

Neutral H<sub>2</sub>O<sub>2</sub> Synthesis by Electrolysis of Water and O<sub>2</sub>

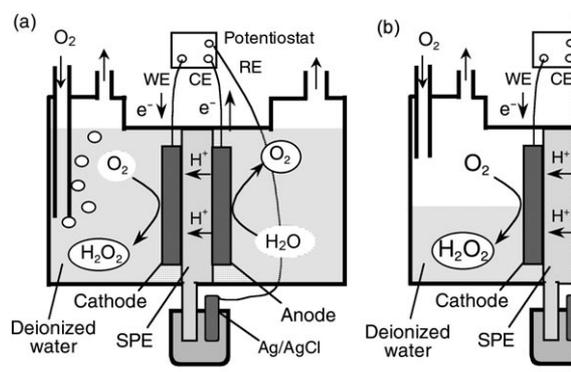
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Growth in demand for hydrogen peroxide is expected due to its wide utilization as a disinfectant and as an oxidant for chemical processes, because it generates only water as byproduct. However, the cost of H<sub>2</sub>O<sub>2</sub> production by multi-step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

We previously reported an H<sub>2</sub>/O<sub>2</sub> fuel-cell system for direct formation of H<sub>2</sub>O<sub>2</sub>.<sup>[9,10]</sup> The fuel cell can be safely operated for H<sub>2</sub>O<sub>2</sub> production because H<sub>2</sub> and O<sub>2</sub> are separated by the electrolytic membrane. Palladium membrane catalysts can be also used for safe synthesis of H<sub>2</sub>O<sub>2</sub>, but the formation rate and concentration of H<sub>2</sub>O<sub>2</sub> need to be improved.<sup>[11,12]</sup> We recently reported an improved fuel-cell system and new electrocatalysts for H<sub>2</sub>O<sub>2</sub> synthesis. In the case of 2 N NaOH as electrolyte, 7 wt % H<sub>2</sub>O<sub>2</sub> was synthesized at the mixed-carbon cathode with 93 % current efficiency (CE).<sup>[13]</sup> With 1.2 N H<sub>2</sub>SO<sub>4</sub> as electrolyte, 3.5 wt % H<sub>2</sub>O<sub>2</sub> was synthesized at a cathode derivatized with Mn porphyrin with 45 % CE.<sup>[14]</sup> The H<sub>2</sub>O<sub>2</sub>/NaOH solution is useful for pulp bleaching, and the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> solution can be used for oxidation in organic synthesis. However, neutral aqueous H<sub>2</sub>O<sub>2</sub> 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<sup>[15]</sup> and for H<sub>2</sub> generation (water decomposition). If we can find a suitable electrocatalyst (cathode) and reaction conditions, formation of neutral H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> and Ar were introduced into the cathode and anode compartments, respectively. Given a suitable cathode, reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> (O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>) and accumulation of H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O and H<sub>2</sub> at the cathode. In addition, water is decomposed at the anode.

