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Detection of OH radicals as the effect of Pt particles in the membrane of polymer electrolyte fuel cells

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Abstract

The formation of OH radicals ($\bullet\text{OH}$) for polymer electrolyte fuel cell (PEFC) was investigated with a home-made test cell by means of a fluorescence probe method for several kinds of membrane electrode assembly (MEA) consisting of Nafion. After 12-h operation under open circuit condition, $\bullet\text{OH}$ was detected at both the anode and the cathode sides but the amount was much larger for the anode side. The formation of $\bullet\text{OH}$ considerably depended on the amount of Pt/C catalyst loaded in the MEA. Dispersion of Pt particles in Nafion membranes increased the $\bullet\text{OH}$ formation, but Pt ions did not. Based on the results, the formation mechanism was discussed.

Keywords:

OH radical, Fluorescence probe, Polymer electrolyte fuel cell, Deterioration, Nafion, Pt dispersion

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1. Introduction

Improvement of duration of polymer electrolyte fuel cells (PEFCs) is one of the tasks which should be attained before forthcoming practical wide applications in the world. Factors affecting the duration of PEFC may be poisoning of catalysts, dissolution of Pt catalyst, and degradation of polymer electrolyte membrane [1]. Among these factors, the degradation of membrane causes decrease of the proton conductivity, and consequently, lowering of the performance as deterioration of the membrane. For the deterioration of membranes, the decomposition with heat and the chemical reaction with active oxygen species have been acknowledged [1]. As for the active oxygen species in PEFC systems, the formation of H₂O₂ has been reported [2]. The presence of H₂O₂ was confirmed in drain water [3], exhaust gas [4], and membranes [5] during operation of PEFCs. Since the reactivity of H₂O₂ is suspected to be not so high to decompose polymer electrolytes, the formation of reactive OH radicals (•OH) from H₂O₂ has been suggested [1]. The formation of reactive •OH from H₂O₂ may be caused by electrode reduction of H₂O₂ and/or reduction with metal ions such as Fe²⁺ which are possibly present as contaminants [6]. The latter reaction is well known as Fenton reaction.



In recent years, the formation of Pt nano crystallites in polymer electrolyte membrane (PEM) has been reported [7]. The dissolved Pt ions from cathode are reduced in the membrane to form Pt particles at a certain position from the cathode where the potential is less positive to reduce Pt ions to metallic Pt particles [7], which is called “Pt band”. On the Pt band, O₂ leaked from the cathode may be reduced to form H₂O₂ since the potential is not so positive as the cathode. The formation of H₂O₂ at the Pt particles may produce a large amount of •OH to deteriorate membranes [8]. On the other hand, it was reported that the dispersed Pt particles in membrane scavenges H₂O₂ and the formation of •OH is suppressed [9], concluding that the Pt band functions to decrease the degradation of PEM.

Though the formation of •OH in the PEFC reaction system is suggested, there are only a few experimental researches dedicated to detect •OH [9-13]. In the literature, a spin-trapping ESR method is often used owing to the high sensitivity. In this method, a stable nitroxide radical is adducted with •OH by a trapping reagent. However, the trapping reagents or adducted radicals are sometimes not stable enough for the quantitative analysis [14]. An alternative method to sensitively detect •OH would be a fluorescence probe method [15]. This method is based on the formation of a stable fluorescent product by the reaction of •OH with a specific molecule, such as coumarin and terephthalic acid. As reported previously [15], by using coumarin, we successfully detected •OH formed in the PEFC reactions for a membrane electrode assembly (MEA) supplied from a company. In the present study, we prepared several kinds of MEAs and used the fluorescence probe method to investigate the effect of the amount of Pt/C catalyst loaded in MEA and the dispersed Pt particles in PEM on the •OH formation.

2. Materials and method

2.1 Materials

Ethanol, sodium hydroxide (Nacalai Tesque), butyl acetate, 1-pentanol, 30-wt% hydrogen peroxide (H₂O₂) solution, 20 wt% Nafion in ethanol, sulfuric acid (Wako Chemicals), coumarin, umbelliferone (Tokyo Kasei), tetra-ammine platinum(II) dichloride (Pt(NH₃)₄Cl₂ H₂O, Kojima Chemicals), hexa-chloro platinum(IV) acid (H₂PtCl₆, Nacalai Tesque) were used without further purification. Pt/C catalyst (46.0 wt% Pt, TEC10E50E) was purchased from Tanaka Kikinzoku. Nafion NRE-212 and Nafion 115 membranes (manufactured by DuPont) were obtained from Aldrich Chemicals. The thicknesses of the membranes are reported from the manufacturer to be 51 and 127 μm, respectively.

