Catalytic Synthesis of Hydrogen Peroxide in a Capillary Microreactor
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Catalytic synthesis of Hydrogen Peroxide in a Capillary Microreactor

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Abstract

The direct synthesis of hydrogen peroxide from hydrogen and oxygen has been investigated in a capillary and a stacked microreactor, where Pd/C catalyst was coated on the silicone wall of a microchannel. In order to make the system of H_2O_2 production compact, a flow-through solid polymer electrolyte (SPE) electrolyzer, which was used for the evolution of H_2 and O_2 instead of gas cylinders, was connected to the microreactor. The influences of gas and liquid flow rates and reaction temperature on the H_2O_2 production were investigated to obtain the optimum operation conditions of the stacked microreactor. As a result, a H_2O_2 concentration of 8.3×10^{-3} mol/L was obtained at 10°C in 0.1 mol/L HCl solution in the short-contact-time microreactor. In addition, H_2O_2 was successfully produced by flowing pure water with H_2 and O_2 in the stacked microreactor.

Keywords: hydrogen peroxide, microreactor, green chemistry, water electrolysis, catalyst

1. Introduction

Hydrogen peroxide is an environmentally friendly chemical as an oxidant and disinfectant in paper manufacturing, waste water treatment, electronics, and pharmaceutical industries. Commercial production of hydrogen peroxide in significant quantities has been performed by the anthraquinone autoxidation (AO) method [1] This process is economically feasible only on large-scale plants because of the complexity of the process and the loss of expensive quinone compounds. Potential hazards of transportation and storage of H_2O_2 solution have to be considered. Direct synthesis of hydrogen peroxide from hydrogen and oxygen has been investigated as an attractive alternative [2] This reaction would be rather suitable for the compact plant on demand.

$$H_2 + O_2 \text{ --- } H_2O_2 \qquad (1)$$

Palladium is the most effective catalyst in the direct synthesis of H_2O_2 [3-6]. Pd is partially transferred to Pd^{2+} in the presence of O_2 and HCl and the reverse reaction of Pd^{2+} to metallic state by hydrogen also occurs. The reaction cycle of Pd^{2+}/Pd^0 is important role to produce H_2O_2 [7]. Pd-Au [8,9] and Au [10] catalysts have been examined in attempts to obtain a high catalytic activity for the H_2O_2 production.

Direct synthesis of H_2O_2 over Pd catalyst was carried out in microreactor [11,12]. To realize the on-demand process of the H_2O_2 production using a microreactor, it would be desirable to produce hydrogen and oxygen by water electrolysis rather obtaining these materials from gas cylinders. H_2O_2 can be produced electrochemically through the reduction of O_2 in an alkaline solution [13], acid solution [14] and neutral solution [15]. Kusakabe et al. [16] used the catalytic slurry reactor inserting a pair of platinum electrodes for water electrolysis into the slurry. The in-situ feeds of H_2 and O_2 into the reactor improved H_2O_2 productivity compared to the result of the catalytic reaction without the electrolysis. H_2O_2 was able to produce through the electrochemical reduction of oxygen. However, the contribution of electrochemical production of H_2O_2 was unclear.

In this study, a capillary or a stacked microreactor was connected to a flow-through solid polymer electrolyte (SPE) electrolyzer for the production of H_2 and O_2. Pd/C catalyst was coated on the wall of microchannel in the reactor. Hydrogen peroxide was safely produced by direct combination of H_2 and O_2 in the presence of Pd/C catalyst. The influences of reaction temperature, liquid flow rate, oxygen flow rate and reaction path length on the reaction were investigated in the microreactors to obtain the optimum operation conditions.

2. Experimenatl

Hydrogen and oxygen were produced by water electrolysis in a flow-through SPE electrolyzer with platinum mesh electrodes as shown in **Figure 1**. The sizes of platinum electrodes were 20 mm x 20 mm. The cathode compartment was separated from the anode compartment by a cation-exchange membrane (Nafion, Du-Pont). Electrolysis was carried out in a constant current operation. The flow rate of oxygen, v_G, at standard temperature and pressure was calculated by the following equation