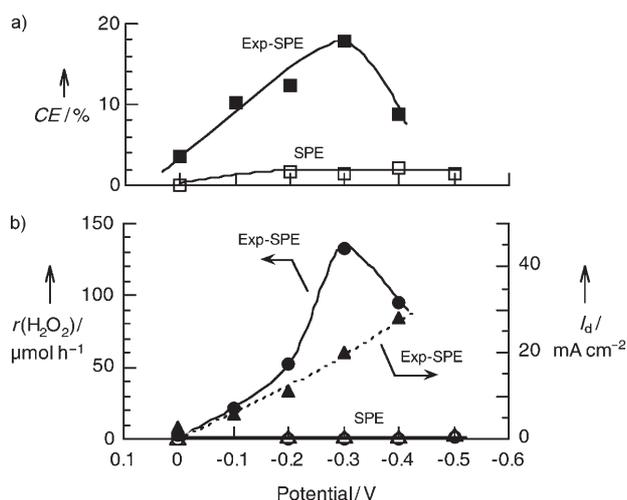
We selected a mixed-carbon cathode (2 cm<sup>2</sup>) prepared from activated carbon (AC), vapor-grown carbon fiber (VGCF), and teflon powder by the hot-press method.<sup>[6]</sup> This [AC + VGCF] cathode is effective for formation of H<sub>2</sub>O<sub>2</sub> by the fuel-cell method with an H<sub>2</sub>SO<sub>4</sub> electrolyte.<sup>[10]</sup> 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<sub>2</sub>O<sub>2</sub> were determined by chemical titration with aqueous KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> solutions. The CE of H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> yield of 0.8 μmol was detected with a low CE of 1.4 %. The majority of the electrolysis current was consumed in H<sub>2</sub> evolution. The electrochemical reduction rate of O<sub>2</sub> was much lower than that of H<sup>+</sup> in H<sub>2</sub> formation. The H<sub>2</sub>O<sub>2</sub> yield was considerably lower than that of the fuel-cell method using H<sub>2</sub>SO<sub>4</sub> solutions.<sup>[10]</sup>

The acidity of nafion-H is as high as that of H<sub>2</sub>SO<sub>4</sub> solution; therefore, its pH conditions on the cathode may be similar and should not be a major reason for formation of less H<sub>2</sub>O<sub>2</sub> in the SPE electrolysis method (Figure 1 a). In the fuel-cell system, the cathode was exposed to gaseous O<sub>2</sub>.<sup>[10,13,14]</sup> The concentration of gaseous O<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> formation by applying the

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**Figure 2.** Effect of cathode potential on a) the rate of formation of neutral H<sub>2</sub>O<sub>2</sub>,  $r(\text{H}_2\text{O}_2)$ , and current density,  $I_d$ , and b) current efficiency CE in the standard SPE [Figure 1 a: cathode soaking in water (O<sub>2</sub>)] and Exp-SPE (Figure 1 b: cathode exposed to O<sub>2</sub>/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<sub>2</sub>O<sub>2</sub>. Current density and formation rate of H<sub>2</sub>O<sub>2</sub> increased with increasingly more negative potential, and the latter showed a maximum rate at -0.3 V. The H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> were 54  $\mu\text{mol h}^{-1}$  (CE 6.8%) at -0.3 V and 254  $\mu\text{mol h}^{-1}$  (23.4%) at -0.4 V. In addition, lower current density and yield of H<sub>2</sub>O<sub>2</sub> were observed at 0 to -0.3 V when the whole cathode was soaked in water. The concentration of O<sub>2</sub> 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  $10^0 \text{ m}^2 \text{ s}^{-1}$ ) is much larger than that of liquid (on the order of  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ). These differences in physical properties suggest that the steady-state concentration of O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> solutions of was only 0.016 M (0.056 wt %).

An attractive feature of the cathode is the accumulation of more highly concentrated H<sub>2</sub>O<sub>2</sub> solutions above 1 wt % (0.29 M), because the reduction rate of H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> synthesis by the Exp-SPE method.<sup>[a]</sup>

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
$I_d$ [ $\text{mA cm}^{-2}$ ]	21.1	18.5	20.0	16.5
$r(\text{H}_2\text{O}_2)$ [ $\mu\text{mol h}^{-1}$ ]	125	103	132	74.2
C(H <sub>2</sub> O <sub>2</sub> ) [wt %]	0.06	0.23	1.30	2.90
CE [%]	15.9	14.9	17.8	12.1

[a]  $T = 281$  K, O<sub>2</sub>/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 H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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 O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> should proceed at the three-phase boundary of nafion-H electrolyte (liquid phase), AC surface (solid phase), and O<sub>2</sub> (gas phase). To increase the formation rate of H<sub>2</sub>O<sub>2</sub>, 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> were significantly increased compared to the results

**Table 2:** Effect of oxidative treatment of AC and nafion coating on neutral H<sub>2</sub>O<sub>2</sub> synthesis by the complete Exp-SPE method.<sup>[a]</sup>

