



Electrolytic Synthesis of Peroxyacetic Acid Using *In Situ* Generated Hydrogen Peroxide on Gas Diffusion Electrodes

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An electrochemical method for the preparation of peroxyacetic acid (PAA) using *in situ* generated hydrogen peroxide on the gas diffusion electrode (GDE) as an oxygen cathode has been described. Effects of several experimental conditions, such as current density, oxygen feed rate, electrolyte concentration, electrolytic cell configuration, flow rate of electrolyte solution, and Pt catalyst incorporated into GDE upon the cathodic reaction of oxygen to hydrogen peroxide as well as the production of PAA solution, have been investigated. Hydrogen peroxide is electrogenerated by the reduction of oxygen on the GDE and the generated hydrogen peroxide can undergo a chemical reaction with acetic acid in the presence of solid superacid, Nafion-H as a catalyst to produce PAA. It is also suggested that the formation of PAA is initiated by the active oxygen, O*, electrogenerated on the cathode surface. The current efficiency for the production of PAA was found to be 28% at a current density of 1 A/dm² and electrolyte flow rate of 160 mL/h. A probable reaction mechanism for the formation of PAA is proposed.
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The use of peroxyacetic acid (PAA) has been progressively increasing as disinfectant agents in the food and beverage industries, as industrial and household bleaching, and as oxidants in organic synthesis because of its environmental benefits (the reaction products are oxygen, water, and acetic acid).^{1,2} PAA is an ideal disinfectant in cleaning-in-place systems (typically used in breweries and dairies). To date, PAA is technically prepared by the reaction of concentrated hydrogen peroxide with acetic acid in the presence of an acid catalyst.^{3,4} However, on-site production of PAA has become of great interest because of the cost and hazards associated with the transport and handling of concentrated hydrogen peroxide and PAA.

The applications of electrogenerated hydrogen peroxide have been described in several recent papers for the synthesis of organic compounds, and for the detoxification and removal of organics from aqueous solution.⁵⁻¹⁵ Our recent report has described an electrochemical application of on-site hydrogen peroxide generator to the synthesis of PAA.¹⁶ The main advantages of the proposed method are (i) transportation of dangerous oxidants is not necessary, (ii) the concentrations of H₂O₂ and PAA solution can be controlled, (iii) no mineral acid is needed as catalyst, and (iv) the operation system is simple. However, the current efficiency for the production of PAA was very low (less than 1%).

In this paper, the preparation of PAA using *in situ* electrogenerated hydrogen peroxide at the gas diffusion electrode (GDE) has been systematically studied to obtain a higher current efficiency for PAA production. The factors affecting the cathodic reduction of oxygen to hydrogen peroxide and the preparation of PAA were examined in detail.

Experimental

Chemicals.—Acetic acid (100%) of reagent grade was obtained from Kanto Chemical Co. Ltd. and used without further purification. The superacid catalyst Nafion-H, a perfluorinated resinsulfonic acid, (Type: NR 50) was obtained from DuPont. Organic solvents for the HPLC obtained from Wako Pure Chemical Industries were of spectroscopic grade. All solutions were prepared with deionized water purified by Milli-Q system (Millipore, Japan).

Apparatus and procedure.—The three-chamber electrolytic cell used was basically of the same type as that described previously.¹⁶ The GDEs with and without Pt catalyst were used as the cathodes to electrogenerate hydrogen peroxide. Both GDEs were obtained from

E-TEK Inc. (Somerset, NJ). The amount of Pt catalyst loaded was 0.4 mg/cm². Pt-mesh (80 mesh) electrodes of geometrical areas of 0.19 dm² were used as the anodes. The anode and cathode chambers, having a 0.19 dm² electrolysis area of circular shape, were made of acrylic resin. The middle chamber (reacting chamber) was composed of Nafion-H beads. A Nafion 112 membrane (DuPont) was used as solid polymer electrolyte which was mechanically attached to the anode. This was pretreated in acid to convert the counter ions in the membrane to protons. The anode chamber contained deionized water. Acetic acid was fed into the middle chamber using a metering pump with a constant flow rate.

