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H_2O_2 Production

Direct and Continuous Production of Hydrogen Peroxide with 93 % Selectivity Using a Fuel-Cell System

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Hydrogen peroxide is currently one of the most essential chemicals for pulp bleaching, waste treatment, and chemical production, and it is the most promising major oxidant for green chemistry in the near future. Most H_2O_2 is manufactured by the anthraquinone process in a multistep operation with high energy consumption.[1] Some pulp-bleaching treatments rely on H_2O_2 manufactured by the electrolysis of O_2 in alkaline solutions over a carbon cathode.[2,3] The cost of the electrolysis process is high and prohibits general H_2O_2 production. Therefore, the development of a catalytic and direct method for the synthesis of H_2O_2 has been desired. It is well known that Pd/carbon catalyzes the formation of H_2O_2 from H_2 and O_2 in acidic aqueous solution. But the mixture of O_2 and H_2 explodes, and the selectivity for H_2O_2 based on H_2 is not high ($<30\%$).[4,5] We have reported a new catalytic system for the synthesis of H_2O_2 utilizing a H_2/O_2 fuel-cell reactor under ambient conditions (Figure 1 a).[6] Advantages of the fuel-cell system over the first catalytic system are, firstly, less opportunity of explosion because O_2 and H_2 are separated by the electrolyte membrane, and secondly, the generation of electric power along with H_2O_2 because of the fuel-cell setup.[7,8]

The concentration of H_2O_2 of 0.2 wt % (59 mM) in our first report was very low, and the concentrations in other industrial applications are also low.[6,9–11] The limit of the H_2O_2 concentration was due to the competitive reduction of H_2O_2 further to H_2O. The H_2O_2 concentration of 59 mM was far higher than that of O_2 ($\approx$ 1 mM), which was limited by its solubility in the aqueous phase (Figure 1 a). We have concluded that the concentrations of O_2 at the cathode must increase to produce a concentrated H_2O_2 solution. It is easy to imagine that the concentration of O_2 would be higher at higher pressures, but the probability of explosion would increase.

We propose a new concept and a new fuel-cell setup for the synthesis of H_2O_2 in order to increase the concentrations of O_2 at the cathode at atmospheric pressure. Our idea is an application of a three-phase boundary (gaseous O_2, aqueous electrolyte, and solid cathode) for the formation of H_2O_2, (Figure 1 b). If a porous membrane electrode is used, a high partial pressure of O_2 (101 kPa, 45 mM) can be applied directly to the active site at the three-phase boundary.[12]

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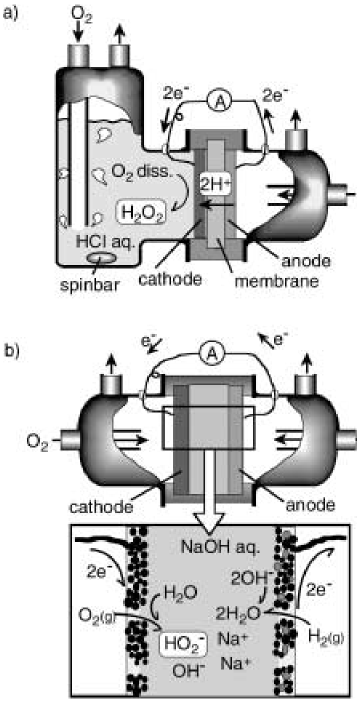

Figure 1. Schematic structure of fuel-cell reactors for H_2O_2 synthesis. a) Previous reactor, b) new reactor.

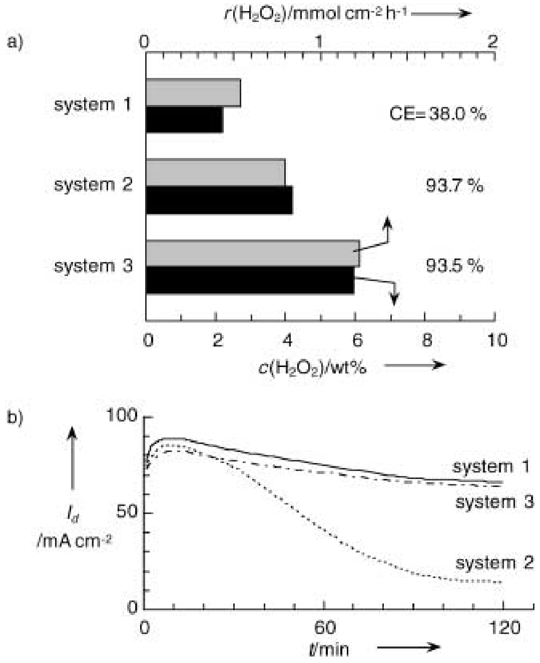

Figure 2. Synthesis of H_2O_2 by three different systems. a) Concentration of H_2O_2 in NaOH produced (2 mol L^{-1}) and rate of formation of H_2O_2. b) Time courses of the current densities of three reaction systems. CE = current efficiency.

