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Catalytic neutral hydrogen peroxide synthesis from O_2 and H_2 by PEMFC fuel

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ABSTRACT

Catalytic and direct synthesis of a neutral hydrogen peroxide solution from O_2 and H_2 was studied using a new conceptual PEMFC reactor with a new active cathode. A particular electrocatalyst of Co-TPP/vapor-grown-carbon-fiber (VGCF) heat-treated in He at 1073 K was found for two electrons reduction of O_2. The most active and efficient cathode was 0.05 wt.%Co-TPP/VGCF (2 mg cm^{-2}) coated on the VGCF base electrode. The maximum concentration of 13.5 wt.% was obtained with 42% CE at 278 K.

1. Introduction

Hydrogen peroxide is expected to use as an oxidant for selective oxidation of hydrocarbons and a disinfectant for living environments. The industrial chemical process of H_2O_2 synthesis is currently limited for use of the anthraquinone method through a multi-step operation [1]. However, the production cost and transport limitations of H_2O_2 are serious disadvantages for its use in a wider range of applications [2]. H_2O_2 is expected as an efficient oxidant for selective oxidation of hydrocarbons and a disinfectant for living environments. Thus, a method for direct production of H_2O_2 from O_2 and H_2 is desired [2]. In the last three decades, catalytic synthesis of H_2O_2 from a gas mixture of H_2 and O_2 has been studied for Pd and Au-Pd catalysts or Pd membrane catalysts in acid or methanol solutions [3–9]; however, these catalytic methods are volatile and explosive. The reduction of anthraquinone by H_2 and the oxidation of hydroantraquinone by O_2 were separated in the antraquinone process, allowing the anthraquinone process to be used safely. We have previously reported the H_2/O_2 fuel cell system for the direct formation of H_2O_2 [10–13]. The fuel cell system can be operated safely for the H_2O_2 production because H_2 and O_2 are separated by NaOH or H_2SO_4 electrolyte membrane [14–16]. Both alkaline and acid H_2O_2 solutions are useful; however, the neutral H_2O_2 aqueous solution is the most useful and flexible form. We recently reported the formation of the neutral H_2O_2 aqueous solution by the electrolysis of water and O_2 using a solid-polymer-electrolyte (SPE) [17,18]. If this electrolysis method can be used under fuel cell conditions, catalytic and direct production of the neutral H_2O_2 solution from O_2 and H_2 can be achieved. Therefore, catalytic and direct production of the neutral H_2O_2 solution from O_2 and H_2 was studied using a polymer-electrolyte-membrane-fuel-cell (PEMFC) reactor in this work.

2. Experimental

Fig. 1 shows a structure of the PEMFC reactor for the neutral H_2O_2 production. A unit of cathode/Nafion-117/anode was fixed to a two-compartment cell. A part of Nafion-117 membrane connected to 0.6 M H_2SO_4/reference electrode of Ag/AgCl (0.197 V vs SHE). The cathode, anode and reference electrode were connected to an electrochemical instrument (Hokuto Denko Co, HZ-5000 system).

Cathodes were prepared using two methods, one is a mixed method and the other is a coated method. The mixed method is as below; (i) electrocatalyst (18 mg), vapor-grown-carbon-fiber (30 mg, VGCF, Showa Denko Co.) and poly-tetrafluoroethylene (3 mg, PTFE, F-104 Daikin Co.) were well mixed using a mortar and pestle, (ii) the clayey mixture was pressed and extended to a round sheet (2 cm^{-2}) using a hot-plate and a roller [19]. The coated method is as below; (i) a base cathode (2 cm^2) was prepared from VGCF (50 mg) and PTFE (3 mg), (ii) a mixture of electrocatalyst (2 mg), Nafion solution (10 μL) and 2-propanol was coated on the base VGCF electrode [20]. Various electrocatalysts were tested for the formation of H_2O_2 at the cathode. For example, a typical