2.2 Preparation of MEA

The catalyst paste used in the present study was prepared with the following procedure based on the report by Uchida et al.[16]. Pt/C catalyst was dispersed in butyl acetate for 30 min by ultrasonic treatment. Into the dispersion, a 5-wt% Nafion ethanol solution and then butyl acetate were added. The mixture was agitated with ultrasonic treatment. The final weight ratio of the paste was 1:1:60 for Pt/C: Nafion(dried):butyl acetate. Carbon cloth (EC-CC1-060, Toray Co. Ltd.) was employed for the functions of a charge collecting electrode and a gas diffusion layer. The carbon cloth used was a rough cloth with the texture of 8 meshes for 10 mm. After the treatment with the 5-wt% Nafion ethanol solution, one side of the carbon cloth was coated with the catalyst paste using an air-brush spray for the area of 25 mm x 25 mm, followed by drying at 80 °C for 10 min under vacuum. This procedure was repeated until the weight of catalysts became a desired value. Finally the coated carbon cloth was dried at 80 °C for 30 min. The tested quantities of catalyst ranged from 0.1 to 1.25 mg_{Pt} cm⁻², but usually 0.5 mg_{Pt} cm⁻² was adopted. MEAs were prepared by sandwiching a PEM with the catalyst-coated carbon clothes prepared above. The contact between the PEM and the catalyst was attained by pressing the layers under 5 MPa at 150 °C for 10 min. The PEM samples used were Nafion NRE-212, acid treated NRE-212, Nafion 115, and Pt-dispersed Nafion 115.

2.3 Dispersion of Pt ions and Pt particles in Nafion

Pt-dispersed Nafion membranes were prepared with the following procedure based on the report by Hagihara et al. [17]. To prepare Pt-dispersed PEM, Nafion 115 was used instead of Nafion NRE-212 because the mechanical strength of the NRE-212 membrane after the Pt dispersion became too weak to construct a test fuel cell. A sheet (5 cm x 5 cm) of Nafion-115 membrane was treated in 100 mL of 0.26 mM Pt(NH₃)₄Cl₂ solution at 80 °C for 24 h to prepare an ion-exchanged membrane. This ion-exchanged membrane was used as one of the test membranes after washing by boiling pure water. To prepare a Pt-particle dispersed membrane, 100 mL of 1-pentanol was mixed with the Pt(NH₃)₄Cl₂ solution containing ion-exchanged membrane and then the mixture was refluxed at 125 °C for 2 h. By this procedure, Pt ions in the membrane were reduced into Pt metal particles and the color of the membrane became black. The membrane was washed by boiling in pure water. According to the literature [17], the acid groups in the PEM are completely exchanged with Pt ions regardless the state of the membrane, and almost all (98%) of Pt ions are reduced to Pt metal. Under the assumption of complete

exchange, the densities of Pt^{2+} and Pt are calculated to be 0.1 mg cm^{-2} .

2.4 Test cells

To apply the coumarin fluorescence probe method to the reaction occurring in a PEFC system, a test cell equipped with reservoirs for the probe solution was devised as illustrated in Figure 1. The cell was built with two pairs of acrylic resin plates (thickness 5 and 1 mm) and shielded from gas with silicone glue. In each reservoir, 1 mL of coumarin solution contacts with the outside of the carbon cloth of a $1 \text{ cm} \times 2 \text{ cm}$ area so that the surface of the MEA was exposed to probe molecules in solution. The upper part of the cathode end-plate was opened to contact with air and had some grooves (2 mm width and 3 mm depth) on the MEA side to allow the diffusion of oxygen into the probe solution. For the anode end-plate, similar grooves were also curved to lead H_2 gas to the carbon cloth and into the probe solution. The flow rate was about 3 mL min^{-1} and the potential difference between the electrodes was about 1.0 V on the open circuit condition. The probe solution at the anode was deoxygenized by bubbling N_2 gas thoroughly before the experiments. The temperature of the cell was not controlled and remained at room temperature. Before building the test cell, the MEA was soaked in a 30 mL of 10 mM coumarin solution for one night. In the previous study [15], the concentration of coumarin was 1 mM and the MEA was not pre-treated by coumarin solution since the MEA did not adsorb coumarin from the solution. Actually, Nafion NRE-212 used in the present study adsorbed 0.52 mmol of coumarin molecules per 1 g membrane.

Four sets of the test cell of the same design were prepared and used, e. g., to examine for 1, 3, 6, and 12 h operations. After the open circuit voltage (OCV) test operation, the coumarin solutions in contact with the electrodes were transferred to a usual fluorescence quartz cell ($10 \times 10 \times 45 \text{ mm}^3$), and the fluorescence spectra were measured with a spectrofluorometer (Hitachi Co., Ltd., Model 850). Because the optical absorbance of 10 mM coumarin at 332 nm was as large as 30 cm^{-1} , the fluorescence spectra were measured with a cell holder for front detection.