To examine the influence of the anode material, a two-chamber cell without Nafion membrane was used with Pt-plate anode in place of Pt-mesh anode. The size of electrodes was the same as that of the three-chamber cell. The anode chamber was composed of Nafion-H beads and acetic acid was fed into this chamber. A schematic view of the cells used for the preparation of PAA is shown in Fig. 1.

The middle chamber of the three-chamber cell is the same as the anode chamber of the two-chamber cell, and its width is 0.5 cm and the volume is 9.5 cm³. Gaskets, fittings, and tubes were all made of poly(tetrafluorethylene) (PTFE). Oxygen gas (99.999%) was supplied to the cathode chamber from a gas cylinder at a feed rate of 10-70 mL/min. Electrolyses in both cells were performed with a constant current. All the experiments were carried out at ambient temperature and under atmospheric pressure.

Analysis procedures of products.—The concentration of electrogenerated hydrogen peroxide was determined by volumetric titration using a standard solution of potassium permanganate. The concentration of PAA solution was determined by the HPLC based on the procedures described by Pinkernell *et al.*¹⁷: 1 mL of sample or standard solution was mixed with 2 mL of a solution of 10 mM methyl-p-tolylsulfide (MTS) in methanol in a volumetric flask. Water-methanol mixtures were added to a total volume of 10 mL. A 100 mg of manganese dioxide was added to each 10 mL sample exactly 1 min after addition of the MTS solution. After centrifugation, each sample was injected directly into the sample loop. The HPLC instrument consisted of the following components: pump TOSOH CCPM, injector valve, column TOSOH ODS Ts (dimension 150 × 4.6 mm), detector JASCO UV-970, and mobile phase 75% methanol/25% water. The injection volume was 20 μL at a flow rate of 1 mL/min and the UV detection wavelength was 230 nm.

Safety note¹⁸.—All preparations of PAA were carried out behind a safety shield. PAA solutions should be handled gently because

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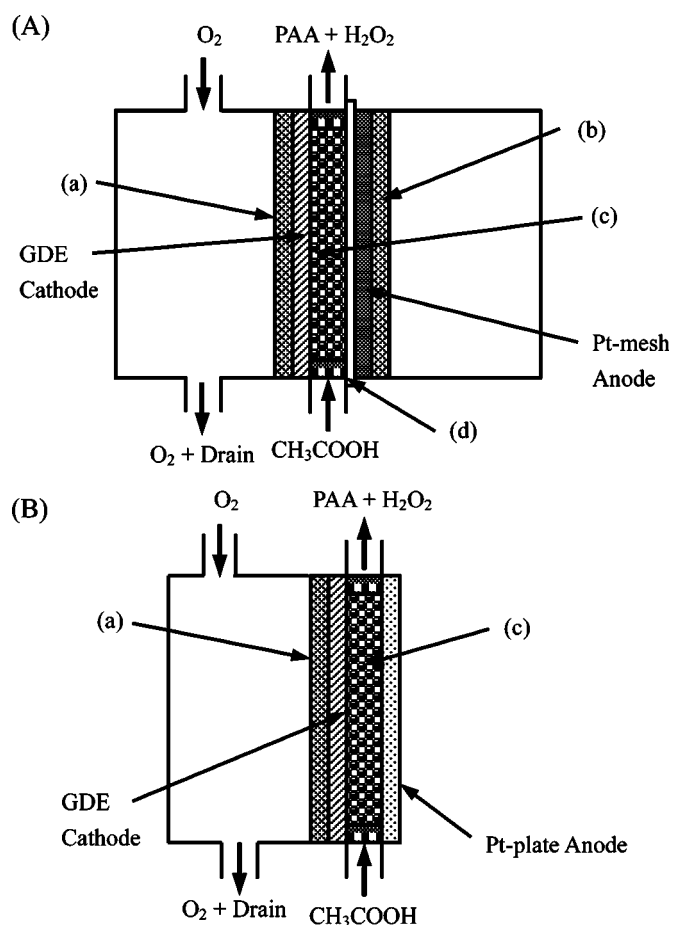