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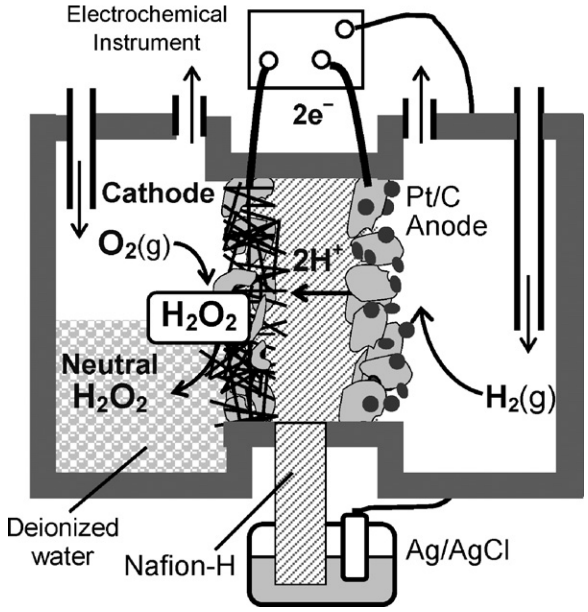

Fig. 1. Diagram of O_2/H_2 fuel cell reactor of mode-1 for direct synthesis of neutral H_2O_2 solution. Geometric area of electrodes: 2 cm^{-2}, solid polymer electrolyte: Nafion-117 (Du Pont), deionized water in cathode: 0.5 mL, O_2: 1 atm, H_2: 1 atm.

electrocatalyst of Co-porphyrin derivative was prepared, as below; (i) Co-TPP (TPP: 5, 10, 15, 20-tetrakis(phenyl)-21*H*, 23*H*-porphyrin) dissolved in CH_2Cl_2, (ii) VGCF powder added to the CoTPP/CH_2Cl_2 solutions, (iii) the mixture was stirred using magnetic spin-bar, (iv) the mixture was dry up on the hot-plate and a electrocatalyst precursor was prepared, (v) the precursor was heat-treated at 973 K in an inert gas (He) and the electrocatalyst omitted as Co-TPP/VGCF(973) was prepared. A loading of Co was 0.30 wt.% against carbon (VGCF). We also used Co-OEP (OEP: 2,3,7,8,12,13,17,18-octaethyl-21*H*, 23*H*-porphyrin).

The anode (2 cm^2) was prepared from 45 wt.% Pt/carbon black (25 mg, Pt/CB), VGCF (25), and PTFE (5). The electrodes were attached to each sides of the Nafion-117 with Nafion solutions under 5 MPa at 140 °C.

As mentioned above, the prepared unit of the cathode/Nafion-117/anode was attached at the center position of the cell. Deionized water (0.5 mL) was poured to the level covering half of the cathode. O_2 (1 atm, 20 mL) and H_2 (1 atm, 20 mL) were introduced to each compartment. This reaction mode was called mode-1 (Fig. 1). Other three different reaction modes were conducted at the later experiments as below, mode-2; deionized water was poured to a level covering half of both the anode and cathode, mode-3; no deionized water was at the cathode and anode, and mode-4; deionized water was poured to a level covering half of the anode. The current and the cathode and anode potentials were monitored using the electrochemical instrument.

When the circuit was shorted, rapid initial decrease in current was observed and stable current continued after 5 min for the four reaction modes. The reaction was continued for 2 h. Current density (I_d) indicated in this paper was average value for 2 h. If we choose a suitable cathode, 2-electron reduction of O_2 to H_2O_2 (Eq. (1)) would proceed at the cathode under the short circuit conditions. A yield of H_2O_2 was determined by a chemical titration with $KMnO_4/H_2SO_4$ aqueous solutions. Another product is water by 4-electron reduction of O_2 (Eq. (2)), successive 2-electron reduction of H_2O_2 (Eq. (3)) or decomposition of H_2O_2 (Eq. (4)). A current efficiency (CE) for the H_2O_2 formation was calculated from a yield of H_2O_2 and a quantity of charge passed for 2 h (Eq. (5)). The CE corresponds selectivity to H_2O_2 based on H_2. Conversion of H_2 (20 mL min^{-1}) depends on the current, 1.44 A cm^{-2} as the 100% conversion. Conversion of O_2 (20 mL min^{-1}) depends on the current and the product selectivity, 1.44 A cm^{-2} with 100% selectivity to H_2O_2 as the 100% conversion.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (3)$$

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \quad (4)$$

$$\mathrm{CE} = 2(H_2O_2\text{yield}) \times 96485/(\text{Quantityofchargedpassed}) \quad (5)$$

