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ONE STEP SYNTHESIS OF HYDROGEN PEROXIDE THROUGH FUEL CELL REACTION

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Abstract—The fuel cell system [O_2, HCl aq. or H_2SO_4 aq., M(cathode)/Nafion–H/Pt(anode), H_2] where M is Pt, Pd, Au, graphite or Au-mesh, cogenerates H_2O_2 and electricity. Current efficiency for the formation of H_2O_2 was 100% at the early stage of the reaction. However, the efficiency dropped sharply as H_2O_2 accumulated in the solution at cathode because of further electrochemical reduction and/or thermal decomposition of the H_2O_2. The rate of formation of H_2O_2 was controlled by mass transfer of oxygen. Thus, less active material such as graphite or Au-mesh was a better electrode for the synthesis of H_2O_2. The best conditions for the accumulation of H_2O_2 were as follows: M = Au-mesh, pH = 1.1 using HCl aq., pressure of hydrogen = 5 kPa, and pressure of oxygen ⩾101 kPa.

INTRODUCTION

Most hydrogen peroxide is manufactured by the well-known anthraquinone process through the successive reduction and oxidation reactions[1]. Among the disadvantages of this method are the necessity to circulate the anthraquinone solution through separate reaction vessels for reduction, oxidation and extraction, and the formation of unwanted by-products both from the anthraquinone and the solvent. The preparation of the hydrogen peroxide by cathodic reduction of oxygen in an alkali metal hydroxide solution has been developed in improving the cell design and the efficiency of the process[2]. However, this process requires expensive electric energy and corrosion resistant equipment. It has been reported that hydrogen peroxide can be produced by a catalytic reaction of hydrogen and oxygen with a supported or homogeneous platinum group metal catalyst suspended or dissolved in an aqueous sulfonic and hydrochloric acid solution[3]. However, the disadvantage of this method is the need to bring hydrogen and oxygen into the same reactor and to circulate an explosive gas mixture.

In this communication, we propose a new method of producing hydrogen peroxide using a fuel cell system at room temperature. This method requires neither electricity nor organic materials of which peroxide is potentially explosive. Oxygen and hydrogen are not directly in contact with each other because the reactants are separated by a solid polymer electrolyte membrane (Nafion–H). This may relieve the danger of an explosion.

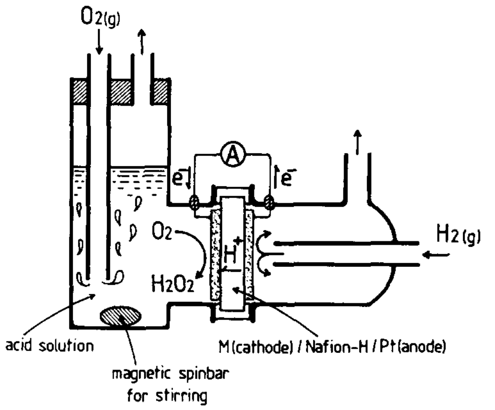


Fig. 1. Schematic diagram of the fuel cell reactor used.

EXPERIMENTAL

Figure 1 shows the schematic diagram of the fuel cell reactor and the gas flow system used in this experiment. The anode and the cathode components are separated by a Nafion 117 (Du Pont) membrane (thickness, 0.2 mm). Pt was deposited on the membrane surface at the anode by the Takenaka–Torikai method[4]. The geometrical area of the Pt deposited was 2.5 cm^2 and the apparent density was 10 mg cm^{-2}. For the cathode electrodes, Pt, Pd and Au were deposited by the same method with approximately the same area and density as those for the Pt electrode at the anode. The graphite electrode (graphite 60 mg + Teflon powder 15 mg) was adhered on the membrane by the hot-press method[5]. Au-mesh electrode (55 mesh, geometrical area was 1.8 cm^2) was contacted physically to the membrane. The apparatus used was a conventional gas-flow system at atmospheric pressure. For cathode compartment, oxygen carried by helium was introduced into aqueous solution of hydrochloric acid (0.1 N, 40 ml) with vigorous stirring of the solution. Preliminary experiments had revealed that the hydrochloric acid solution of 0.1 N (pH = 1.1) gave the optimum production of hydrogen peroxide. For anode compartment, hydrogen was introduced with helium. The flow rate of the gases for both compartments was 50 ml min^{-1}.