Figure 1. Schematic drawing of (A) three-chamber and (B) two-chamber cells used for the preparation of PAA. (a) Porous carbon plate as the current collector for the cathode, (b) porous Ti-plate as the current collector for the anode, (c) Nafion-H beads, and (d) cation exchange membrane (Nafion).

they cause severe irritant to eyes, skin, and mucous membranes. Concentrated PAA solutions should never be mixed with organic substances including solvents.

Results

Effect of current density.—Figure 2 shows the current density dependence of the current efficiency for the hydrogen peroxide accumulation using a three-chamber cell at 25°C. Here it should be noted that hydrogen peroxide accumulation in the effluent after its electrogeneration at the GDE and further decomposition in the corresponding system, and thus the term “current efficiency for hydrogen peroxide accumulation” is preferable to “current efficiency for hydrogen peroxide production.” The current efficiency is low compared with the usual electrolytic preparation of hydrogen peroxide.^{6,7} This fact can be attributed to a chemical reaction between hydrogen peroxide and acetic acid. Moreover, hydrogen peroxide could undergo decomposition via different chemical and/or electrochemical processes in the solution as well as at the GDE surface.¹⁰ It is also obvious from Fig. 2 that the current efficiency for hydrogen peroxide accumulation decreases from 22.5 to 9% with increasing the current density from 1 to 10 A/dm². The observed decrease of the current efficiency with increasing current density may be mainly due to the formation of hydrogen gas as a side reaction on the cathode. Moreover, further reduction of hydrogen peroxide to water and/or chemical and electrochemical decomposition of hydrogen peroxide significantly can occur as the current density is increased.^{7,10}

Figure 3 shows the effect of current density on the concentration

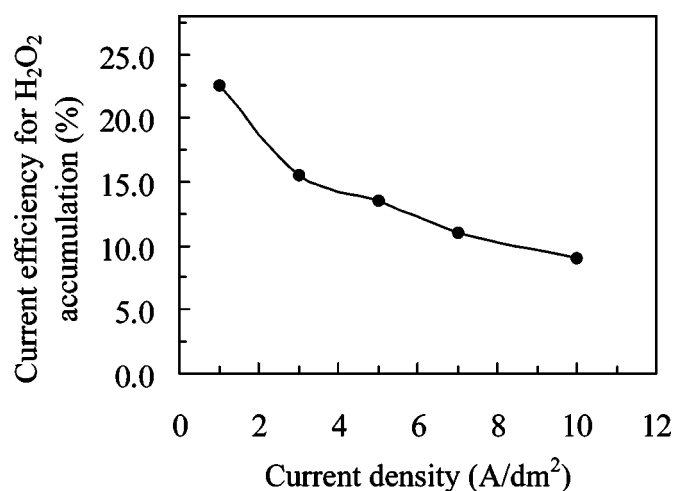


Figure 2. Effect of current density on the current efficiency for hydrogen peroxide accumulation at the GDE in a three-chamber cell. Electrolyte flow rate: 160 mL/h; oxygen feed rate: 10 mL/min; acetic acid concentration: 1 M.

and current efficiency for the formation of PAA via electrogenerated hydrogen peroxide in a three-chamber cell. The PAA solutions of 2.0–2.6 mM were found to be prepared when hydrogen peroxide was electrogenerated in acetic acid. The concentration of PAA slightly increased with increasing current density. The current efficiency for the formation of PAA was observed to decrease with increasing the current density. A current efficiency of *ca.* 9.5% was found at a current density of 1 A/dm².