3. Results and discussions

3.1. Screening of electrocatalysts and supports for formation of neutral H_2O_2

A potential of the Pt/CB anode in P(H_2) = 1 atm was −0.28 V (Ag/AgCl) under open-circuit conditions; therefore, a candidate cathode must reduce O_2 to H_2O_2 at >−0.28 V. We tested a mixed-carbon cathode prepared from activated carbon (AC) and vapor growing carbon fiber using the reaction mode-1. The AC + VGCF cathode was active for the formation of a neutral H_2O_2 solution by the Exp-SPE electrolysis of water and O_2 [18]. When the circuit was shorted, stable current flowed after 5 min and steady formation rate of H_2O_2 was obtained for 2 h. H_2O_2 accumulated in the deionized water in the cathode and the concentration increased with the process time in mode-1. The cathode and the anode potentials were −0.24 V (Ag/AgCl) under short-circuit conditions. The H_2O_2 concentration of 0.40 wt.% and the CE of 9.8% at 2 h were not excellent but the direct formation of neutral H_2O_2 solution from O_2 and H_2 was performed.

We prepared various electrocatalyst candidates (0.3 wt.% loading based on metal) supported on AC and VGCF for the H_2O_2 synthesis. We have reported that the heat-treated Mn-porphyrin/AC was active for the formation of H_2O_2/H_2SO_4 solutions [15]. Therefore, various metal-porphyrin derivatives were examined for the neutral H_2O_2 formation and well-known catalysts of Pd and Au were also examined [3–9].

Fig. 2 shows the electrocatalytic activity of electrocatalyst/AC + VGCF cathode for the neutral H_2O_2 formation in mode-1, (a) I_d and CE, (b) formation rate (R(H_2O_2)) and concentration of H_2O_2 (C(H_2O_2)). The result of the AC + VGCF cathode was also indicated. Mn-TPP/AC heat-treated at 823 K (Mn-TPP/AC(823)) showed very low electrocatalytic activity for the neutral H_2O_2 formation in this system. Co-TPP, Ni-TPP and Pd-OEP/AC(823) were also not efficient. On the other hand, Au^0/AC showed higher electrocatalytic activity for the neutral H_2O_2 formation than AC, but the advantage was a little. The electrocatalysis of Au^0 on AC was not significant in our system. The Co-TPP/AC(823) and Pd^0/AC showed higher I_d but H_2O_2 did not accumulated for 2 h; therefore, the CE, R(H_2O_2) and C(H_2O_2) were zero. These results suggested that AC was not suitable support for the neutral H_2O_2 formation although it was good for the H_2O_2/H_2SO_4 formation.

Next, VGCF was examined as a support of electrocatalysts for the neutral H_2O_2 formation in mode-1, as shown in Fig. 3. We found that Co-TPP/VGCF(823) and Co-OEP/VGCF(823) remarkably enhanced the neutral H_2O_2 formation. In contrast, VO-TPP, Mn-OEP, Ni-TPP, and Ru-TPP were not efficient. Other Co complexes, Co-Pc and Co(acac)$_2$ were used as the electrocatalyst precursor. The Co-Pc/VGCF(823) showed a higher I_d but the formation rate of H_2O_2 was very low. The Co(acac)$_2$/VGCF(823) did not function at all. These results indicate that the heat-treated Co-porphyrin/VGCF has particular and efficient electrocatalysis for the neutral H_2O_2 formation; however, the Co-TPP/AC(823) should have high catalytic