The experiments were usually carried out at 298 K for 3 h without putting any external load in the outer circuit in order to produce hydrogen peroxide as much as possible. The hydrogen peroxide accumulated in the solution was analyzed quantitatively by the titration method using $KMnO_4$ in sulfuric acid solutions.

RESULTS AND DISCUSSION

Under open circuit conditions, the formation of hydrogen peroxide was negligible at any conditions in this work. When the lead wires of Au from both electrodes were connected (closed circuit), a current of 10–30 mA flowed depending on experimental conditions. Hydrogen peroxide was formed in the aqueous solution in the cathode compartment. Figure 2 shows the results observed for different cathode materials attached to the membrane. The amount of accumulated hydrogen peroxide and current efficiency are plotted against reaction time. The current efficiency was calculated from the accumulated hydrogen peroxide and from the amount of electricity flowing in the outer circuit within the reaction time for each point in Fig. 2.

The results in Fig. 2 show that a catalytically inactive electrode such as graphite or Au-mesh gives better accumulation of hydrogen peroxide and current efficiency. The current efficiencies observed for most of the electrode materials at the cathode can be extrapolated to 100% when the amount of hydrogen peroxide approaches zero in Fig. 2. On the other hand, the efficiencies dropped sharply with the amount of accumulated hydrogen peroxide. The decrease was most striking for the electrocatalytically active materials such as Pd and Pt. The results in Fig. 2 strongly suggest that hydrogen peroxide is electrochemically produced with 100% selectivity (step 1) at a very early stage of the reaction, but is reduced electrochemically further into water (step 2):

$$\begin{array}{ccccc} O_2 & \xrightarrow[1]{2H^+ + 2e^-} & H_2O_2 & \xrightarrow[2]{2H^+ + 2e^-} & 2H_2O \\ & & 3 \downarrow \text{cat.} & & \\ & & H_2O + 1/2O_2 & & \end{array} \qquad (1)$$

Figure 3 shows the changes in current with reaction time measured for each kinetic curve in Fig. 2. The current increased with time for most of the curves in Fig. 3. This increase in current as well as a larger current observed for Pt and Pd in Fig. 3 can be ascribed to the reaction of step 2 in equation (1). In the cases of catalytically active Pt and Pd electrodes, we cannot exclude the thermal decomposition of hydrogen peroxide (step 3). This must be the another reason for the lower production of hydrogen peroxide for these electrode materials (Fig. 2).

It is to be noted that the steady currents observed for different cathode materials in Fig. 3 did not differ too greatly. The difference was 30% at most between Pt and Au-mesh electrodes. This is surprising because the relative surface area of the Pt electrode is two to three orders of magnitude greater than that of the Au-mesh considering the roughness factor of the former (estimated by Kita *et al.*[6]). These observations suggest that the rate of step 1 in equation (1) is controlled by mass transfer of oxygen at gas–liquid or liquid–electrode interface. In fact, the current and the amount of hydrogen peroxide formed were strongly affected with stirring of the solution. Thus, less active electrodes in step 2 are better for the accumulation of hydrogen peroxide under the experimental conditions in Figs 2 and 3.

When 0.5 V potential was externally applied between both electrodes of the cell of Pd(cathode)/Nafion–H/Pd(anode), *ca* 200 mA of current flowed steadily. This value was about eight times greater than that observed in Fig. 3 for the fuel cell reaction using Pd-cathode. However, the amount of hydrogen peroxide formed in 3 h was only 56 μmol, which is less than 20% of that observed in the fuel cell reaction (see Fig. 2). Pumping of hydrogen from anode to cathode