2.5 Formation of $\bullet\text{OH}$ from H_2O_2 on Pt

The formation of $\bullet\text{OH}$ was examined with the following separate batch experiments. A sheet (5 mm x 50 mm) of Pt-modified Nafion membrane or a piece (5 mm x 20 mm) of Pt-mesh was immersed for one night in 20 mL of a 3% H_2O_2 solution containing 10 mM coumarin. After the immersion, the fluorescence spectra of the solutions were measured to estimate the concentration of umbelliferone.

3. Results and discussion

3.1 Formation of $\bullet\text{OH}$

Figure 2 shows fluorescence spectra of 10 mM coumarin solution which was contacted with the electrodes during OCV tests up to 12 h. A large fluorescence band peaked at 393 nm is attributed to coumarin and a small peak observed at 455 nm is assigned to umbelliferone. The increase of the 455-nm peak in the fluorescence spectra indicates the detection of $\bullet\text{OH}$ on OCV

operation of fuel cells. Thus it was confirmed that $\bullet\text{OH}$ can be detected in PEFC reaction as shown in the previous report [15], where the commercially prepared MEA rarely adsorbed coumarin molecules and the coumarin concentration used was one tenth of that in the present experiment.

For quantitative analysis, the fluorescence spectra of authentic umbelliferone in 10 mM coumarin solution were measured. Figure 3 shows the fluorescence intensity at 455 nm as a function of the umbelliferone concentration. The data lay on a linear line, indicating the validity of the fluorescence method to measure the small amount of the probed molecule. By using the linear line in Figure 3, the concentration of umbelliferone, namely the probed $\bullet\text{OH}$, can be calculated from the fluorescence intensity at 455 nm in Figure 2. Since the yield of umbelliferone by the reaction of coumarin with $\bullet\text{OH}$ was reported to be 7% [15, 18], the generated amount of $\bullet\text{OH}$ can be estimated from the umbelliferone concentration by dividing by 0.07.

Figure 4 shows the concentrations of $\bullet\text{OH}$ probed at the both electrode sides on the OCV operations for various periods of time. After 12 h of OCV operation, the concentrations of probed $\bullet\text{OH}$ were about 1 μM and 0.5 μM at the anode and cathode sides, respectively. Since the volume of probe solution was 2 mL and the contact area with electrodes was 2 cm^2 , the amounts of probed $\bullet\text{OH}$ in 12 h were calculated to be 1.0 and 0.5 nmol cm^{-2} for the anode side and the cathode side, respectively.

3.2 Effect of the amount of Pt/C catalyst in MEA

Since the amount of catalyst is known to affect the performances of PEFCs, the effect of the amount of Pt on the formation of $\bullet\text{OH}$ was examined. Figure 5 shows the fluorescence spectra of probe solution at both electrodes with various amounts of Pt/C catalyst. From the fluorescence intensity at 455 nm of these spectra, the amount of $\bullet\text{OH}$ was calculated by the method described above and plotted in Figure 6. When the amount of Pt was as small as 0.1 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$, the formation of $\bullet\text{OH}$ increased compared to the case of 0.25-0.75 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$. Inaba et al. [19] showed that, for a Pt-dispersed glassy carbon rotating ring-disk electrode, a small amount of Pt increased the formation of H_2O_2 because of the incomplete reduction of O_2 . Although under OCV condition the reduction at the cathode does not take place as usual fuel cell reaction, keeping the positive potential against the H_2/Pt anode electrode means the presence of some electrode reactions involving O_2 and Pt, which are considered to be similar to the O_2 reduction reaction of fuel cells. Therefore, the increase of the H_2O_2 formation for the small amount of Pt catalyst probably lead to the increase of $\bullet\text{OH}$ formation at the cathode side as shown in Figure 6. The $\bullet\text{OH}$ increase at the anode side as well as the cathode side is attributable to the diffusion of H_2O_2 from the cathode side to the anode side.

When the amount of Pt was 0.5 - 0.75 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$, lower formation of $\bullet\text{OH}$ was detected. At a higher amount of Pt content, the $\bullet\text{OH}$ formation gradually increased as shown in Figure 6. This increase can be explained by the increase of H_2O_2 formation at the anode by cross leaked O_2 with the increase of the amount of Pt catalyst. The cross leakage of gasses to generate $\bullet\text{OH}$ is supported by the observation that the $\bullet\text{OH}$ formation became about a half when the thickness of the membrane increased from 51 μm (Nafion NRE-212) to 127 μm (Nafion 115) as shown in Figure 7. The increase of the $\bullet\text{OH}$ formation at the cathode side with large amount of Pt seems to

contradict to the observation by Inaba et al. [19], where the formation of H_2O_2 as a byproduct of oxygen reduction decreased with increasing the amount of Pt. In the present experiment under OCV condition, however, with large amount of Pt, H_2O_2 is initially generated by the leaked O_2 at the anode and then diffuses to the cathode. The formation of $\bullet\text{OH}$ from H_2O_2 under the electrode potential of cathode has been proved by our previous ESR study [14].