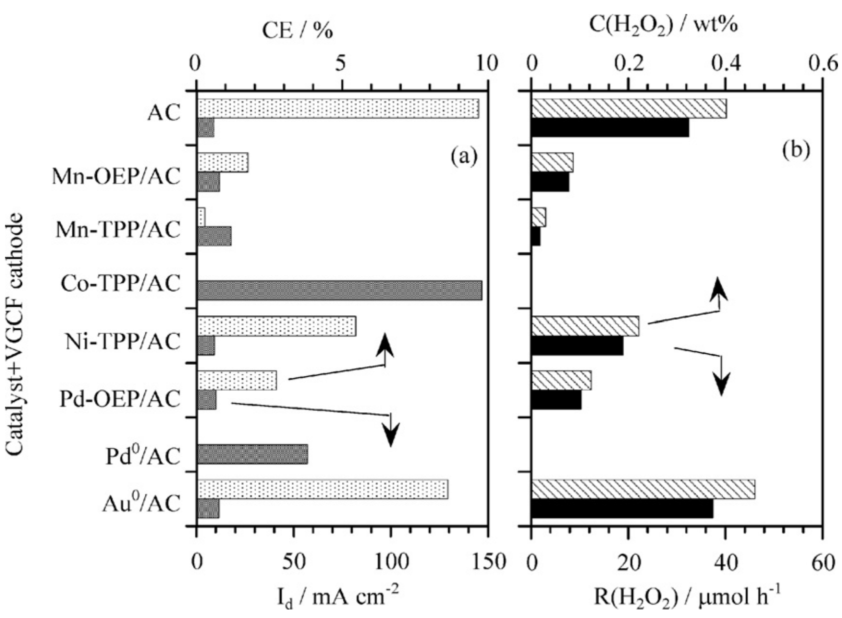

Fig. 2. Screening of various electrocatalyst supported on AC for the formation of H_2O_2 using the PEMFC reactor (mode-1). (a) Current density (I_d) and current efficiency (CE), (b) formation rate ($R(H_2O_2)$) and concentration ($C(H_2O_2)$). $T = 278$ K, cathode: metal-porphyrin/AC(823) + VGCF, 0.3 wt.% metal loading against AC, 0.5 mL of deionized water, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, H_2 20 mL min^{-1}. Pd^0/AC and Au^0/AC prepared by reduction with H_2 at 573 K.

activity for 4-electron reduction of O_2 (Eq. (2)), successive reduction of H_2O_2 (Eq. (3)), or decomposition of H_2O_2 (Eq. (4)). Properties of carbon supports strongly affect electrocatalysis of heat-treated Co-porphyrin.

3.2. Optimization of heat-treated Co-TPP/VGCF electrocatalyst and cathode

The Co-TPP/VGCF(823) and Co-OEP/VGCF(823) showed significant electrocatalysis for the neutral H_2O_2 formation; in contrast, none heat-treated one did not show the electrocatalytic activity of the reduction of O_2. Therefore, effects of heat-treatment temperature of the Co-TPP/VGCF on the H_2O_2 formation in mode-1 were studied in Fig. 4. The electrocatalytic activity of the Co-TPP/VGCF for the H_2O_2 formation generated by a heat treatment above 673 K and the formation rate of H_2O_2 increased with heat-treatment temperatures. The maximum formation rate was obtained at 1073 K. The I_d corresponding to electrochemical reduction rate of O_2 varied as similar as the formation rate of H_2O_2, and showed the maximum at 1073 K. The concentration of H_2O_2 achieved 1.0 wt.% using Co-

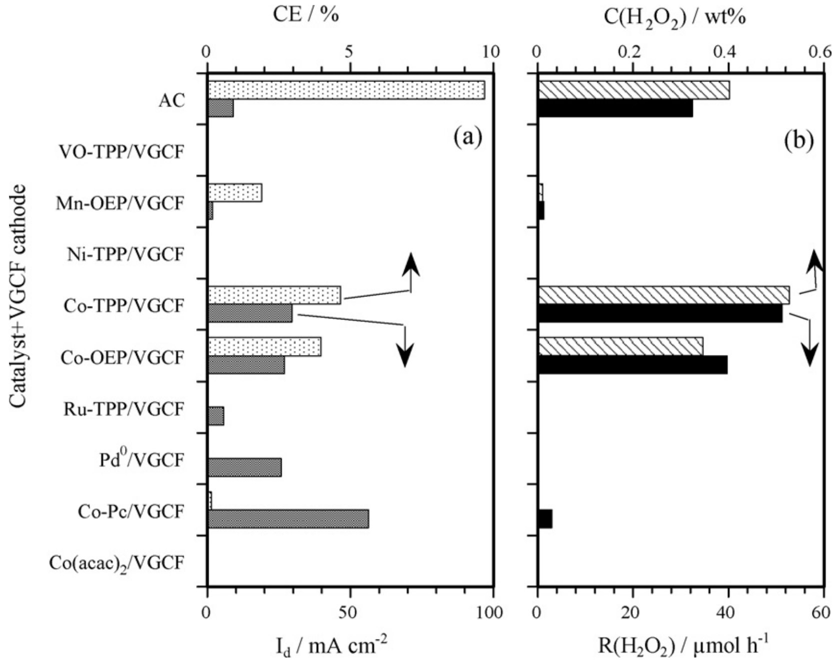

Fig. 3. Screening of various electrocatalyst supported on VGCF for the formation of H_2O_2 using the PEMFC reactor (mode-1). (a) I_d and CE, (b) $R(H_2O_2)$ and $C(H_2O_2)$. $T = 278$ K, cathode: metal-porphyrin/VGCF(823) + VGCF, 0.3 wt.% metal loading against VGCF, 0.5 mL of deionized water, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, H_2 20 mL min^{-1}. Pd^0/VGCF prepared by reduction with H_2 at 573 K.