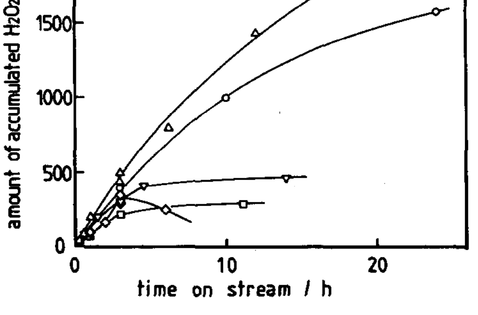


Fig. 2. Kinetic curves of accumulation of H_2O_2 and current efficiencies for different cathode materials. Reaction conditions: $T = 298$ K, anode; Pt electrode, $P(H_2) = 4$ kPa (except for Pd, 20 kPa), cathode; HCl(0.1 N) aq. 40 ml, $P(O_2) = 101$ kPa. Cathode electrodes: △, Au-mesh; ○, graphite; ▽, Au; □, Pt; ◇, Pd.

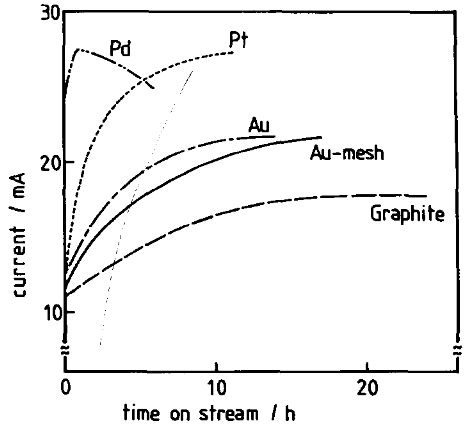


Fig. 3. Changes in current with reaction time for different electrodes at cathode.

by applying the potential must enhance the reduction[step 2 in equation (1)] and decomposition (step 3) of hydrogen peroxide. However, the applied potential cannot enhance the rate of step 1 because the rate is controlled by mass transfer of oxygen. Consequently, the application of potential must have reduced the formation of hydrogen peroxide as described above.

The effects of oxygen pressure at the cathode on the amount of hydrogen peroxide accumulated in 3 h are shown in Fig. 4 for the different electrode materials at the cathode on the membrane. Here, the pressure of hydrogen at the anode was 4 kPa except for Pd (101 kPa). The amount of hydrogen peroxide increased proportionally to the pressure of oxygen for each electrode. This observation suggests that the rate of step 1 in equation (1) depends on first order in oxygen pressure, which supports the assumption that the reaction is controlled by mass transfer of oxygen. Thus, higher pressures of oxygen is desirable for the synthesis of hydrogen peroxide.

The effects of hydrogen pressure are shown in Fig. 5. The amount of hydrogen peroxide accumulated in 3 h are plotted against the hydrogen pressure in the anode compartment. The experiments were carried out at constant pressure of oxygen of 101 kPa in the cathode side. A maximum in the amount of hydrogen peroxide can be seen for every electrode material of cathode in the range of hydrogen pressure lower than 30 kPa. The results in Fig. 5 suggest that there is an optimum pressure of hydrogen for each electrode in order to get the best production of hydrogen peroxide. It is not easy to explain the

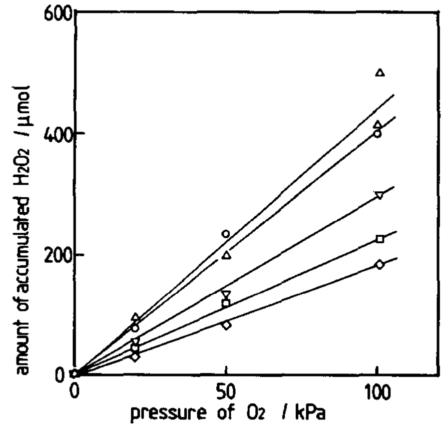


Fig. 4. Effects of pressure of oxygen at cathode on the amount of H_2O_2 accumulated in 3 h. Reaction conditions and the meaning of symbols are the same as those in Fig. 2.

