Direct Synthesis of Hydrogen Peroxide (>1 wt%) over the Cathode Prepared from Active Carbon and Vapor-Grown-Carbon-Fiber by a New H$_2$–O$_2$ Fuel Cell System

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A higher concentration of H$_2$O$_2$ solution (>1 wt%) was catalytically and directly synthesized from O$_2$ and H$_2$ over a [active carbon + vapor-grown-carbon-fiber] cathode by a new type of fuel cell system at 1 atm.

Hydrogen peroxide is one of the most essential chemicals in the current chemical industry. Most of H$_2$O$_2$ is manufactured by the anthraquinone process through multi step operations with a large amount of energy consumption. A part of H$_2$O$_2$ is manufactured by the electrolysis of O$_2$ in alkaline solutions over the graphite cathode, as the on-site process for the pulp breaching.[1] Process cost of the electrolysis method is expensive and cannot be applied for the general H$_2$O$_2$ production. Therefore, development of catalytic and direct synthesis method of H$_2$O$_2$ from O$_2$ and H$_2$ has been desired. It is well known that Pd/carbon catalyzes the formation of H$_2$O$_2$ from H$_2$ and O$_2$ in acidic aqueous solution, but it could not prevent the explosion of a mixture of O$_2$ and H$_2$.[2] We have reported a new catalytic system utilizing a H$_2$–O$_2$ fuel cell reactor for the direct synthesis of H$_2$O$_2$ from O$_2$ and H$_2$ under ambient conditions, as shown in Figure 1a.[3] Advantages of the fuel cell system compared with the conventional catalytic system are (i) less opportunity of the explosion because of separation of O$_2$ and H$_2$ by the electrolyte membrane and (ii) high flexibility of application of catalysts for the activation of H$_2$ and the reduction of O$_2$. In our previous work, the maximum concentration of H$_2$O$_2$ (0.2 wt%, 59 mM) was low with a low current efficiency (CE) <10%, because the successive reduction of H$_2$O$_2$ to water was accelerated with accumulating H$_2$O$_2$. The formation reactions of H$_2$O$_2$ and water are competitive. The H$_2$O$_2$ concentration of 59 mM is far higher than that of O$_2$ ($\approx$1 mM) limited by the solubility in an electrolyte
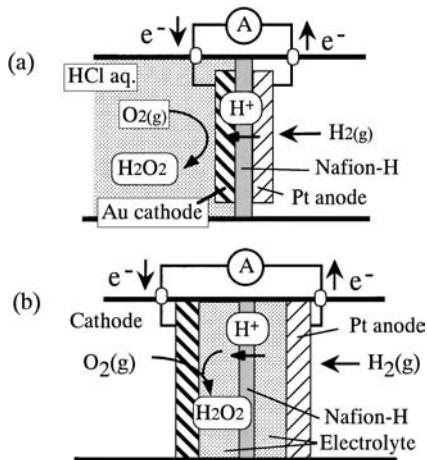
at atmospheric pressure. We have concluded that the concentrations of O$_2$ at the cathode must be increased to produce higher concentrated H$_2$O$_2$ solution.

We propose a new concept and a new fuel cell system for the H$_2$O$_2$ synthesis to enable to increase the concentrations of O$_2$ at the cathode at atmospheric pressure. Our idea is that a three-phase boundary (gas phase (O$_2$), liquid phase (acid solutions), and solid phase (cathode)),[4] is applied for the electrochemical formation of H$_2$O$_2$, as shown in Figure 1b. Electrolyte solutions (HCl 1.2 N) filled two spaces between the gas-diffusion cathode and the Nafion-117 membrane and between the anode and the membrane (each volumes as 2.1 ml), as shown in Figure 1b. The apparent surface area of the both electrode is 1.3 cm^{-2}. Pure O$_2$ (10 ml min^{-1}) and H$_2$ (10 ml min^{-1}) were supplied to the cathode and anode, respectively at atmospheric pressure. A high partial pressure of O$_2$ (101 kPa, 45 mM) should be directly supplied to the active site at the three-phase boundary in the cathode. Therefore, the reduction of O$_2$ to H$_2$O$_2$ should be accelerated and the successive reduction of H$_2$O$_2$ should be decelerated, respectively.

