

Neutral H₂O₂ Synthesis by Electrolysis of Water and O₂

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Growth in demand for hydrogen peroxide is expected due to its wide utilization as a disinfectant and as an oxidant for chemical processes, because it generates only water as byproduct. However, the cost of H₂O₂ production by multi-step anthraquinone-based processes and transport restrictions^[1] are major factors in meeting this demand.^[2] Therefore, an on-site production method for H₂O₂, for example, direct synthesis of H₂O₂ from H₂ and O₂ with Pd and Au/Pd catalysts in acid or methanol solutions have been studied.^[3–8] However, a gaseous mixture of H₂ and O₂ has the possibility of exploding, so a safer procedure is essential.

We previously reported an H₂/O₂ fuel-cell system for direct formation of H₂O₂.^[9,10] The fuel cell can be safely operated for H₂O₂ production because H₂ and O₂ are separated by the electrolytic membrane. Palladium membrane catalysts can be also used for safe synthesis of H₂O₂, but the formation rate and concentration of H₂O₂ need to be improved.^[11,12] We recently reported an improved fuel-cell system and new electrocatalysts for H₂O₂ synthesis. In the case of 2 N NaOH as electrolyte, 7 wt % H₂O₂ was synthesized at the mixed-carbon cathode with 93 % current efficiency (CE).^[13] With 1.2 N H₂SO₄ as electrolyte, 3.5 wt % H₂O₂ was synthesized at a cathode derivatized with Mn porphyrin with 45 % CE.^[14] The H₂O₂/NaOH solution is useful for pulp bleaching, and the H₂O₂/H₂SO₄ solution can be used for oxidation in organic synthesis. However, neutral aqueous H₂O₂ solution without salts is the most useful and flexible form.

If we use a solid polymer electrolyte (SPE), except for soluble supporting electrolytes, electrolyte-free product solutions can be obtained. This SPE electrolysis method has been used for several kinds of electrochemical syntheses^[15] and for H₂ generation (water decomposition). If we can find a suitable electrocatalyst (cathode) and reaction conditions, formation of neutral H₂O₂ can be expected.

An SPE electrolysis cell unit was prepared from a cathode, an anode, and nafion-H membrane. This cell unit was fixed in a two-compartment glass cell, as shown in Figure 1. Deionized water was infused into both compartments, and O₂ and Ar were introduced into the cathode and anode compartments, respectively. Given a suitable cathode, reduction of O₂ to H₂O₂ (O₂ + 2H⁺ + 2e[−] → H₂O₂) and accumulation of H₂O₂ in the deionized water are expected.

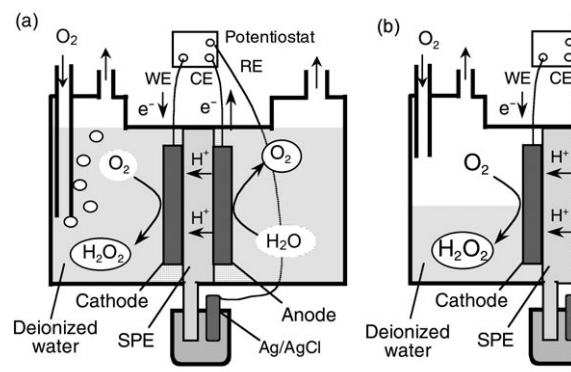


Figure 1. Diagram of a) standard SPE method and b) exposure SPE (Exp-SPE) method. WE = working electrode, CE = counter-electrode, RE = reference electrode.

Other possible reactions are formation of H₂O and H₂ at the cathode. In addition, water is decomposed at the anode.

We selected a mixed-carbon cathode (2 cm²) prepared from activated carbon (AC), vapor-grown carbon fiber (VGCF), and teflon powder by the hot-press method.^[6] This [AC + VGCF] cathode is effective for formation of H₂O₂ by the fuel-cell method with an H₂SO₄ electrolyte.^[10] The anode was prepared from 45 wt % Pt supported on carbon black (Pt/CB), VGCF, and teflon powder. The electrodes were attached on each side of a nafion-117 membrane (DuPont) under 5 MPa at 413 K. Yields of H₂O₂ were determined by chemical titration with aqueous KMnO₄/H₂SO₄ solutions. The CE of H₂O₂ formation was calculated as a two-electron reaction against the quantity of charge passed.