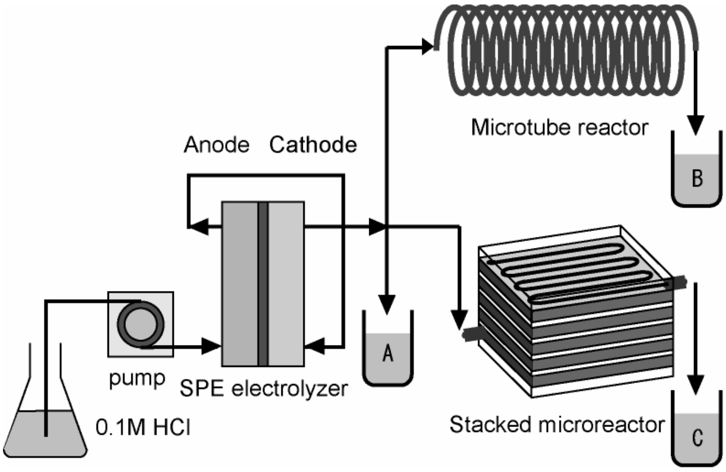
$$v_G = 0.0224I/(nF) \qquad (1)$$

where I is the electric current, n the charge number of ionic species, and F the Faraday's constant. Reaction liquid was aqueous HCl solution and introduced from the bottom of the anode compartment. Flow rate of the solution was controlled by a tubing pump and was in the range of 1.8-6.8 $mm^3\ s^{-1}$. The liquid containing oxygen, produced electrochemically at the anode was fed into the cathode compartment. As shown in Fig. 1, outlet of the cathode compartment in SPE electrolyzer was connected to the capillary microreactor or the stacked microreactor for catalytic synthesis of H_2O_2. The sample was taken from outlet of the cathode compartment to determine the amount of H_2O_2 production during the electrolysis.

The silicone capillary microreactor (outer diameter: 3mm, inner diameter: 1 mm, length: 1-6 m) was used to facilitate contact among gas, liquid and solid catalyst. A 5 wt%Pd/C catalyst (Wako Chemicals Co. ltd., Japan) for the direct synthesis of H_2O_2 was used. Inner surface coating of the capillary was realized by passing through the slurry solution of Pd/C catalyst. Pd/C catalyst was strongly adhered on the surface. About 94 mg of the catalyst were homogeneously deposited on 1 m silicone capillary tube, resulting in a catalyst loading of 30 g/m^2. After the coating treatment, no efflux of catalyst was observed during continuous flow experiments.

The stacked microreactor was designed for the compactness of the whole system. Pattern of microchannel (width: 1mm) as shown in **Figure 2** was cut out from a polymethylmethacrylate (PMMA) plate (width: 30mm, length 70mm, thickness: 1mm) using end milling. Silicone plate equivalent to the size of the PMMA plate was used as a spacer and a catalytst support. The stacked microreactor was assembled with alternating layers of five sheets of the PMMA plates and six sheets of the silicone plates. Total length of microchannel was 1.36 m. The coating method of catalyst in the stacked microreactor was as same as that in the capillary microreactor. In the stacked microreactor, about 82 mg of the catalyst were deposited. The whole system including the SPE electrolyzer and the microreactors was put in a thermostatic chamber. Reaction temperature was varied from 5 to 20^{o}C

The amount of H_2O_2 in the sample was determined by colorimetry after complexation with the $TiOSO_4/H_2SO_4$ reagent.



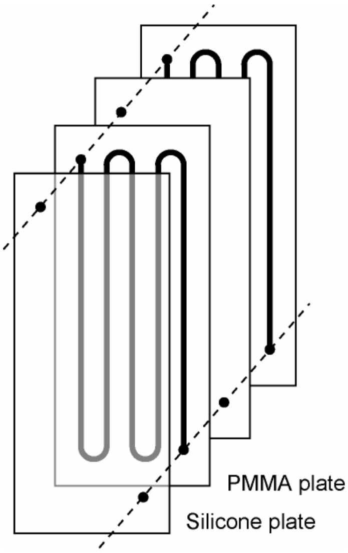


Fig. 1 Experimental set-up for H_2O_2 synthesis.

Fig. 2 Stacked microreactor

3. Results and discussion

The production of H_2O_2 in the flow-through SPE electrolyzer was first investigated in HCl solution with different concentration (10^{-9}–10^{-1} mol/L). H_2O_2 was electrochemically formed by the reduction of the dissolved O_2 as follows.

$O_2 + 2H^+ + 2e$ --- H_2O_2 at the cathode, $E_0 = 0.440$ V vs SCE. (2)

When the electrolysis was carried out under the standard conditions in this study (reaction temperature = 10°C, electric current = 0.1 A, liquid flow rate = 3 mm^3/s), H_2O_2 concentration at the outlet of the SPE electrolyzer increased with increasing HCl concentration and reached 2×10^{-3} mol/L in 0.1 mol/L HCl solution. Hereafter, 0.1 mol/L HCl solution was used in all experiments.