First, various cathodes prepared from precious metal compounds (Pd-black, PdO, H$_2$PdCl$_4$, Au-black, HAuCl$_4$) of 20 mg,[2,3] vapor-grown-carbon-fiver (VGCF, 13 m^2 g^{-1}, Showa-Denko Co.) of 50 mg, and PTFE powder of 5 mg by the hot-press method[4] were tested for the H$_2$O$_2$ formation under short circuit conditions at 298 K. The VGCF was used as a support for cathode because of a high electric conductivity and a high chemical stability. When Pd-black was added to the VGCF cathode, the concentrations of H$_2$O$_2$ were determined over 0.6 wt% for 2 h by KMnO$_4$ titration, which was higher than the maximum of 0.2 wt% by the previous system for 24 h. This result clearly proves that the new cell system (Figure 1b) is effective for the synthesis of higher concentrated H$_2$O$_2$ solutions. After screening to find more effective electrocatalysts for the H$_2$O$_2$ formation, we have found the strong enhancement of addition of active carbon (AC, Wako Co., 1500 m^2 g^{-1}) to VGCF on the H$_2$O$_2$ formation. The concentration of H$_2$O$_2$ of 0.52 wt% over the [AC + VGCF] cathode (17% CE) was as well as 0.6 wt% for the [Pd-black + VGCF] cathode (9% CE). Therefore, we have focused our interest to the [AC + VGCF] cathode.

Figure 2 shows the effect of amount of AC (x mg) in the [AC (x) + VGCF (80-x) + PTFE (7)] cathode on the formation of H$_2$O$_2$. The VGCF cathode without addition of AC was not active for the formation of H$_2$O$_2$. The current density and the formation rate of H$_2$O$_2$ increased with increasing in the addition of AC. The maximum formation rate of H$_2$O$_2$ was observed around at the AC addition of 20 mg. Excess addition of AC to VGCF did not accelerate the formation rate of H$_2$O$_2$ and the electrochemical reduction rate of O$_2$. An AC cathode without VGCF didn't show any electrocatalytic activity for reduction of


Figure 1. Diagram of the fuel cell reactor for H$_2$O$_2$ synyhesis. a: The previous type of the cell, b: a new type of the cell in this work.
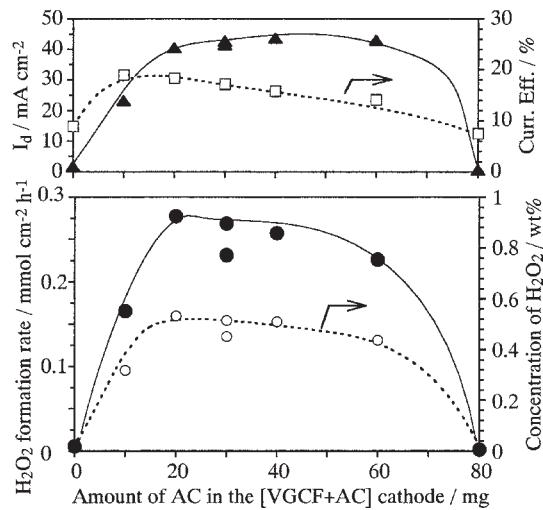
Figure 2. Effect of amount of AC in the [VGCF + AC] cathode on the formation of H_2O_2 solutions during H_2–O_2 fuel cell reactions for 2 h at 298 K. Electrolyte; HCl (1.2 N) 2 ml, anode; Pt-black (20 mg) + VGCF (70 mg)+ PTFE (7 mg), H_2 101 kPa, cathode; [AC + VGCF] (80 mg) + PTFE (7 mg), O_2 101 kPa.

O_2. The current efficiency for the formation of H_2O_2 increased from 8% to 19% by the addition of AC of 10 mg to the VGCF cathode. These results clearly propose a strong synergism of AC and VGCF on the electrochemical reduction of O_2 and on the formation of H_2O_2.