First, we filled the cathode and anode compartments (30 mL) with deionized water and applied a cathode potential of −0.5 V (vs. Ag/AgCl) for 2 h. A very low H₂O₂ yield of 0.8 μmol was detected with a low CE of 1.4 %. The majority of the electrolysis current was consumed in H₂ evolution. The electrochemical reduction rate of O₂ was much lower than that of H⁺ in H₂ formation. The H₂O₂ yield was considerably lower than that of the fuel-cell method using H₂SO₄ solutions.^[10]

The acidity of nafion-H is as high as that of H₂SO₄ solution; therefore, its pH conditions on the cathode may be similar and should not be a major reason for formation of less H₂O₂ in the SPE electrolysis method (Figure 1 a). In the fuel-cell system, the cathode was exposed to gaseous O₂.^[10,13,14] The concentration of gaseous O₂ (1 atm) of 41 mM at 298 K is much higher than that in an aqueous electrolyte (ca. 1 mM).

On the basis of the above considerations, we exposed half of the [AC + VGCF] cathode to an O₂ stream by decreasing the amount of deionized water to 15 mL, to give what we call the exposure SPE (Exp-SPE) method (Figure 1 b). We found a dramatic improvement in H₂O₂ formation by applying the

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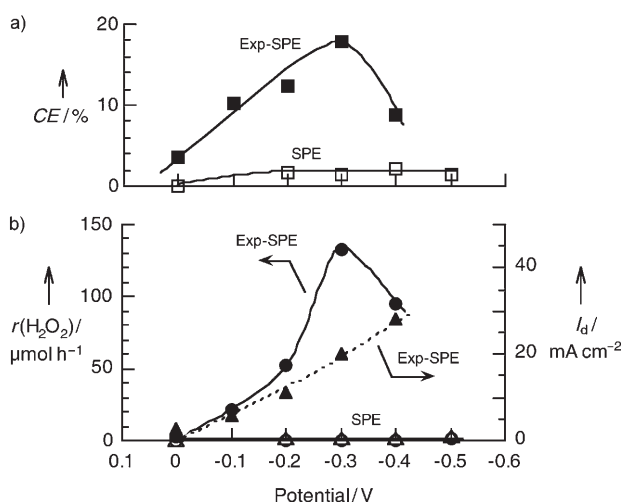


Figure 2. Effect of cathode potential on a) the rate of formation of neutral H₂O₂, $r(\text{H}_2\text{O}_2)$, and current density, I_d , and b) current efficiency CE in the standard SPE [Figure 1 a: cathode soaking in water (O₂)] and Exp-SPE (Figure 1 b: cathode exposed to O₂/water) setups. Experimental conditions: |AC + VGCF cathode|nafion-117|Pt/CB anode|water(Ar), $T = 281$ K, reaction time 2 h.

Exp-SPE method. Figure 2 shows the effects of cathode potential on the formation of H₂O₂. Current density and formation rate of H₂O₂ increased with increasingly more negative potential, and the latter showed a maximum rate at -0.3 V. The H₂O₂ solutions in the cathode were found to be neutral. The CE also showed its maximum of 18% at -0.3 V. The formation rates of H₂ were 54 μmol h⁻¹ (CE 6.8%) at -0.3 V and 254 μmol h⁻¹ (23.4%) at -0.4 V. In addition, lower current density and yield of H₂O₂ were observed at 0 to -0.3 V when the whole cathode was soaked in water. The concentration of O₂ in the gas phase (43 mm) is much higher than that in water (1.8 mm) at 1 atm and 281 K. In addition, the diffusion coefficient of gas (on the order of 10⁰ m² s⁻¹) is much larger than that of liquid (on the order of 10⁻⁹ m² s⁻¹). These differences in physical properties suggest that the steady-state concentration of O₂ on the cathode in the Exp-SPE method should be dramatically larger than that with the conventional method and accelerate the formation rate. However, the concentration of 15-mL H₂O₂ solutions of was only 0.016 M (0.056 wt %).

