photovoltaic solar cell. H_2O_2 thus produced was used as a fuel of a direct fuel cell, which has a very simple one-compartment structure, to generate electric power. Although the power density of an H_2O_2 fuel cell still needs to be improved, combination of H_2O_2 production with a solar cell and power generation with an H_2O_2 fuel cell provides an ideal sustainable energy conversion and preservation system.

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- Abbreviations of porphyrin ligands; TCPP: 5,10,15,20-tetraphenyl porphinate, OEP: 2,3,7,8,12,13,17,18-octaethyl porphinate, TCPP: 5,10,15,20-tetra(4-carboxylphenyl) porphinate, DPP: 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphinate.
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- Ag-Pb nanoparticles were prepared by reducing Pb ion with formalin in the presence of Ag nanoparticles seeds and the molar ratios of Ag to Pb were varied among 6 : 4, 7 : 3 and 9 : 1 (see ESI† for preparations and characterization).
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