Effect of oxygen feed rate.—The effect of oxygen feed rate into the cathode chamber on the current efficiencies for hydrogen peroxide accumulation and PAA production in a three-chamber cell is shown in Fig. 4. When the oxygen feed rate was increased, the current efficiency for hydrogen peroxide accumulation gradually increased and attained a constant value (*ca.* 29%). The current efficiency for producing PAA remained almost constant when the oxygen feed rate was increased from 10 to 70 mL/min.

Effect of electrolytic cell configuration.—To find the influence of the anode material, a two-chamber cell without Nafion membrane was used with Pt-plate anode in place of Pt-mesh anode (see Fig. 1). In this case, the concentration of hydrogen peroxide was 20 mM at

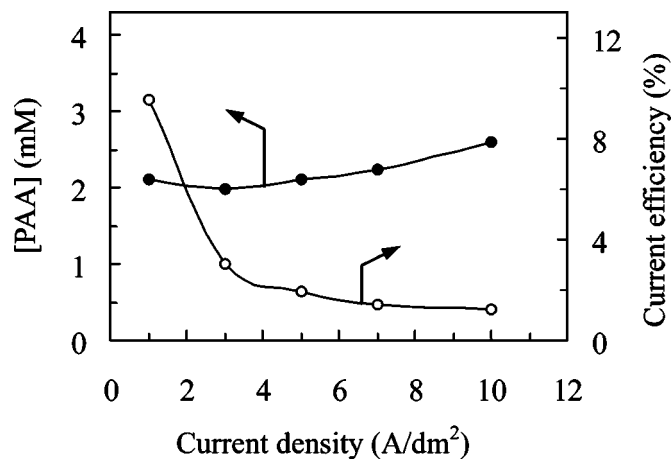


Figure 3. Effect of current density on the concentration and current efficiency for the formation of PAA by electrogenerated hydrogen peroxide at the GDE cathode. Other experimental conditions are the same as in Fig. 2.

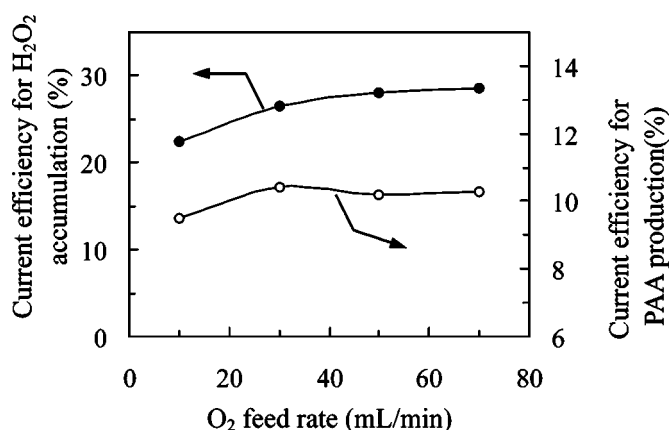


Figure 4. Effect of oxygen feed rate on the current efficiencies for hydrogen peroxide accumulation and PAA production at the GDE cathode in a three-chamber cell. Current density: 1 A/dm²; electrolyte flow rate: 160 mL/min; acetic acid concentration: 1 M.

a current density of 1 A/dm² and electrolyte flow rate of 10 mL/h. Under the same experimental conditions, its concentration was 50 mM when the electrolysis was carried out in a three-chamber cell with Nafion membrane as a separator. The lower concentration of hydrogen peroxide in a two-chamber cell can be attributed to its decomposition at the Pt anode surface.¹⁰

The effect of electrolytic cell type on the formation of PAA using *in situ* generated hydrogen peroxide was insignificant: PAA of the same concentration was produced when the electrolysis was carried out in the three-chamber and two-chamber cells. This result suggests that the decomposition of PAA does not occur at the anode surface, in contrast to the case of hydrogen peroxide.