An attractive feature of the cathode is the accumulation of more highly concentrated H₂O₂ solutions above 1 wt % (0.29 M), because the reduction rate of H₂O₂ to water is usually very fast. We reduced the volume of deionized water by decreasing the thickness of the cathode bath (Table 1, runs 1–3). We note that current density and the formation rate of H₂O₂ were almost constant among runs 1 (15 mL), 2 (3 mL), and 3 (0.6 mL), with no dependence on the initial volume of deionized water. Therefore, concentrations of H₂O₂ dramatically increased to 0.23 wt % (0.065 M) and 1.30 wt % (0.38 M) due to the reductions in volume. These results suggest that successive reduction of H₂O₂ to water is very slow at the [AC + VGCF] cathode.

Peculiarly, the solution volume increased from 3.00 to 3.14 mL (Table 1, run 2) and from 0.60 to 0.76 mL (Table 1,

Table 1: Effect of initial volume of deionized water in the cathode compartment on the neutral H₂O₂ synthesis by the Exp-SPE method.^[a]

Run	1	2	3	4
initial V [mL]	15	3.0	0.6	0.0
final V [mL]	15	3.1	0.76	0.17
I_d [mA cm ⁻²]	21.1	18.5	20.0	16.5
$r(\text{H}_2\text{O}_2)$ [μmol h ⁻¹]	125	103	132	74.2
C(H ₂ O ₂) [wt %]	0.06	0.23	1.30	2.90
CE [%]	15.9	14.9	17.8	12.1

[a] $T = 281$ K, O₂/water |AC + VGCF cathode|nafion-117|Pt/CB anode|Ar, cathode potential -0.3 V(Ag/AgCl), reaction time 2 h. Experimental errors: $V \pm 0.1$ mL and $C \pm 0.01$ wt %.

run 3) after electrolysis. We determined that the increase in volume corresponded to the amount of charge passed. In detail, three molecules of water of hydration per proton moved from the anode to the cathode. This suggests that initial presence of water at the cathode is not essential for the formation of neutral H₂O₂ solutions, because water of hydration accumulates in the cathode bath during electrolysis. Therefore, we performed Exp-SPE electrolysis without initial water in the cathode bath, that is, with complete exposure of the cathode (complete Exp-SPE method, Table 1, run 4). A higher H₂O₂ concentration could be obtained (0.85 M (2.9 wt %), 0.17 mL), but the formation rate and CE were slightly lower than in runs 1–3.

The electrochemical reduction of O₂ to H₂O₂ should proceed at the three-phase boundary of nafion-H electrolyte (liquid phase), AC surface (solid phase), and O₂ (gas phase). To increase the formation rate of H₂O₂, the area of the three-phase boundary should be expanded. Therefore, we attempted to modify the [AC + VGCF] cathode by coating treatment with nafion solutions to increase the three-phase boundary. Nafion solutions (5 wt % in 2-propanol and water, Aldrich Co.) were painted on one side of the [AC + VGCF] cathode, which dried during decompressing. The loading of nafion was determined by the difference in weight before and after coating. This cathode was denoted [AC + VGCF/nafion]. Neutral H₂O₂ synthesis was conducted at the [AC + VGCF/nafion] cathode by the complete Exp-SPE method (Table 2, run 8). The current density and the formation rate of H₂O₂ were significantly increased compared to the results

Table 2: Effect of oxidative treatment of AC and nafion coating on neutral H₂O₂ synthesis by the complete Exp-SPE method.^[a]