To get information for the synergism of AC and VGCF and for the reaction mechanism of the H_2O_2 formation, electrochemical studies were carried out. The cathode potentials (vs Ag|AgCl) changed from 0.4 V (open circuit condition) to -0.06 V (short circuit condition) and anode potentials changed from -0.2 V (open) to -0.07 V (short). Most of electric motive force (0.6 V) was consumed for the cathode reactions; reduction of O_2. Thus, the cathode reaction determined the H_2O_2 formation. A cyclic voltammetry (CV) for the VGCF electrode and the [VGCF + AC] electrode were studied under the same reaction conditions of the H_2O_2 formation in Figure 3. In the CV of the VGCF electrode (Figure 3a) at atmospheric pressure of O_2, the reduction current was observed below -0.5 V, no reduction current of O_2 was observed at around 0 to -0.1 V, corresponding to the cathode potential for H_2O_2 formation under short circuit conditions. This observation is corresponding to low electrocatalytic activity of the VGCF cathode for the H_2O_2 formation. In the CV of the [VGCF + AC] electrode (Figure 3b), significant reduction current of O_2 was observed below 0 V. A large and broad shoulder peak around -0.5 V was observed. When the CV was scanned to a positive potential until $+1.0$ V, no oxidation peak was observed over the [VGCF + AC] electrode. Thus, the reduction peak in Figure 3b was irreversible one. Some standard redox potentials of O_2 in aqueous media at pH = 1 were well-known in eq. 1–3.[5] On the basis of these standard potentials, the shoulder peak at around -0.5 V should be formation of $HO_2\bullet$ (eq. 3). It is reported that two $HO_2\bullet$ molecules heterogeneously convert to H_2O_2 and O_2.[5]

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (1.43 \text{ V vs Ag|AgCl}) \quad (1)$$

$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad (0.85 \text{ V}) \quad (2)$$

$$O_2 + H^+ + e^- = HO_2\bullet \qquad (-0.30 \text{ V}) \quad (3)$$
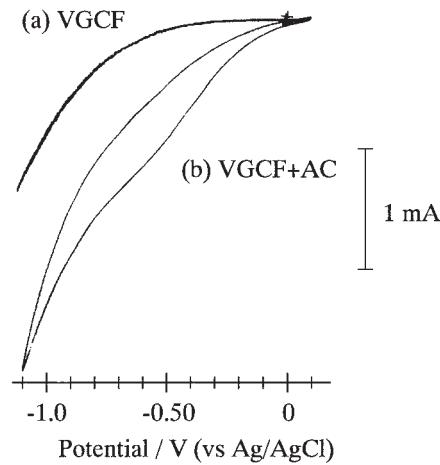

Figure 3. Cyclic voltammograms over (a) the VGCF and (b) the (AC + VGCF) electrodes in 1.2 N HCl aq at atmospheric pressure of O_2. Scan rate; 50 mV/s.

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \qquad (4)$$
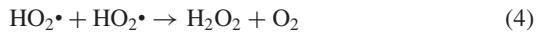
If this reaction route through eq. 3 and 4 for the H_2O_2 formation was true, more negative cathode potentials should be suitable for the formation of H_2O_2. In fact, we observed increases in the formation rate of H_2O_2, the current density, and the CE with decreasing in cathode potentials in potentiostatic experiments. The maximum formation rate of H_2O_2 and the current efficiency were observed at -0.5 V, this potential is corresponding to the potential of the shoulder peak in Figure 3b. The concentration of H_2O_2 at -0.5 V for 2 h was more than 2.5 wt% with a CE of 40%. These results strongly suggest the formation route of H_2O_2 through eq. 3 and 4 over the [VGCF + AC] cathode. The active phase for the electrochemical reduction of O_2 should be AC. However, the AC electrode without VGCF didn't show the electrochemical activity for the reduction of O_2 (Figure 2). These results proposed that AC functioned as an active site for reduction of O_2 to H_2O_2 and VGCF functioned as an electron conductor, a lead wire.

The [VGCF + AC] cathode is active for the formation of H_2O_2 by the new fuel cell system. However, the CE is not high under short circuit conditions, as shown in Figure 2. In order to increase the CE with keeping a high formation rate of H_2O_2, various factor of the cathode (contents of VGCF, AC, PTFE, and other additives, total weight of cathode, thickness of cathode, etc.) have been studied. Then, we have found that a content of PTFE strongly affected the CE of the H_2O_2 formation. The CE increased from 19 to 46% with increasing the amount of PTFE from 7 to 40 mg. A time course for the H_2O_2 formation has been studied over the [VGCF (60 mg) + AC (20 mg) + PTFE (40 mg)] cathode. After the reaction for 6 h, the concentration of H_2O_2 achieved to 1.1 wt% with a good CE of 40%. This result shows the high potential of the new fuel cell system for the direct synthesis of H_2O_2 solution with a higher concentration under mild conditions.

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