Therefore, the reduction of O_2 to H_2O_2 should be accelerated, and the successive reduction of H_2O_2 to H_2O should be decelerated.

The porous cathode was prepared from carbon powder (vapor-grown carbon-fiber (VGCF), 13 m^{2}g^{-1}, Showa-Denko Co.) and poly(tetrafluoroethylene) powder (PTFE, Daikin Co.) by the hot-press method.[13] The anode was also prepared from VGCF, PTFE, and Pt-black powders by the hot-press method. Pure O_2 (20 mL min^{-1}) and H_2 (20 mL min^{-1}) were supplied. The yield of H_2O_2 was determined by titration against $KMnO_4$, and the current efficiency was calculated based on the two-electron reaction. The current efficiency corresponds to H_2O_2 selectivity based on H_2.

It is well known that graphite electrodes are active for the electrolysis of O_2 to H_2O_2 in alkaline solution.[2,3] We chose VGCF as the cathode material because it has good graphitic structure and high chemical stability. First, the one-compartment cell (system 1) was used for the direct synthesis of H_2O_2 over the VGCF cathode with NaOH solutions (2 mol L^{-1}) at 298 K (Figure 2 a). The concentration of H_2O_2 increased with reaction time and showed an upper limit of 2.2 wt % at 2 h. The current density gradually decreased with reaction time and was almost constant (70 mA cm^{-2}) at 2 h (Figure 2 b). Therefore, current efficiency (H_2 selectivity) decreased with reaction time from 80 % at 10 min to 38 % at 2 h. In other words, the H_2O_2 yield decelerated with reaction time.

Although the one-compartment fuel cell described above (Figure 1 b) was indeed effective for the production of more concentrated H_2O_2 solutions, the final current efficiency of 38 % was not enough. We assumed that catalytic decomposition or reduction of H_2O_2 over Pt-black is occurring. Therefore, the electrolyte compartment was divided into two compartments (1.18 mL each) separated by a cation membrane (Nafion-117, DuPont) to prevent diffusion of H_2O_2 from the cathode to the anode sides (system 2). Cationic species can pass from one side to the other but anionic species cannot. In alkaline solution hydrogen peroxide is present as HO_2^-.[2,3] Therefore, we assumed that the diffusion of HO_2^- could be controlled by the Nafion membrane.

When we tested the two-compartment reactor the concentration of H_2O_2 increased with the reaction time and reached 4.2 wt % after 2 h with a high current efficiency of 93.7 % (Figure 2 a). The separation of the electrolyte compartment was very effective for H_2O_2 production. In contrast to system 1, however, the current density in the system 2 decreased remarkably with reaction time (Figure 2 b), which is a serious problem. We have observed that the electrolyte volumes in the cathode and the anode smoothly increased and decreased, respectively, with charge passed. It could be estimated that six to seven molecules of H_2O diffused from the anode to the cathode per each electron passed. In system 2, H_2O coordinated to Na^+ should be carried from the anode to the cathode. The decrease in the amount of electrolyte in the anode should cause the decrease in the current density.

To fill up the anode, the NaOH electrolyte was injected (1.5 mL h^{-1}) with a microsyringe pump (system 3). The stability of current density was considerably improved (Figure 2 b). The concentration of H_2O_2 smoothly increased and reached 6.0 wt % after 2 h with a high current efficiency of 93.5 % (Figure 2 a). The upper limit of the concentration of H_2O_2 was observed after 2 h, but the H_2O_2 yield increased linearly with reaction time. The upper limit of the H_2O_2

concentration was due to the increase in the volume of the H_2O_2 solution. That is, system 3 produced H_2O_2 solution at a concentration of 6 wt% continuously with high current efficiencies $>90\%$.