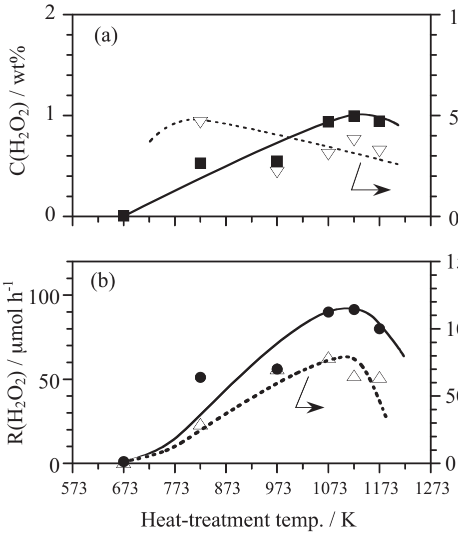

Fig. 4. Effects of heat-treatment temperature of electrocatalyst precursor of Co-TPP/VGCF on the H_2O_2 formation using the PEMFC reactor (mode-1). (a) The C(H_2O_2) and CE, and (b) R(H_2O_2) and I_d. T = 278 K, cathode: 0.3 wt.% CoTPP/VGCF + VGCF, 0.5 mL of deionized water, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, H_2 20 mL min^{-1}.

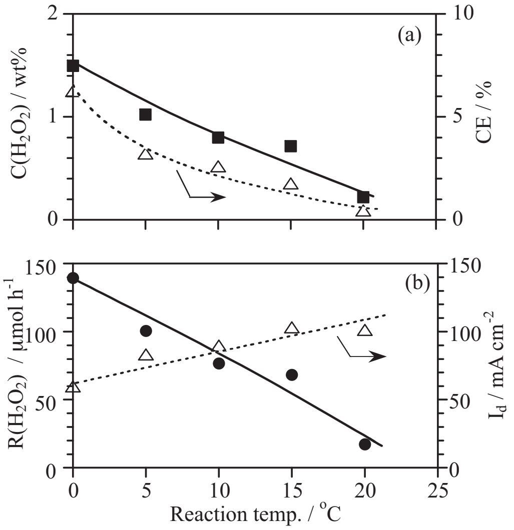

Fig. 6. Effects of reaction temperature on the H_2O_2 formation using the PEMFC reactor (mode-1). (a) The C(H_2O_2) and CE, and (b) R(H_2O_2) and I_d. Cathode: 0.3 wt.% CoTPP/VGCF(1073) + VGCF, 0.5 mL of deionized water, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, H_2 20 mL min^{-1}.

TPPP/VGCF(1073); however, the CEs of 3–4% were low for all heat treatments from 823 to 1173 K. A higher CE, selectivity based on H_2, is essential for the production of H_2O_2.

Effects of Co loadings from 0 to 0.50 wt.% on the formation of H_2O_2 were studied in Fig. 5. The I_d increased with Co loadings and achieved to a plateau at 0.50 wt.%. The formation rates of H_2O_2 were almost constant below 0.30 wt.%. Therefore, the CE increased by decreasing the Co loading from 0.3 to 0.05 wt.% and was over 8%. These results indicated a lower loading of Co of the Co-TPP/VGCF(1073) was efficient for the H_2O_2 formation; of course, no loading of Co was inactive.

Effects of reaction temperatures on the H_2O_2 formation were studied in Fig. 6. The I_d decreased with decreasing reaction temperatures from 20 to 0 °C; in contrast, the formation rate of H_2O_2 increased. Therefore, higher CE and concentration of H_2O_2 were obtained at 0 °C. These dependences of the formation rate on reaction temperatures suggested that successive reduction or decomposition of H_2O_2 should determine the final yield of H_2O_2. In other words, suppression of the successive reactions is essential for the efficient production of H_2O_2.

