Short communication

Reduction of hydrogen peroxide production at anode of proton exchange membrane fuel cell under open-circuit conditions using ruthenium–carbon catalyst

Un Ho Jung, Seong Uk Jeong, Kook Chun, Ki Tae Park, Hyang Mee Lee,
Dong Woong Choi, Sung Hyun Kim*

*Department of Chemical & Biological Engineering, Korea University, 1 Anam-Dong,
Sungbuk-Ku, Seoul 136-701, Republic of Korea*

Abstract

This study examines the effect of hydrogen peroxide (H_2O_2) on the open-circuit voltage (OCV) of a proton exchange membrane fuel cell (PEMFC) and the reduction of H_2O_2 in the membrane using a ruthenium/carbon catalyst (Ru/C) at the anode. Each cathode and anode potential of the PEMFC in the presence of H_2O_2 is examined by constructing a half-cell using $1.0\,M\ H_2SO_4$ solution as an electrolyte and Ag/AgCl as the reference electrode. H_2O_2 is added to the H_2SO_4 solution and the half-cell potential is measured at each H_2O_2 concentration. The cathode potential is affected by the H_2O_2 concentration while the anode potential remains stable. A Ru catalyst is used to reduce the level of H_2O_2 formation through O_2 cross-over at the interface of a membrane and the anode. The Ru catalyst is known to produce less H_2O_2 through oxygen reduction at the anode of PEMFC than a Pt catalyst. A Ru/C layer is placed between the Nafion® 112 membrane and anode catalyst layer and the cell voltage under open-circuit condition is measured. A single cell is constructed to compare the OCV of the Pt/C only anode with that of the Ru/C-layered anode. The level of hydrogen cross-over and the OCV are determined after operation at a current density of $1\,A\,cm^{-2}$ for 10 h and stabilization at open-circuit for 1 h to obtain an equilibrium state in the cell. Although there is an increase in the OCV of the cell with the Ru/C layer at the anode, excessive addition of Ru/C has an adverse effect on cell performance.
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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are receiving much attention due to their promising properties as a power sources for small-scale [1–3] and large-scale [4–6] applications. Several degradation mechanisms for the long-term stability have been investigated. In particular, studies of the degradation of Nafion® membranes due to hydrogen peroxide, which is formed as a by-product [7–9] have been conducted by many research groups [10–14]. The membrane and membrane electrode assembly (MEA) become very unstable in the presence of H_2O_2 due to its strong oxidative characteristics. There are two different mechanisms for H_2O_2 generation. The first is O_2 reduction at the cathode during operation, as expressed by [11]

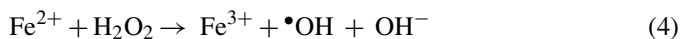$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

The other pathway is based on O_2 cross-over from the cathode through membrane to the anode side, which provides the O_2 needed to react with hydrogen and produce H_2O_2 [11,12], i.e.:

$$2Pt + H_2 \rightarrow 2PtH \tag{2}$$

$$2PtH + O_2 \rightarrow Pt + H_2O_2 \tag{3}$$
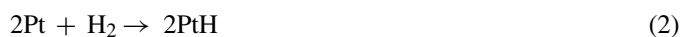
Hydrogen peroxide in itself does not attack the polymer electrolyte membrane. Rather, it reacts with trace metal ions to form $OH^\bullet$ and $HO_2^\bullet$ radicals that attack membrane [15,14]. The process for producing hydroxyl radicals is known as the Fenton

* Corresponding author. Tel.: +82 2 3290 3297; fax: +82 2 926 6102.
E-mail address: kimsh@korea.ac.kr (S.H. Kim).

reaction [16–20], i.e.:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{4}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}OOH \tag{5}$$

Thus, research on the reduction of hydrogen peroxide generation must be investigated to prevent degradation of the membrane and to obtain long-term PEMFC stability.

This study investigates the direct effect of H_2O_2 on the OCV of the cell instead of membrane degradation. The presence of H_2O_2 in the membrane, which was produced by O_2 cross-over, is confirmed by measuring the OCV using half-cell equipment. In addition, a Ru/C catalyst is used at the anode to reduce the level of H_2O_2 production.