Influences of electric current, liquid flow rate and reaction temperature on electrochemical H_2O_2 production in the SPE electrolyzer were investigated. The results are shown in **Figure 3**. The H_2O_2 concentration increased nonlinearly with increasing electric current as shown in Figure 3(a). As a result, current efficiency for H_2O_2 production was tend to become high at low electric current and was as high as 1.2 % at the electric current of 0.1 A. This low current efficiency was caused by the use of platinum electrode in stead of carbon electrode, which was usually used for H_2O_2 production [13, 14]. Figure 3(b) indicates that the H_2O_2 concentration became low at high liquid flow rate due to short residence time. However total amount of H_2O_2 production was high at the liquid flow rate of 3 mm^3/s. Electrochemical H_2O_2 production was not greatly affected on reaction temperature as shown in Figure 3(c) and mainly controlled by electric current. Qiang et al. [14] reported that the electrochemical production rates of H_2O_2 in acidic solutions were favored at lower temperatures. However the low apparent activation energy (3.5kJ/mol) was evaluated from their results. Accordingly the SPE electrolyzer used in this study mainly acts to form hydrogen and oxygen for the subsequent catalytic reaction in the microreactor.

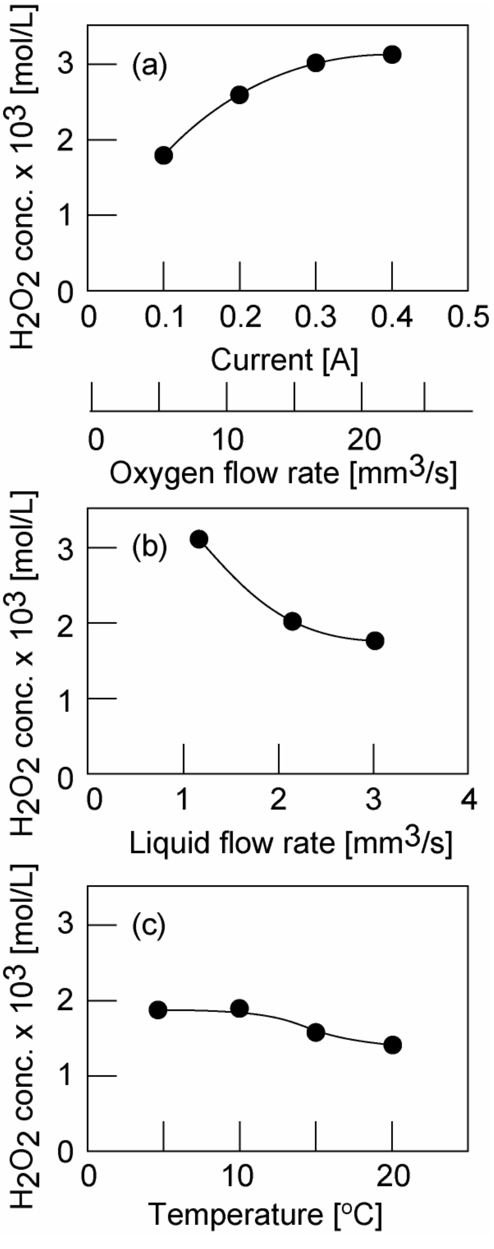


Fig. 3 H_2O_2 production in flow through SPE electrolyzer.
Reaction conditions: 0.1mol/L HCl solution, reaction temperature 10°C, liquid flow rate = 3 mm^3/s, electric current = 0.1 A

We examined the direct synthesis of hydrogen peroxide by connecting the SPE electrolyzer to the microreactor for catalytic reaction. Initially, capillary microreactors with different lengths were used to determine change in H_2O_2 concentration along flow path in the capillary tube. Experiments were carried out by varying the value of electric current. As a result, oxygen gas flow rates, which was controlled by electric current according to Eq. (1), were varied from 0.58–11.6 mm^3/s. The other experimental conditions were the same as the conditions described above for the electrochemical synthesis of H_2O_2 in the SPE electrolyzer (0.1 mol/L HCl, liquid flow rate = $3mm^3/s$, reaction temperature = 10^oC). **Figure 4** indicates the H_2O_2 concentration at the outlet of capillary microreactors with different capillary lengths. H_2O_2 concentration at the capillary length of 0 m in Figure 4 indicates the results obtained by the electrochemical reduction of O_2 in the SPE electrolyzer. The H_2O_2 concentrations became almost constant when capillary length exceeded 2 m in all experiments. According to the previously reported results [16] in the catalytic slurry reactor, reduction of H_2O_2 by hydrogen was significantly influenced under the hydrogen-rich condition.