3.3 Effect of Pt dispersed in membrane

In order to investigate the effect of Pt band and dissolved Pt ions on the degradation of PEM, the formation of $\bullet\text{OH}$ was examined for Nafion 115 membranes modified with dispersing Pt particles and ions. Since the mechanical strength of the membrane was decreased by the modification, Nafion 115 was used in place of Nafion NRE-212. Three sheets of MEA for each modified membrane were fabricated and tested under OCV condition for 12 h. The amounts of detected $\bullet\text{OH}$ for each MEA were averaged and presented in Figure 7, where the error bars indicate the dispersion of the data for three cells. For MEA without membrane modification, the amount of $\bullet\text{OH}$ formed at the anode was about twice of that at the cathode for both Nafion NRE-212 and Nafion 115. This observation indicates that the thickness of the membrane does not affect the formation mechanism, and the effect of Pt on Nafion 115 can be discussed for Nafion NRE-212 as well.

By dispersing Pt particles in the membrane, the formation of $\bullet\text{OH}$ increased by twice at both electrode sides as shown in Figure 7. The increase at the cathode side is likely due to the reduction of H_2O_2 at the surface of dispersed Pt particles, while the increase at the anode side is explained by the increase in the H_2O_2 formation at Pt particles from the leaked O_2 and the H_2 at the anode. When the Nafion membranes were treated to impregnate Pt^{2+} and Pt^{4+} ions, no increase in $\bullet\text{OH}$ was detected. This observation suggests that dissolved Pt ions, as a precursor of the Pt band, do not accelerate the formation of $\bullet\text{OH}$.

The experimental results described above indicated that at the surface of Pt particles $\bullet\text{OH}$ was formed from H_2O_2 . Thus the generation of $\bullet\text{OH}$ was tested in a separate batch experiment with a 3% H_2O_2 solution. Figure 8 shows the umbelliferone concentrations estimated from the fluorescence intensity as the amount of probed $\bullet\text{OH}$. Since the absorbance of 3% H_2O_2 at 332 nm is 0.1 cm^{-1} , the excitation light for fluorescence measurements caused photodecomposition of H_2O_2 into $\bullet\text{OH}$. Then, $0.74 \mu\text{M}$ of umbelliferone (dotted line in Figure 8), which was estimated from the measurement without test samples, is not attributable to the $\bullet\text{OH}$ probed in the each test reaction. Then, the actual concentration of $\bullet\text{OH}$ formed on the test reactions is that exceeded this value.

As exhibited in Figure 8, about $1.7 \mu\text{M}$ of $\bullet\text{OH}$ (actually $0.9 \mu\text{M}$ by subtracting the blank) were formed by the reaction with a Pt-particle modified membrane. When the piece of platinum mesh was immersed, the formation of $\bullet\text{OH}$ was about $6.2 \mu\text{M}$ ($5.5 \mu\text{M}$ by subtracting blank). Thus it was confirmed that at the Pt surface a part of H_2O_2 is converted to $\bullet\text{OH}$. The oxygen gas was evolved from H_2O_2 at the Pt surface, indicating the decomposition of H_2O_2 represented by reaction (2). Then, the $\bullet\text{OH}$ formation may be explained by two side reactions of the decomposition of H_2O_2 ; one electron reduction (3) or oxidation (4) of H_2O_2 would take place at the Pt surface as discussed in the previous reports [12, 14].



Thus, by employing the coumarin fluorescence probe method, the $\bullet\text{OH}$ formation from H_2O_2 at Pt particles in Nafion membrane was evidenced. This observation contradicts to the report by Aoki et al. [9], where the DMPO spin-trapping ESR method was applied to detect $\bullet\text{OH}$. They concluded that $\bullet\text{OH}$ formation was suppressed by the Pt particles dispersed in Nafion membranes. In our experiments connecting to the previous researches [12, 14], the Pt catalysts also decreased the $\bullet\text{OH}$ formation by using the DMPO spin-trapping ESR. Where, with the careful examination of the change of UV spectrum of DMPO, we found that DMPO molecules decomposed at the Pt surface [14]. The decomposition can take place through the H adducts [13, 20] of DMPO at the Pt surface. Therefore, the decrease in the trapped adduct of $\bullet\text{OH}$ is attributable to the decomposition of DMPO spin trap reagent. Thus it may be difficult to detect $\bullet\text{OH}$ by using trapping reagents in the presence of Pt.