Thickness of the Co-TPP/VGCF(1073) + VGCF cathode was controlled by reduction of amounts of components with keeping their proportion. Fig. 7 showed effects of the thickness of the cathode on the formation rate of H_2O_2. The standard thickness was 0.5 mm. The formation rate of H_2O_2, I_d, CE and concentration of H_2O_2 were almost constant between 0.6 and 0.3 mm thickness of the cathode. Significant increases of the formation rate, CE, and concentration were observed at 0.2 mm thickness. If we could prepare a thinner cathode than 0.2 mm, a better result would be obtained.

The electrochemical reduction of O_2 to H_2O_2 should proceed at the three-phases boundary of Nafion-H (liquid-like phase), Co-TPP/VGCF surface (solid phase), and O_2 (gas phase). In other words,

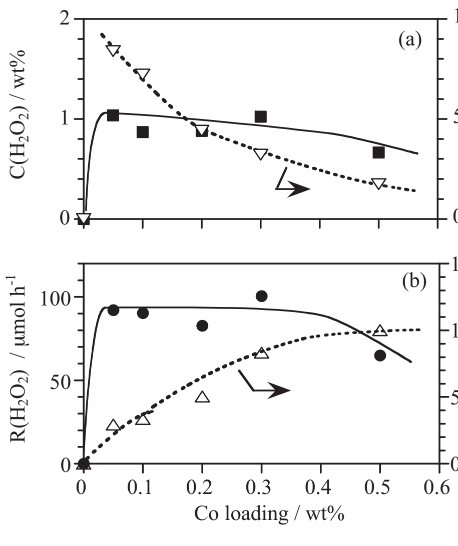

Fig. 5. Effects of Co loading of Co-TPP/VGCF (1073) electrocatalyst on the H_2O_2 formation using the PEMFC reactor (mode-1). (a) The C(H_2O_2) and CE, and (b) R(H_2O_2) and I_d. T = 278 K, cathode: CoTPP/VGCF(1073) + VGCF, 0.5 mL of deionized water, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, H_2 20 mL min^{-1}.

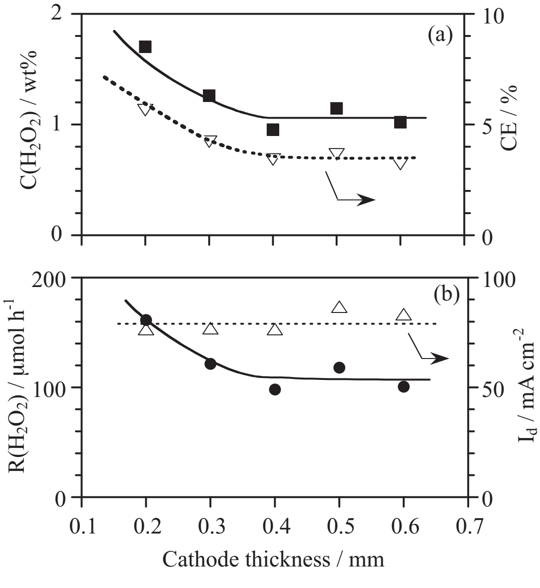

Fig. 7. Effects of thickness of the 0.3 wt.% CoTPP/VGCF(1073) + VGCF cathode on the H_2O_2 formation using the PEMFC reactor (mode-1). (a) The C(H_2O_2) and CE, and (b) R(H_2O_2) and I_d. T = 278 K, cathode: CoTPP/VGCF:VGCF:PTFE = 18:30:3 (wt.%), 0.5 mL of deionized water, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, H_2 20 mL min^{-1}.

Table 1
Effects of reaction modes on the formation of H_2O_2 using the Co-TPPP/VGCF(1073) electrocatalyst at 5 °C.

Run	Conditions mode[a], method[b]	I_d (mA cm^{-2})	R(H_2O_2) (μmol cm^{-2} h^{-1})	C(H_2O_2) (wt.%)	CE (%)	Volume (mL)
1	Mode-1, mixed	29.4	46	1.0	8.4	0.58
2	Mode-1, coated	69.6	139	2.9	12.5	0.65
3	Mode-2, coated	64.4	524	6.5	43.7	1.10
4	Mode-3, coated	69.2	135	12.3	10.4	0.15
5	Mode-4, coated	58.6	475	10.5	43.4	0.61

Cathode: 0.05 wt.%Co-TPP/VGCF(1073) electrocatalyst-VGCF electrode; O_2: 1 atm, 40 mL min^{-1}. Anode: Pt/CB + VGCF electrode; H_2: 1 atm, 40 mL min^{-1}.