Effect of electrolyte concentration.—Effect of acetic acid concentration on hydrogen peroxide accumulation and PAA production in a three-chamber cell is shown in Fig. 5. It was found that hydrogen peroxide of *ca.* 35 mM can be produced in 0.1 M acetic acid. The concentration of hydrogen peroxide was observed to increase with increasing the acetic acid concentration.

The concentration of the PAA prepared was highly affected by the electrolyte concentration of acetic acid. The concentration of PAA increased from 1 to 3.6 mM with increasing the concentration of acetic acid from 0.1 to 5 M (Fig. 5). This result can be expected from the fact that the PAA is produced from a chemical reaction of

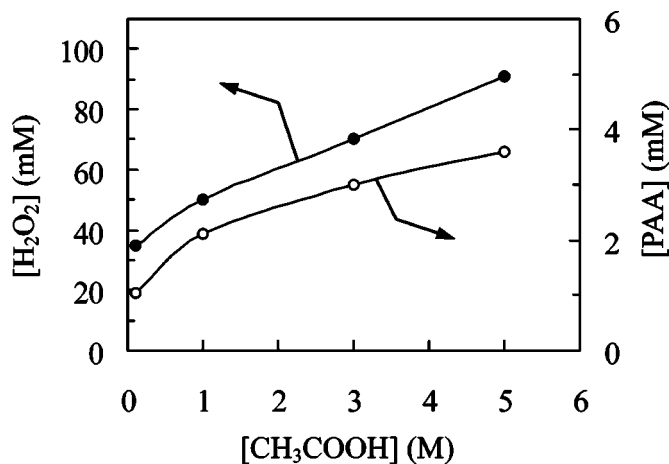


Figure 5. Effect of acetic acid concentration on the concentrations of hydrogen peroxide and PAA in a three-chamber cell. Current density: 1 A/dm²; electrolyte flow rate: 10 mL/h; oxygen feed rate: 10 mL/min.

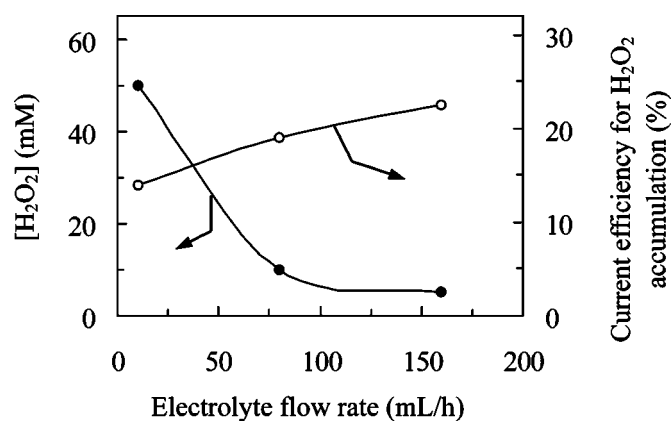


Figure 6. Effect of electrolyte flow rate on the concentration of hydrogen peroxide and current efficiency for its accumulation at the GDE in a three-chamber cell. Current density: 1 A/dm²; oxygen feed rate: 10 mL/min; acetic acid concentration: 1 M.

acetic acid with hydrogen peroxide that is produced from the reduction of oxygen in the presence of Nafion-H beads.^{16,20}

Effect of flow rate of electrolyte solution.—Influence of the electrolyte flow rate on the concentration of hydrogen peroxide and current efficiency for its accumulation in a three-chamber cell is shown in Fig. 6. The concentration of hydrogen peroxide was observed to decrease from 50 to 5 mM with increasing the electrolyte flow rate from 10 to 160 mL/h. But the molar quantity of hydrogen peroxide increased with increasing electrolyte flow rate. Thus a higher current efficiency for hydrogen peroxide accumulation was obtained as the flow rate was increased.