4. Conclusions

We demonstrated that a coumarin fluorescence probe method is applicable to detect $\bullet\text{OH}$ formed in PEFC systems. On the 12-h OCV operation of test cells with the prepared MEA, it was confirmed that the $\bullet\text{OH}$ formation is larger at the anode side, though the significant amount of $\bullet\text{OH}$ was detected at the cathode side as well. The formation of $\bullet\text{OH}$ depended on the amount of Pt/C catalyst in MEA. For Pt loading of 0.5 – 1.0 mgPt cm⁻², $\bullet\text{OH}$ formation was barely varied. Above and below these values the increase of $\bullet\text{OH}$ formation was observed. Dispersion of Pt particles in PEM increased the $\bullet\text{OH}$ formation, while Pt ions did not. The present observation supports the reports that the Pt band in PEM accelerates the PEFC deterioration [8], although this is based on the limited observation of the present study.

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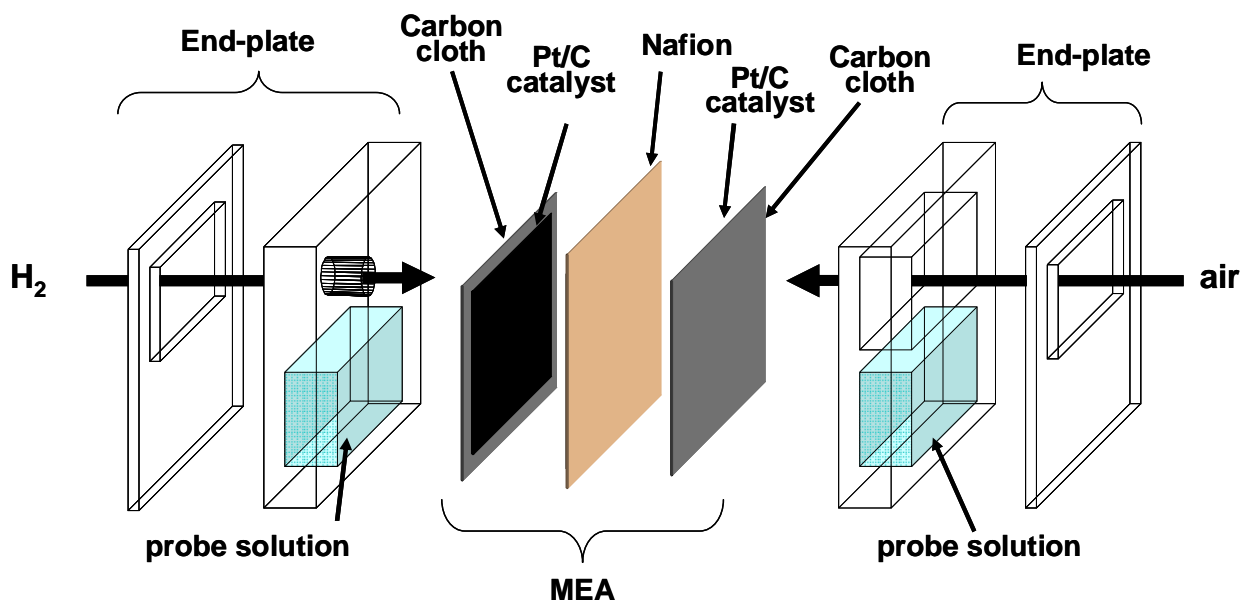
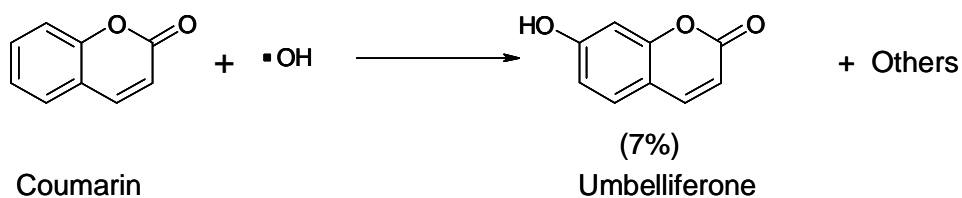


Figure 1. (Color online) Expanded illustration of the test cell. The thicknesses of the acrylic resin plates for these end plates are 1 and 5 mm, and the dimension of the MEA is 30 mm x 30 mm. These parts were secured by four bolts of 4 mm diameter.