To further optimize the production of H_2O_2 the rate-determining step in the system 3 was studied electrochemically. The open circuit voltage of the system 3 was 0.919 V (cathode potential: -0.102 V, anode potential: -1.021 V vs Ag | AgCl). The over potential of cathode was 0.550 V and that of anode was 0.230 V at 70 mA cm^{-2}. IR drop of the electrolyte was 0.095 V (electric resistance of NaOH electrolyte: 1.35 Ω cm) and that of the Nafion membrane was 0.044 V (resistance of Nafion in NaOH: 34.6 Ω cm). These data suggest that the cathode reaction, the reduction of O_2 to H_2O_2, limits the reaction rate of the system 3.

We have improved the electrocatalytic activity of the VGCF cathode by including several additives. We found that the addition of a small amount of carbon-black materials, Black Pearls 2000 (1475 m^2 g^{-1}, Cabot Co) and Valcan XC-72 (254 m^2 g^{-1}, Cabot Co.), to the VGCF cathode increased the current density and the formation rate of H_2O_2 by a factor of more than 1.4 with high current efficiency. We chose cathode components of VGCF (70 mg), XC72 (10 mg), and PTFE powder (7 mg) after many tests, because high activity and good reproducibility were obtained. The time course of H_2O_2 formation by the cell using the new cathode and anode (system 4) was shown in Figure 3. The concentration of H_2O_2 increased rapidly, comparable to that in system 3, and reached 7.0 wt% with 94% current efficiency at 2 h. The rate of H_2O_2 formation (2.0 mmol h^{-1} cm^{-2}) in system 4 was 1.7 times greater than that in system 3 (1.2 mmol h^{-1} cm^{-2}). The current density of system 4 (100 mA cm^{-2}) was comparable to that of the electrolysis method (80–120 mA cm^{-2}).[2,3]

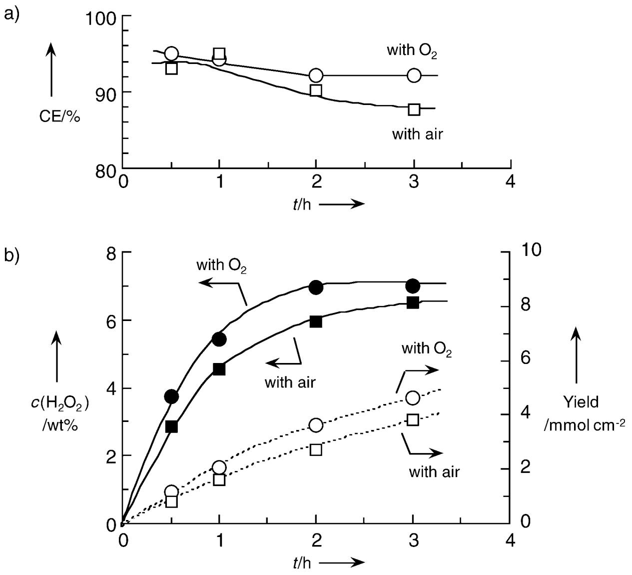

Figure 3. Time courses of the H_2O_2 synthesis by system 4. a) Concentrations and yields of H_2O_2, b) current densities.

In all of the experiments described pure oxygen ($P(O_2) = 1$ atm) was used for the synthesis of H_2O_2. If we could use air ($P(O_2) = 0.21$ atm), production costs could be cut tremendously. When air was used for system 4, the concentration of H_2O_2 increased smoothly with reaction time and reached 6.5 wt% with 88% current efficiency at 3 h. The formation rate of H_2O_2 (1.3 mmol h^{-1} cm^{-2}) and a current density (78 mA cm^{-2}) were slightly reduced when air was used, but performance was still very good. This result suggests that the fuel-cell method (system 4) has a great advantage for the industrial production of H_2O_2.

In conclusion, the H_2/O_2 fuel-cell method showed very good performance for the selective and continuous synthesis of H_2O_2 because gaseous O_2 could be supplied directly to the active site (the three-phase boundary) in the cathode, and the successive reduction of H_2O_2 over the anode could be avoided. If the apparent surface area of the electrodes of the system 4 could be increased to 1 m^2 with the same performance (current density: 100 mA cm^{-2} (1000 A m^{-2}) and current efficiency: 93%), aqueous alkaline solutions of 7 wt% H_2O_2 could be produced continuously at a rate of 8.3 L h^{-1} m^{-2}.

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