$$H_2O_2 + H_2 \rightarrow 2H_2O \qquad (3)$$

Thus, H_2O_2 decomposition occurred simultaneously on the Pd/C catalyst during the H_2O_2 production. For the capillary microreactor with long channel, the rates of H_2O_2 of production and decomposition were fully balanced at the downstream region in capillary tube, causing a plateau of H_2O_2 concentration.

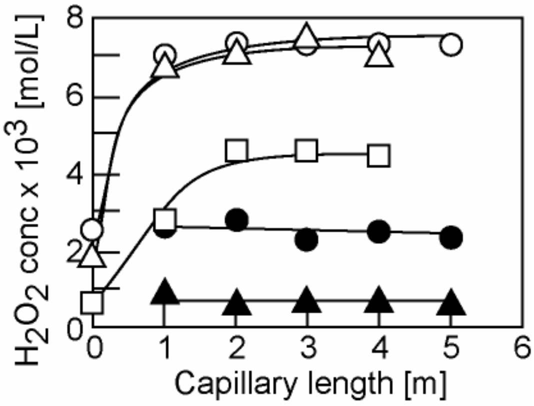


Fig.4 H_2O_2 production in capillary microreactor.
Electric current: ○; 0.2A, △; 0.1A,□; 0.07A, ●; 0.05A, ▲; 0.01A.
Reaction conditions: 0.1mol/L HCl solution, reaction temperature 10^oC, liquid flow rate = 3 mm^3/s

Considering the results of these experiments of capillary microreactor, a stacked microreactor was designed. For the stacked microreactor, the H_2O_2 synthesis was performed to investigate the effects of gas flow rate, liquid flow rate and reaction temperature, and the summary of the results is shown in Figure 5. H_2O_2 concentration at the outlet of stacked microreactor increased with increasing oxygen flow rate and approached to 6.7 x 10^{-3} mol/L, which was equivalent to the value obtained in the capillary microreactor. Compared to the result of the capillary microreactor, high H_2O_2 concentration was observed at low oxygen flow rate in the stacked microreactor, which would be explained by the mass transfer properties in the microchannels. When the capillary and the stacked microreactor without catalysts were used, stable slug flow was observed in both reactors. Turbulence was generated at the points of perpendicular flow between PMMA plates and hair-pin curves of microchannel in the stacked microreactor, enhancing the dissolution of oxygen and hydrogen due to good gas-liquid contact.

As shown in Figure 5(b), the H_2O_2 production in the stacked microreactor was not greatly affected by liquid flow rate. The H_2O_2 concentration became constant for long capillary microreactor under the sufficient residence time for achieving the equilibrium relation between H_2O_2 formation and decomposition as indicated in Fig. 4. The same situation occurred at low liquid flow rate in the stacked microreactor.

As the reaction temperature rise, the formation of H_2O_2 was promoted but the gas solubility of hydrogen and oxygen decreased. In addition, the decomposition rate of H_2O_2 also increased with temperature. Therefore the effect of temperature on the H_2O_2 production was investigated in the stacked microreactor depicted in Figure 5(c). The H_2O_2 concentration reached a maximum at 10°C. In the previous research [16], H_2O_2 production was carried out batch slurry reactor suspended with the same Pd/C catalyst and reached a maximum at 10°C.

For the stacked microreactor, the residence time of liquid was evaluated to be 93 s from the calculation of Eq. (4).

$$\text{residence time} = V(1 - \varepsilon_G)/v_L \qquad (4)$$

where V is the volume of microchannel, ε_G the gas holodup, and v_L the liquid flow rate. The in situ production of H_2, O_2 and H_2O_2 was performed in the slurry batch reactor with two sheet of platinum electrode [16]. As a result, a H_2O_2 concentration of 3.4×10^{-3} mol/L was attained after 3-hour reaction by the assistance of electrochemically generated species. Although the elecrolyzer and the catalytic microreactor were separated in this study, a H_2O_2 concentration of 8.3×10^{-3} mol/L was attained at