Figure 7 shows the effect of electrolyte flow rate on the concentration and current efficiency for producing PAA using a three-chamber cell. The PAA concentration slightly decreased with increasing the electrolyte flow rate. On the other hand, the current efficiency for the formation of PAA was observed to increase with increasing the electrolyte flow rate as a result of the increased molar quantity of PAA. The current efficiency of 9.5% was achieved at a current density of 1 A/dm² and electrolyte flow rate of 160 mL/h.

Effect of Pt catalyst incorporated into the GDE.—A significant influence of Pt catalyst incorporated into the GDE on the formation of hydrogen peroxide and PAA in a three-chamber cell was ob-

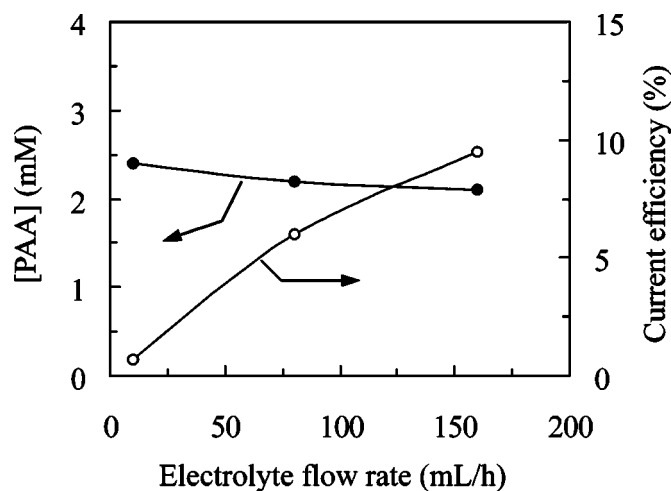


Figure 7. Effect of electrolyte flow rate on the concentration and current efficiency for the formation of PAA by electrogenerated hydrogen peroxide at the GDE cathode. Other experimental conditions are the same as in Fig. 6.

Table I. Effect of Pt catalyst incorporated into the GDE on the formation of H₂O₂ and PAA in a three-chamber cell. Electrolyte flow rate: 160 mL/h; oxygen feed rate: 10 mL/min; acetic acid concentration: 1 M; temperature: 25°C.

Current density (A/dm ²)	Cell voltage (V)	Concentrations (mM)		Current efficiencies (%)	
		PAA ^c	H ₂ O ₂ ^d	PAA ^e	H ₂ O ₂ ^f
1 ^a	3.0	6.2	0.94	28	4.2
1 ^b	3.4	2.1	5	9.5	22.5

^a GDE with Pt catalyst.^b GDE without Pt catalyst.^c The concentrations were determined by HPLC method.^d The concentrations were determined by titration method.^e Current efficiency for PAA production.^f Current efficiency for H₂O₂ accumulation (see text).

served. The results are summarized in Table I. A lower concentration of hydrogen peroxide (0.94 mM) was produced at the Pt catalyst-incorporated GDE, compared with the GDE without Pt catalyst (5 mM). Thus, a lower current efficiency for hydrogen peroxide accumulation was obtained at the Pt catalyst-incorporated GDE. The main pathway for the reduction of oxygen in aqueous media has been well-known to be a four-electron process producing water when Pt is used as electrocatalyst.¹⁹ Moreover, Pt is an efficient catalyst for hydrogen peroxide decomposition.¹⁰

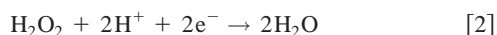
Interestingly, a higher concentration of PAA was produced at the Pt catalyst-incorporated GDE compared with the GDE without Pt catalyst. The concentrations of PAA and hydrogen peroxide were 6.2 and 0.94 mM, respectively, at a current density of 1 A/dm² and electrolyte flow rate of 160 mL/h when the Pt catalyst-incorporated GDE was used as the cathode (Table I), while those concentrations were 2.1 and 5 mM at the GDE without Pt catalyst.