Run	5	6	7	8	9	10
electrocatalyst	AC	AC(air)	AC(HNO <sub>3</sub> )	AC	AC(air)	AC(HNO <sub>3</sub> )
nafion [mg]	–	–	–	5.5	5.1	6.5
$I_d$ [ $\text{mA cm}^{-2}$ ]	16.5	22.5	24.1	24.6	46.8	59.4
$r(\text{H}_2\text{O}_2)$ [ $\mu\text{mol h}^{-1}$ ]	74.2	169	147	191	352	577
CE [%]	12.1	20.2	16.6	20.9	20.2	26.5
final V [ $\mu\text{L}$ ]	174	218	250	217	343	489
C(H <sub>2</sub> O <sub>2</sub> ) [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<sub>3</sub>): AC oxidized by 3.8 N HNO<sub>3</sub> for 1 h under reflux.  $T = 281$  K, O<sub>2</sub> | electrocatalyst + VGCF cathode | nafion-117 | Pt/CB anode | water(Ar), cathode potential -0.3 V (vs. Ag/AgCl), reaction time 2 h. Experimental errors:  $V \pm 1$   $\mu\text{L}$  and  $C \pm 0.01$  wt %.

with the [AC + VGCF] cathode (Table 2, run 5). The concentration of H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>H, OH, =O, etc.) catalyze the electrochemical reduction of O<sub>2</sub>, and VGCF was used as a current collector (lead wire) for the [AC + VGCF] cathode in the fuel-cell system.<sup>[10]</sup> In fact, the electrocatalytic activity of the cathode for H<sub>2</sub>O<sub>2</sub> 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<sub>3</sub> solutions under reflux conditions for 1 h, and the effect of oxidative treatment of AC on H<sub>2</sub>O<sub>2</sub> formation at –0.3 V (Ag/AgCl) in the complete Exp-SPE setup was studied. The AC oxidized with 3.8 M HNO<sub>3</sub> (AC(HNO<sub>3</sub>)) was suitable for H<sub>2</sub>O<sub>2</sub> synthesis. The formation rate, CE, and concentration of H<sub>2</sub>O<sub>2</sub> significantly increased at the [AC(HNO<sub>3</sub>) + 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<sub>2</sub>O<sub>2</sub>. The electrocatalytic activity of the [AC(air) + VGCF] cathode was as good as that of the [AC(HNO<sub>3</sub>) + VGCF] cathode (Table 2, run 7). Nafion coating for neutral H<sub>2</sub>O<sub>2</sub> formation was also effective on both [AC(air) + VGCF/nafion] and [AC(HNO<sub>3</sub>) + VGCF/nafion] cathodes (Table 2, runs 9 and 10, respectively). In particular, the [AC(HNO<sub>3</sub>) + VGCF/nafion] cathode performed best with respect to H<sub>2</sub>O<sub>2</sub> formation: C(H<sub>2</sub>O<sub>2</sub>) = 2.4 M (8.06 wt %) with 26.5% CE over 2 h.

Time trials of neutral H<sub>2</sub>O<sub>2</sub> synthesis were carried out at the [AC(HNO<sub>3</sub>) + 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<sub>2</sub>O<sub>2</sub> linearly increased with a constant CE of 25%. However, the concentration of H<sub>2</sub>O<sub>2</sub> remained constant at 8 wt % because the volume of the solutions linearly increased with reaction time. When H<sub>2</sub>O<sub>2</sub> synthesis was performed in air (P(O<sub>2</sub>) = 0.21 atm) at –0.3 V, neutral 3 wt % H<sub>2</sub>O<sub>2</sub> solutions were obtained with 11% CE.

In conclusion, neutral aqueous H<sub>2</sub>O<sub>2</sub> solutions (max 8 wt %) can be continuously produced from O<sub>2</sub> and water

without any toxic byproducts by using the complete Exp-SPE method with [AC(HNO<sub>3</sub>) + VGCF/nafion] cathode. The neutral H<sub>2</sub>O<sub>2</sub> 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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