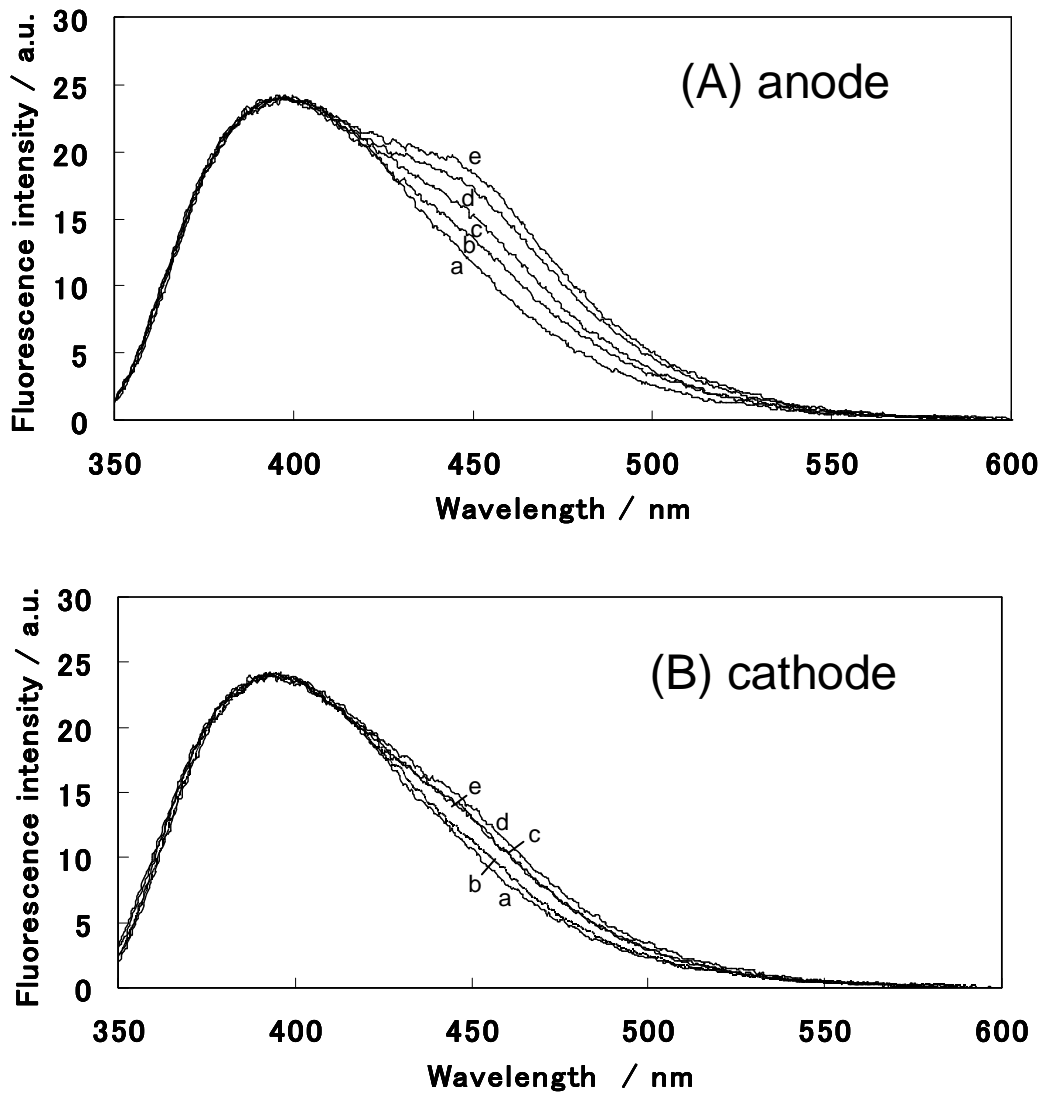


Figure 2. Fluorescence spectra of 10 mM coumarin solutions contacted with (A) anode and (B) cathode for detecting OH radicals after OCV tests for (a) 0, (b) 1, (c) 3, (d) 6, and (e) 12 h. Increase of the intensity at 455 nm indicates the formation of umbelliferone. Excitation wavelength; 332 nm.

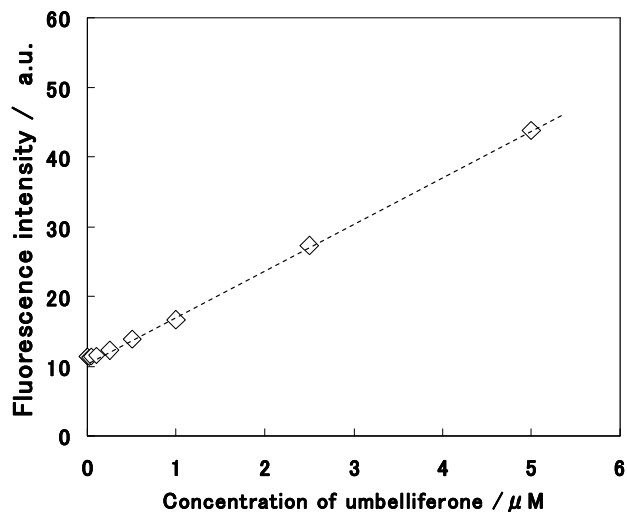


Figure 3. Fluorescence intensity at 455 nm as a function of the concentration of umbelliferone in 10-mM coumarin aqueous solution. Excitation wavelength; 332 nm.