[a] Reaction modes; mode-1: 0.5 mL deionized water in the cathode, mode-2: 0.5 mL deionized water in the anode and cathode, mode-3: no deionized water in the cathode and anode, and mode-4: 0.5 mL deionized water in the anode.

[b] Preparation method of the cathode, mixed: cathode prepared by mixing CoTPP/VGCF(1073) and VGCF, coated: cathode prepared by coating solutions of CoTPP/VGCF(1073) and Nafion on the VGCF base electrode.

in the area of the three-phases boundary, the Co-TPP/VGCF electrocatalyst should function for the H_2O_2 formation; however, in the outer area, it should suppress the accumulation by the decomposition of H_2O_2 to water and O_2 (Eq. (4)). In addition, a thick active phase (three-phases boundary) should accelerate the electrochemical reduction of O_2 to H_2O_2 as well as the successive electrochemical reduction of H_2O_2 to water (Eq. (3)). A fast diffusion of O_2 from the gas phase to the active site, a selective electrochemical reduction of O_2 to H_2O_2, and a fast diffusion of H_2O_2 at the outer area should be essential for the neutral H_2O_2 formation.

Based on above hypothesis, we prepared a new cathode which has a thin three-phases boundary by coating 0.05 wt.%Co-TPP/VGCF(1073) on the VGCF base electrode, as mentioned in the experimental section. We compared the results of the H_2O_2 formation using the mixed cathode and the coated cathode, respectively, at run 1 and 2 in Table 1. As you can see clearly, the 0.05 wt.%Co-TPP/VGCF(1073) coated VGCF cathode has advantage for the H_2O_2 formation to compare the mixed cathode, a higher H_2O_2 concentration of 2.9 wt.% and a higher CE of 12.5%. This result proved our hypothesis that the thin layer of the active site (three-phase-boundary) is favorable for the neutral H_2O_2 formation.

3.3. *Effect of reaction modes on H_2O_2 production*

To improve the CE and the formation rate of neutral H_2O_2 at the Co-TPP/VGCF-coated cathode, different reaction modes of mode-2, 3 and 4 were studied at run 3, 4 and 5 in Table 1, respectively. Their I_d's were very similar; however, the results of the H_2O_2 formation drastically differed.

Mode-2 and -4 showed higher formation rates of H_2O_2 than mode-1. The CE in mode-2 and -4 were also 3.5 times higher than that in mode-1. The electrocatalytic activities of the CoTPP/VGCF(1073)-coated cathode in mode-2 and -4 were very similar; however, the concentration of H_2O_2 in mode-4 was twice of that in mode-2, because of dilution of H_2O_2 with initial water (0.5 mL) in the cathode. A higher concentrated H_2O_2 solution of 12.3 wt.% was obtained in mode-3, although the formation rate and CE were as low as that in mode-1. Volumes of cathode solutions varied before and after the reaction. The initial volume of deionized water of 0.5 mL in mode-1 increased to 0.65 mL after the reaction, and that in mode-2 increased to 1.1 mL. On the other hand, H_2O_2 solutions of 0.15 mL in mode-3 and 0.61 mL in mode-4 accumulated in the empty cathode compartment, as summarized in Table 1.

Table 1 indicated that mode-4 was a better reaction mode for the H_2O_2 formation. When we poured deionized water up to the top of the anode in mode-4, the I_d drastically decreased to 1 mA and H_2O_2 was not produced. The exposure operation of the anode to H_2 and the cathode to O_2 is essential. Pouring deionized water to cover half of the anode remarkably enhanced the formation rate and CE of H_2O_2 (mode-2 and -4). On the other hand, pouring deionized water to cover half of the cathode did not affect the formation rate and CE of H_2O_2 (mode-1 and -3). The accumulation of water in the cathode compartment was observed by transport of coordinated water to H^+ from the anode to cathode compartments [14,17]. The quantity of water transported to the cathode was estimated from the solution volume in the cathode, sum of coulomb and H_2O_2 yield. The ratio of the quantity of transported water (mol) per transported H^+ (mol), water/H^+, was 2.8 for mode-2 and 3.2 for mode-4. An effect of pouring deionized water to the level covering half of the anode may be washing away of H_2O_2 from the thin three-phase boundary (active site) at the cathode. Quick desorption of H_2O_2 from the three-phase boundary suppresses the successive reduction or decomposition of H_2O_2; therefore, the formation rate and CE of H_2O_2 increased remarkably by covering half of the anode with deionized water.