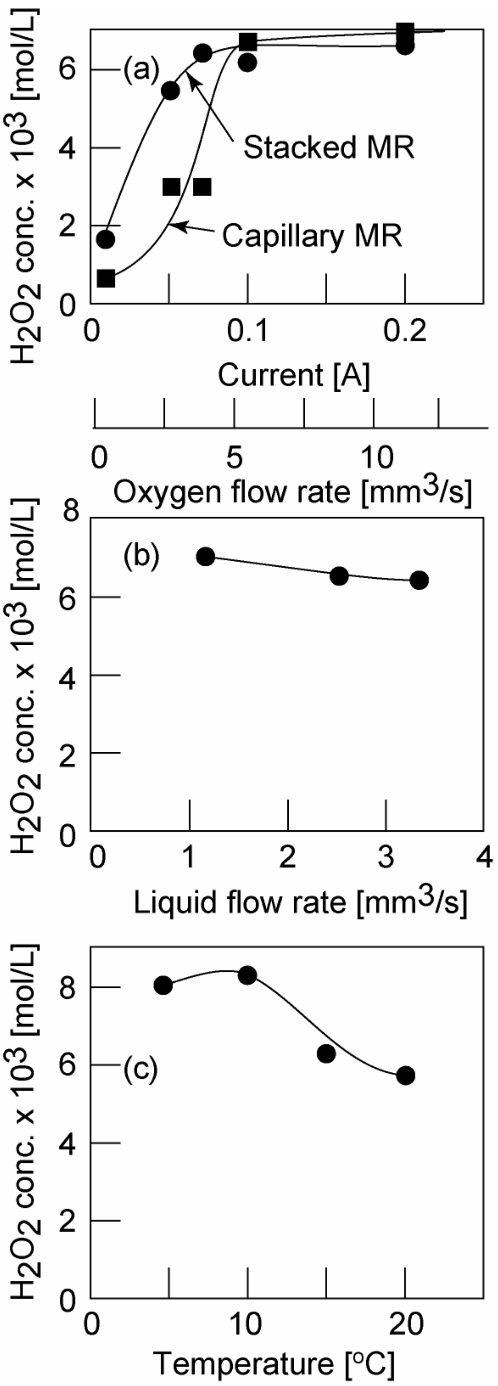


Fig. 5 H_2O_2 production in stacked microreactor.
Reaction conditions: 0.1mol/L HCl solution, reaction temperature 10°C, liquid flow rate = 3 mm^3/s, electric current = 0.2 A

the residence time of only 93 s in the stacked microreactor. The enhancement of production rate in the microreactor was caused by the greatly improved mass transfer under plug flow conditions.

In order to use a H_2O_2 solution without any separation process on demand, reduction of HCl concentration is desired. H_2O_2 production was carried out by 10^{-1}-10^{-7} mol/L HCl solution and pure water. The results are indicated in Table 1. The H_2O_2 production in the stacked microreactor was not significantly affected by HCl concentration. In addition, it is found that H_2O_2 could formed at the concentration comparable to those in HCl solution even when using pure water

Table 1 Effect of liquid phase on H_2O_2 formation

Liquid phase	Concentration [mol/L]	H_2O_2 concentration [mmol/L]
HCl soln.	10^{-1}	6.48
	10^{-3}	7.56
	10^{-5}	6.92
	10^{-7}	6.68
Pure water	-	5.64

4. Conclusions

We have proposed the compact H_2O_2 production system for direct synthesis of H_2O_2 from H_2 and O_2 in the presence of Pd/C catalyst. The production of H_2 and O_2 was performed in a flow-through SPE electrolyzer. Oxygen generated at the anode was fed into the cathode chamber. As a result, small amount of H_2O_2 was formed through electrochemical reduction of O_2. However, current efficiency was as high as 1.2 %. By connecting the SPE elecrolyzer to the stacked microreactor coated with Pd/C catalyst in microchannel, catalytic synthesis of H_2O_2 was enhanced because of the existence of active components generated during water electrolysis as well as the high mass transfer properties in microchannel. As a result, a H_2O_2 concentration of 8.3 x 10^{-3} mol/L was obtained at 10°C in 0.1 mol/L HCl solution. In addition, H_2O_2 was successfully produced by flowing pure water with H_2 and O_2 in the stacked microreactor.

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Nomenclature

E	= electrode potential	[V]
F	= Faraday's constant	[C]
I	= electric current	[A]

n	= charge number of ionic species	[-]
V	= volume of microchannel	[m^3]
v_G	= gas flow rate	[m^{3}s-1]
v_L	= liquid flow rate	[m^{3}s-1]
ε_G	= gas holdup	[-]

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