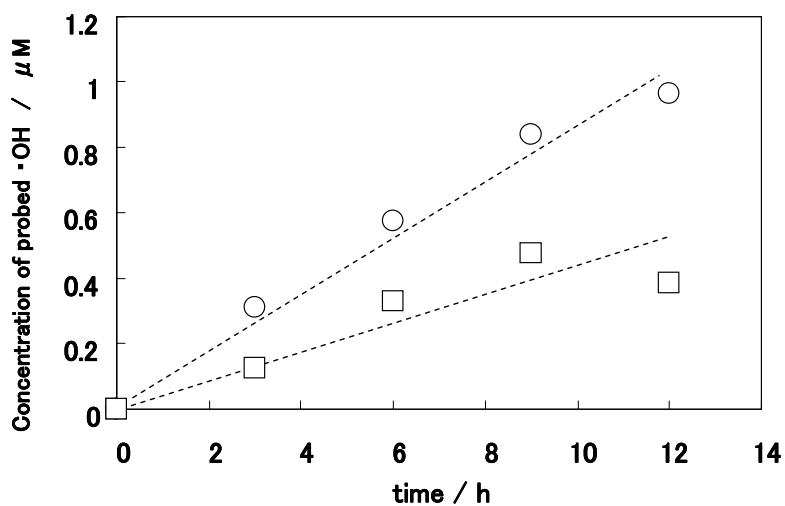


Figure 4. Concentration of umbelliferone as probed OH radicals which were formed at the anode side (\circ) and the cathode side (\square) on the OCV operations of various periods of time.

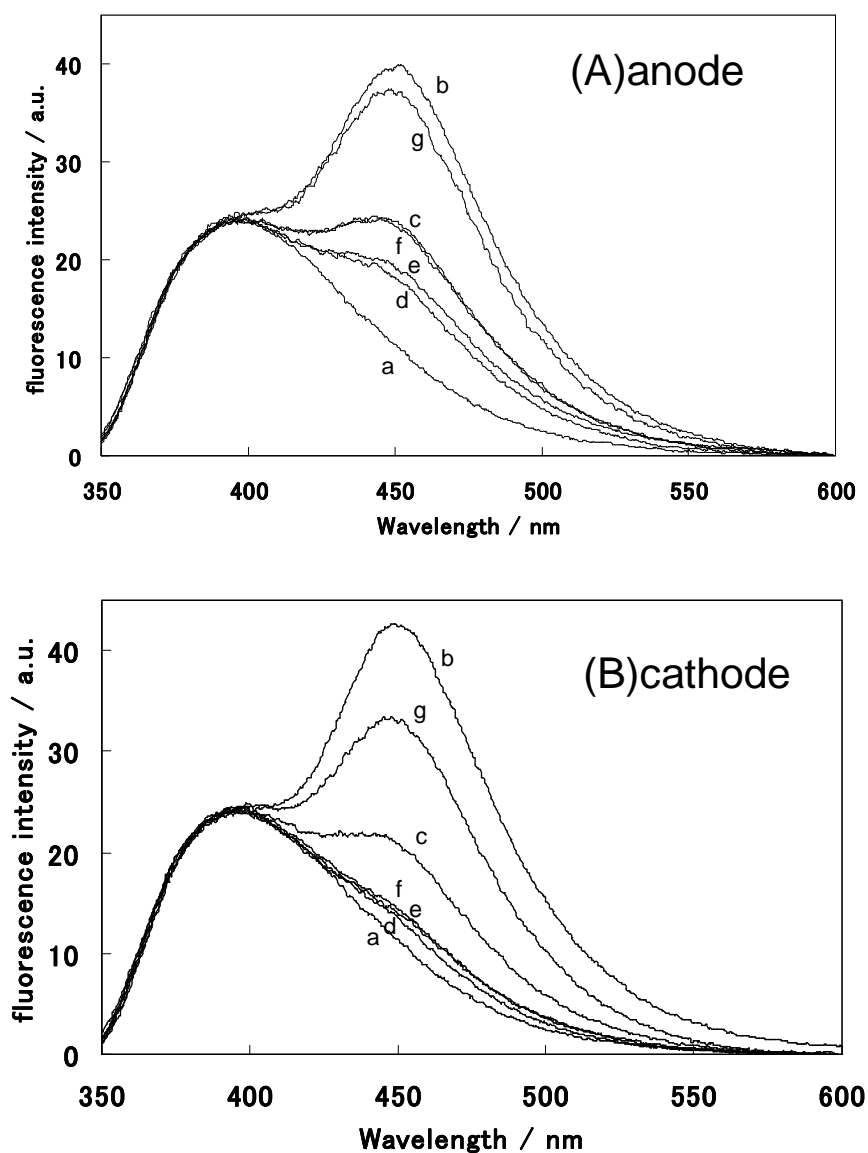


Figure 5 Fluorescence spectra of 10 mM coumarin solutions (a) and those contacted with (A) anode and (B) cathode for detecting $\bullet\text{OH}$ radicals after OCV tests for 12 h. Pt/C catalyst loaded were (b) 0.1, (c) 0.25, (d) 0.5, (e) 0.75, (f) 1.0, and (g) 1.25 mg cm^{-2}