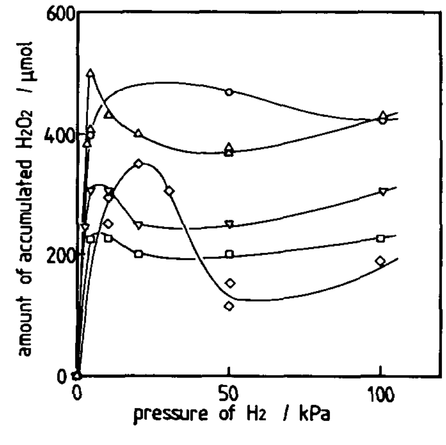
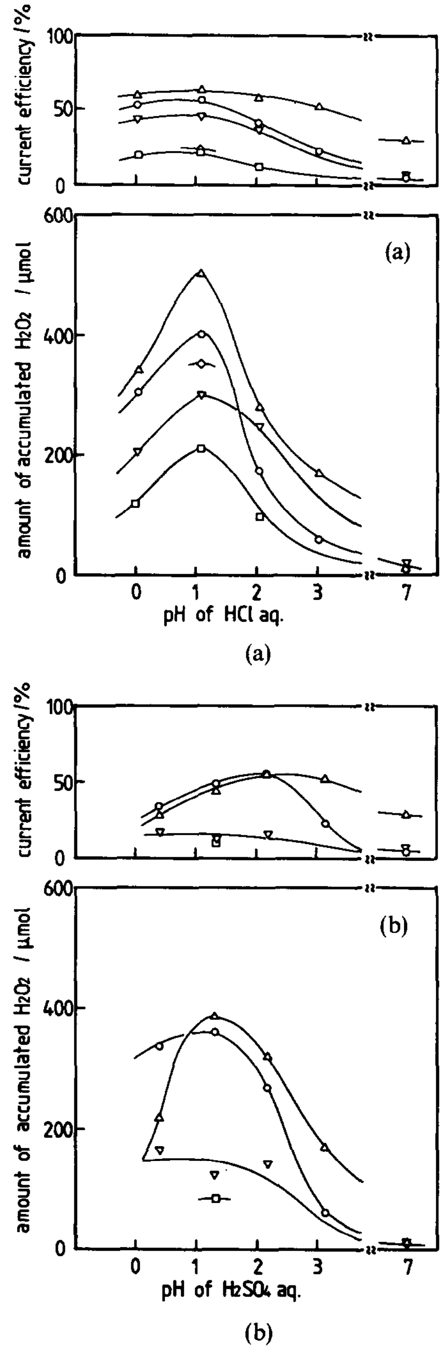


Fig. 5. Effects of pressure of hydrogen at the anode on the amount of H_2O_2 accumulated in 3 h for different electrodes. Reaction conditions and the meaning of symbols are the same as those in Fig. 2.



(a)

(b)

Fig. 6. Effects of pH on the H_2O_2 formation and current efficiencies. The pH was controlled with HCl (a) or H_2SO_4 (b). Experimental conditions and the meaning of the symbols are the same as those in Fig. 2.

complicated effects of hydrogen pressure in Fig. 5 at present. The amount of hydrogen peroxide shown depends on the relative rates of steps 2 and 3 in equation (1). The effects of hydrogen pressure on the rates of these steps could be quite different. Thus, the quantity of hydrogen peroxide accumulated in 3 h may depend on the pressure of hydrogen in a complicated way (Fig. 5).

Figure 6 shows the effect of pH on the amount of hydrogen peroxide accumulated in 3 h and on the current efficiency of the product. The pH control was performed either by adding hydrochloric acid [Fig. 6(a)] or sulfuric acid[Fig. 6(b)]. The experiments were carried out under the pressures of hydrogen and oxygen of 4 and 101 kPa, respectively. The maximum quantities of hydrogen peroxide were observed at $pH = 1.1$ irrespective of electrode materials tested or of hydrochloric acid or sulfuric acid used. It is reasonable to assume that the rates of steps 1–3 depend on pH of the solution. Therefore, the amount of hydrogen peroxide accumulated would depend strongly on pH (Fig. 6). The results in Fig. 6 show that the optimum conditions for the production of hydrogen peroxide are to adjust pH to 1.1 by HCl and to use Au-mesh electrode. The current efficiency for the formation of hydrogen peroxide under these experimental conditions exceeded 60% [Fig. 6(a)].

In conclusion, the fuel cell system in Fig. 1 worked well for generation of hydrogen peroxide. This method does not require any electricity but generates electricity. The method is very simple and may remove the danger of explosion.

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