Run	5	6	7	8	9	10
electrocatalyst	AC	AC(air)	AC(HNO ₃)	AC	AC(air)	AC(HNO ₃)
nafion [mg]	–	–	–	5.5	5.1	6.5
I_d [mA cm ⁻²]	16.5	22.5	24.1	24.6	46.8	59.4
$r(\text{H}_2\text{O}_2)$ [μmol h ⁻¹]	74.2	169	147	191	352	577
CE [%]	12.1	20.2	16.6	20.9	20.2	26.5
final V [μL]	174	218	250	217	343	489
C(H ₂ O ₂) [wt %]	2.90	5.27	4.07	5.99	6.98	8.06

[a] AC(air): AC oxidized by air for 1 h at 537 K, AC(HNO₃): AC oxidized by 3.8 N HNO₃ for 1 h under reflux. $T = 281$ K, O₂ |electrocatalyst + VGCF cathode|nafion-117|Pt/CB anode|water(Ar), cathode potential -0.3 V (vs. Ag/AgCl), reaction time 2 h. Experimental errors: $V \pm 1$ μL and $C \pm 0.01$ wt %.

with the [AC + VGCF] cathode (Table 2, run 5). The concentration of H_2O_2 increased to 1.76 M (5.99 wt %) with 20.9 % CE over 2 h.

We have proposed a primitive reaction scheme in which functional groups on AC surfaces (CO_2H , OH , $=\text{O}$, etc.) catalyze the electrochemical reduction of O_2 , and VGCF was used as a current collector (lead wire) for the [AC + VGCF] cathode in the fuel-cell system.^[10] In fact, the electrocatalytic activity of the cathode for H_2O_2 formation disappeared when functional groups on the AC surface were removed by thermal treatment in He at 1073 K. We attempted to increase electrocatalytic activity of the AC surface by oxidative treatment.

The surface of AC was oxidized with 1.0–13.8 M HNO_3 solutions under reflux conditions for 1 h, and the effect of oxidative treatment of AC on H_2O_2 formation at -0.3 V (Ag/AgCl) in the complete Exp-SPE setup was studied. The AC oxidized with 3.8 M HNO_3 (AC(HNO_3)) was suitable for H_2O_2 synthesis. The formation rate, CE, and concentration of H_2O_2 significantly increased at the [AC(HNO_3) + VGCF] cathode (Table 2, run 7). Oxidation of the surface of AC in air at 473–673 K was studied. The AC oxidized in air at 523 K (AC(air)) was suitable for formation of H_2O_2 . The electrocatalytic activity of the [AC(air) + VGCF] cathode was as good as that of the [AC(HNO_3) + VGCF] cathode (Table 2, run 7). Nafion coating for neutral H_2O_2 formation was also effective on both [AC(air) + VGCF/nafion] and [AC(HNO_3) + VGCF/nafion] cathodes (Table 2, runs 9 and 10, respectively). In particular, the [AC(HNO_3) + VGCF/nafion] cathode performed best with respect to H_2O_2 formation: $C(\text{H}_2\text{O}_2) = 2.4$ M (8.06 wt %) with 26.5 % CE over 2 h.

Time trials of neutral H_2O_2 synthesis were carried out at the [AC(HNO_3) + VGCF/nafion] cathode in the complete Exp-SPE setup at -0.3 V for 6 h. The current densities were almost constant over 6 h. The total yield of H_2O_2 linearly increased with a constant CE of 25 %. However, the concentration of H_2O_2 remained constant at 8 wt % because the volume of the solutions linearly increased with reaction time. When H_2O_2 synthesis was performed in air ($P(\text{O}_2) = 0.21$ atm) at -0.3 V, neutral 3 wt % H_2O_2 solutions were obtained with 11 % CE.

In conclusion, neutral aqueous H_2O_2 solutions (max 8 wt %) can be continuously produced from O_2 and water

without any toxic byproducts by using the complete Exp-SPE method with [AC(HNO_3) + VGCF/nafion] cathode. The neutral H_2O_2 solution can be used as a disinfectant for bathrooms, air conditioners, and running water, and as an abstergent for semiconductors and an oxidant for the synthesis of fine chemicals.

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