Fig. 8 shows time courses for the H_2O_2 formation at the Co-TPP/VGCF(1073)-coated cathode using mode-4. Fig. 8(a) shows the yield of H_2O_2 and I_d, and (b) shows the solution volume and concentration of H_2O_2. The I_d slightly decreased with process time but steady formation of H_2O_2 was observed with higher CE than 40% for 8 h. Drops of neutral H_2O_2 solution from the surface of cathode and accumulation at the bottom of cathode compartment were observed for 8 h. As shown in Fig. 8, the yield and volume of H_2O_2 linearly increased and the concentration was higher than 11 wt.% for 8 h. The turnover frequency of Co for the H_2O_2 formation was 14 s^{-1}; thus the total turnover number achieved 4×10^5 for 8 h.

As described above, concentrated H_2O_2 solution dropped from the cathode. In other words, the H_2O_2 solution separated from the cathode; therefore the successive reduction of H_2O_2 (Eq. (3)) and

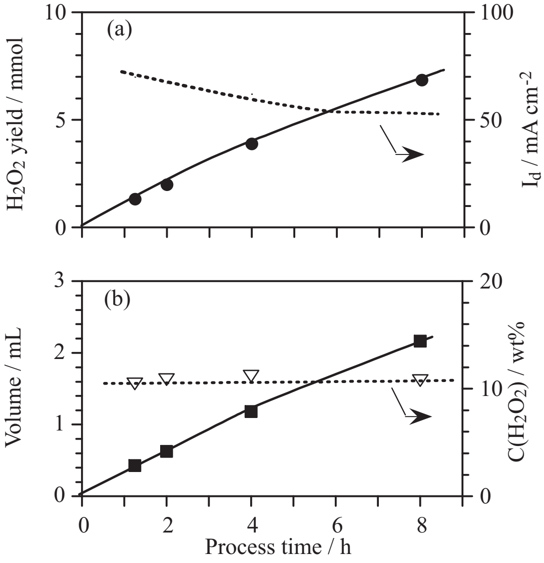

Fig. 8. Time courses of the H_2O_2 formation using the PEMFC reactor (mode-4). (a) H_2O_2 yield and I_d, and (b) solution volume and C(H_2O_2). T = 278 K, 0.05 wt.% CoTPP/VGCF(1073) + VGCF, O_2 20 mL min^{-1}, anode: Pt/CB + VGCF, 0.5 mL of deionized water, H_2 20 mL min^{-1}.

the decomposition of H_2O_2 (Eq. (4)) could be suppressed in our reaction system (mode-4).

Effects of the amount of the electrocatalyst (0.05 wt.%Co-TPP/VGCF) coated on the VGCF cathode ($2\,cm^2$) were studied on the H_2O_2 formation in mode-4. The I_d increased with increasing the amount of the electrocatalyst from 0.1 to 6 mg. The maximum formation rate of H_2O_2 ($0.7\,mmol\,h^{-1}\,cm^{-2}$) was obtained at 4 mg electrocatalyst with $90\,mA\,cm^{-2}$ and the maximum concentration of 13.5 wt.% (4.0 M) was obtained with 42% CE. At this experiment, the conversions of H_2 and O_2 were 6.3 and 4.4%, respectively.

4. Conclusions

The direct production of neutral H_2O_2 solution from O_2 and H_2 was studied using the PEMFC reactor and the heat-treated Co-TPP/VGCF electrocatalyst. Preparation methods of cathode (mixed and coated methods) and the reaction modes (mode-1, 2, 3 and 4) strongly affected the electrocatalysis and the H_2O_2 formation. The most active and efficient cathode was the 0.05 wt.%Co-TPP/VGCF ($2\,mg\,cm^{-2}$) coated on the VGCF electrode. Neutral and no halide of 13.5 wt.% H_2O_2 solution was obtained with 42% CE at 278 K. We have recently clarified the structure of the active site on the heat-treated Co-TPP/VGCF electrocatalyst using XAFS [21]. If the active site can be selectively synthesized on suitable carbon surface, more selective and efficient production of neutral H_2O_2 solution will be performed using the PEMFC reactor.

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