Hydrogen Peroxide Production

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Neutral H_2O_2 Synthesis by Electrolysis of Water and O_2

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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 H_2O_2 production by multistep anthraquinone-based processes and transport restrictions[1] are major factors in meeting this demand.[2] Therefore, an on-site production method for H_2O_2, for example, direct synthesis of H_2O_2 from H_2 and O_2 with Pd and Au/Pd catalysts in acid or methanol solutions have been studied.[3–8] However, a gaseous mixture of H_2 and O_2 has the possibility of exploding, so a safer procedure is essential.

We previously reported an H_2/O_2 fuel-cell system for direct formation of H_2O_2.[9,10] The fuel cell can be safely operated for H_2O_2 production because H_2 and O_2 are separated by the electrolytic membrane. Palladium membrane catalysts can be also used for safe synthesis of H_2O_2, but the formation rate and concentration of H_2O_2 need to be improved.[11,12] We recently reported an improved fuel-cell system and new electrocatalysts for H_2O_2 synthesis. In the case of 2 N NaOH as electrolyte, 7 wt% H_2O_2 was synthesized at the mixed-carbon cathode with 93% current efficiency (*CE*).[13] With 1.2 N H_2SO_4 as electrolyte, 3.5 wt% H_2O_2 was synthesized at a cathode derivatized with Mn porphyrin with 45% *CE*.[14] The H_2O_2/NaOH solution is useful for pulp bleaching, and the H_2O_2/H_2SO_4 solution can be used for oxidation in organic synthesis. However, neutral aqueous H_2O_2 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 H_2 generation (water decomposition). If we can find a suitable electrocatalyst (cathode) and reaction conditions, formation of neutral H_2O_2 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 O_2 and Ar were introduced into the cathode and anode compartments, respectively. Given a suitable cathode, reduction of O_2 to H_2O_2 ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) and accumulation of H_2O_2 in the deionized water are expected. Other possible reactions are formation of H_2O and H_2 at the cathode. In addition, water is decomposed at the anode.

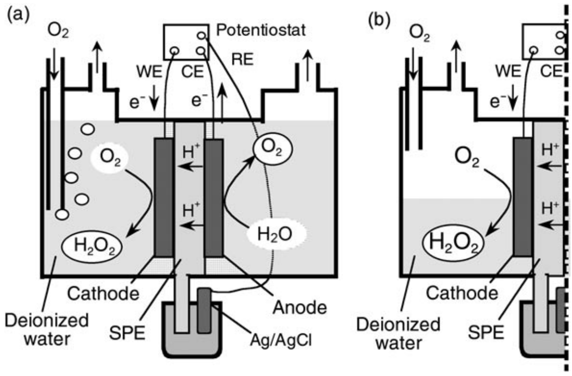

Figure 1. Diagram of a) standard SPE method and b) exposure SPE (Exp-SPE) method. WE = working electrode, CE = counterelectrode, RE = reference electrode.

We selected a mixed-carbon cathode (2 cm^2) 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 H_2O_2 by the fuel-cell method with an H_2SO_4 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 H_2O_2 were determined by chemical titration with aqueous $KMnO_4/H_2SO_4$ solutions. The *CE* of H_2O_2 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 H_2O_2 yield of 0.8 μmol was detected with a low *CE* of 1.4%. The majority of the electrolysis current was consumed in H_2 evolution. The electrochemical reduction rate of O_2 was much lower than that of H^+ in H_2 formation. The H_2O_2 yield was considerably lower than that of the fuel-cell method using H_2SO_4 solutions.[10]

The acidity of nafion-H is as high as that of H_2SO_4 solution; therefore, its pH conditions on the cathode may be similar and should not be a major reason for formation of less H_2O_2 in the SPE electrolysis method (Figure 1 a). In the fuel-cell system, the cathode was exposed to gaseous O_2.[10,13,14] The concentration of gaseous O_2 (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 O_2 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 H_2O_2 formation by applying the

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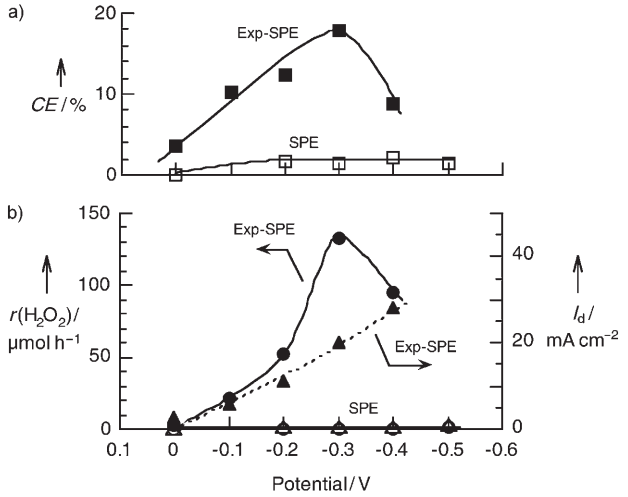

Figure 2. Effect of cathode potential on a) the rate of formation of neutral H_2O_2, $r(H_2O_2)$, and current density, I_d, and b) current efficiency *CE* in the standard SPE [Figure 1 a: cathode soaking in water (O_2)] and Exp-SPE (Figure 1 b: cathode exposed to O_2/water) setups. Experimental conditions: |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 H_2O_2. Current density and formation rate of H_2O_2 increased with increasingly more negative potential, and the latter showed a maximum rate at -0.3 V. The H_2O_2 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 H_2 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 H_2O_2 were observed at 0 to -0.3 V when the whole cathode was soaked in water. The concentration of O_2 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 10^0 m^2 s^{-1}) is much larger than that of liquid (on the order of 10^{-9} m^2 s^{-1}). These differences in physical properties suggest that the steady-state concentration of O_2 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 H_2O_2 solutions of was only 0.016 M (0.056 wt %).

An attractive feature of the cathode is the accumulation of more highly concentrated H_2O_2 solutions above 1 wt % (0.29 M), because the reduction rate of H_2O_2 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 H_2O_2 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 H_2O_2 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 H_2O_2 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, 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 H_2O_2 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 H_2O_2 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.

Table 1: Effect of initial volume of deionized water in the cathode compartment on the neutral H_2O_2 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
$r(H_2O_2)$ [μmol h^{-1}]	125	103	132	74.2
$C(H_2O_2)$ [wt %]	0.06	0.23	1.30	2.90
CE [%]	15.9	14.9	17.8	12.1

[a] $T = 281$ K, O_2/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 %.

The electrochemical reduction of O_2 to H_2O_2 should proceed at the three-phase boundary of nafion-H electrolyte (liquid phase), AC surface (solid phase), and O_2 (gas phase). To increase the formation rate of H_2O_2, 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 H_2O_2 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 H_2O_2 were significantly increased compared to the results

Table 2: Effect of oxidative treatment of AC and nafion coating on neutral H_2O_2 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
$r(H_2O_2)$ [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
$C(H_2O_2)$ [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(HNO_3): AC oxidized by 3.8 N HNO_3 for 1 h under reflux. $T = 281$ K, O_2|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, =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: $C(H_2O_2) = 2.4$ 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 ($P(O_2) = 0.21$ 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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