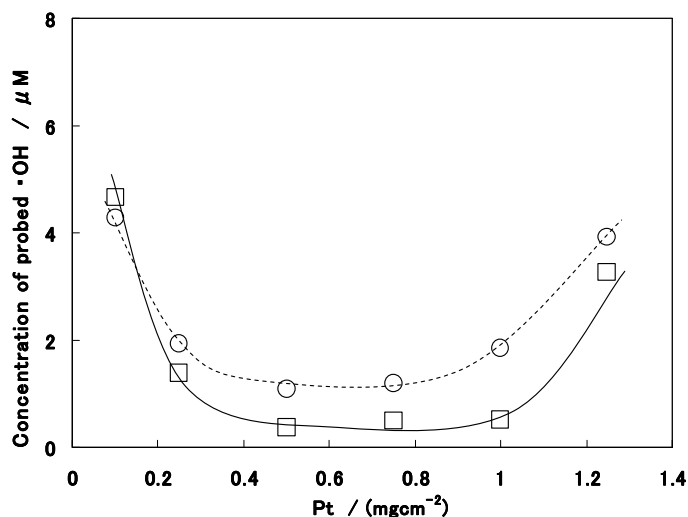


Figure 6. Concentration of probed •OH radicals at the anode side (○) and the cathode side (□) on 12-h OCV operation for the PEFC prepared with Nafion NRE-212.

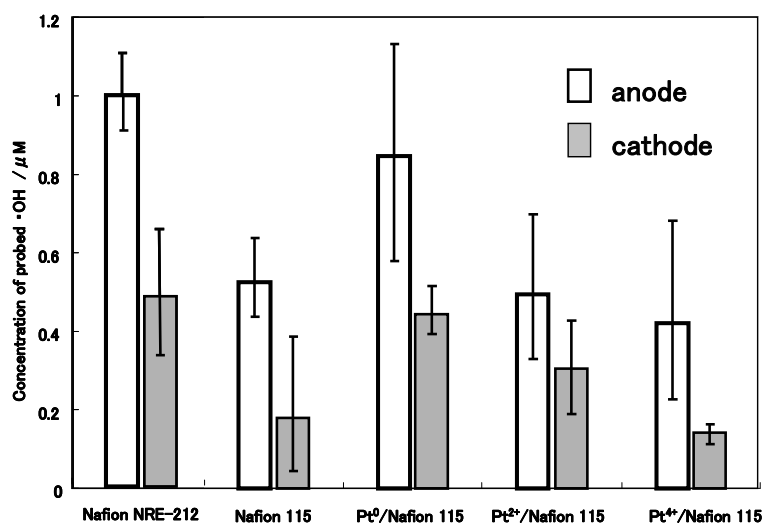


Figure 7. Concentration of probed OH radicals at the anode side (□) and the cathode side (■) on the 12-h OCV operation for the PEFC prepared with various Nafion membranes; Nafion NRE-212, Nafion 115, Pt-dispersed Nafion 115, and Pt ion (2+ and 4+) exchanged Nafion 115

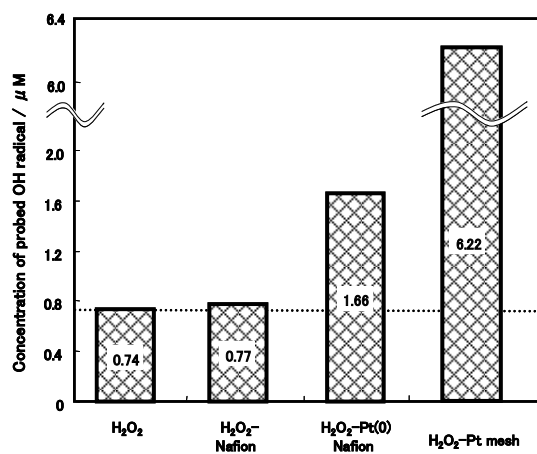


Figure 8. Concentration of OH radicals detected by 10-mM coumarin solution on the reaction of 3% H_2O_2 with the modified Nafion-115 membranes. Without membrane OH radicals were produced by the 332 nm irradiation for fluorescence measurements because the H_2O_2 concentration in the reaction solution was very high.