Discussion

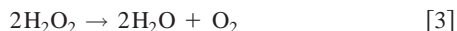
The reduction of oxygen at the GDE cathode in acidic media is mainly two-electron process, which produces H₂O₂.^{6,9}



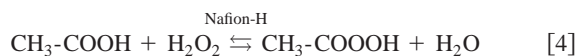
H₂O₂ produced at the GDE cathode can be further reduced to H₂O



or H₂O₂ can be decomposed chemically to generate oxygen



These two pathways are alternatives for the four-electron process, a so-called series mechanism. The formation of PAA can be achieved by a nucleophilic attack of electrogenerated hydrogen peroxide on the protonated acetic acid in the presence of Nafion-H catalyst.^{4,20} The overall reaction is expressed as follows



It should be noted here that Nafion-H beads used as a catalyst accelerate the formation of PAA as sulfuric acid catalyzes the formation of PAA from acetic acid and hydrogen peroxide.^{3,4}

Equation 4 allows us to expect that a higher concentration of PAA can be prepared using a higher concentration of hydrogen peroxide when the concentration of acetic acid is constant. However, the results given in Table I are not consistent with such an expectation from Eq. 4. This may suggest that PAA is not prepared only by an acid-catalyzed reaction, as discussed above. On the basis of previous reports^{14,15,21-24} and the present results, it can be assumed that an active oxygen (O*) might be generated on the cathode surface during the reduction of O₂ by



The activation and oxidation of acetic acid are initiated by the O* to produce PAA



It was also reported that an introduction of metal catalyst to the carbon cathode enhanced the formation of active oxygen.^{14,24} The results in Table I show that the addition of Pt catalyst into the GDE resulted in the preparation of PAA of a higher concentration and at the same time suggest that O* might be more favorably formed at the GDE with Pt catalyst. The detailed mechanism for the generation of O* is not clear at the present state but the mechanism may be similar to the generation of O* by P-450.²¹⁻²³ Otsuka *et al.* have reported the O*-catalyzed partial oxidation of cyclohexane and benzene on the oxygen reduction cathode with Pd, carbon, and Fe catalysts during O₂-H₂ fuel cell reactions.^{14,15}

Other possible actions of Pt as catalyst could also be envisaged, for example, a relatively large proportion of hydroperoxyl radical (HO₂·) or hydroperoxide ion (HO₂⁻) generated during O₂ reduction could remain adsorbed on the Pt surface. Simultaneous adsorption of acetic acid could then favor a heterogeneous reaction between such species at the Pt cathode giving PAA. Reaction between hydroperoxide ion and acetic acid probably could also take place, although with less efficiency, on Nafion-H surface placed in the middle- and anode-chambers. The increase of current efficiency for hydrogen peroxide accumulation and PAA production with increasing electrolyte flow rate is (shown in Fig. 6 and 7) can be simply explained by the faster desorption of hydrogen peroxide and PAA retained on Nafion-H.

Conclusions

Electrochemical preparation of PAA has been achieved from acetic acid in the presence of solid superacid, Nafion-H, as a catalyst using *in situ* generated hydrogen peroxide on GDE at ambient temperature and atmospheric pressure.

The current efficiency for hydrogen peroxide accumulation at the GDE was primarily governed by current density, oxygen feed rate, electrolyte concentration, electrolytic cell configuration, electrolyte flow rate, and Pt catalyst loaded on the GDE. The preparation of PAA by electrogenerated hydrogen peroxide largely depended on the acetic acid concentration and on whether Pt catalyst is loaded on the GDE or not, but it was slightly affected by the current density, electrolyte flow rate, oxygen feed rate, and type of electrolytic cell. The maximum current efficiencies obtained for the production of PAA were 28 and 9.5% at the GDEs with and without Pt catalyst, respectively.

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