2. Experimental

2.1. Half-cell test

Fig. 1 shows a schematic diagram of the half-cell structure. The working electrode was composed of Pt/C, a gas-diffusion layer (GDL) and a Pt wire. The Pt/C was coated with as much as 0.4 mg Pt cm^{-2} on one side of the Nafion® 112 membrane and the opposite side of the membrane was left uncoated in order to come in direct contact with the H_2SO_4 solution. The counter electrode, reference electrode and electrolyte were glassy carbon, Ag/AgCl and 1.0 M H_2SO_4, respectively. Either O_2 or H_2 was fed to the cell at a rate of 50 mL per min with no humidification. When O_2 was fed into the cell, the reaction at the working electrode corresponded to the cathodic reaction of the PEMFC. Hydrogen was applied to the anodic side of the PEMFC. Therefore, the potential of the anodic and the cathodic half-cell could be measured. 1.0 wt.% H_2O_2 was added slowly to the 1.0 M H_2SO_4 solution to determine the effect of H_2O_2 on
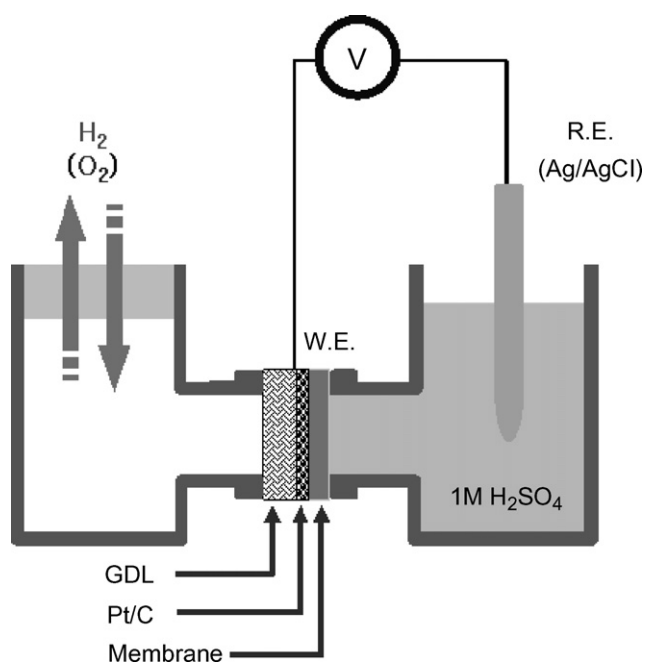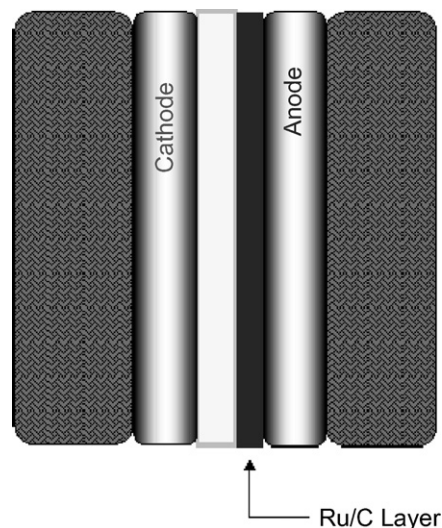

Fig. 1. Schematic diagram of half-cell.

Fig. 2. Schematic diagram of Ru/C layered MEA.

half-cell potential. The H_2O_2 concentration in the H_2SO_4 solution was increased to 100 ppm. Dilution of the H_2SO_4 solution was ignored because the amount of H_2O_2 added was very small. At each concentration, the potential was measured after allowing 30 min for stabilization. All measurements were carried out at 25 °C and at atmospheric pressure.

2.2. Unit-cell test

2.2.1. Preparation of membrane electrode assembly (MEA)

Standard MEA. A Nafion® 112 membrane was pretreated sequentially with 5 wt.% H_2O_2, de-ionized water, 1.0 M H_2SO_4 and de-ionized water at 80 °C for 30 min. A 40 wt.% Pt/C (Johnson Matthey) catalyst, a 5 wt.% Nafion® solution (Dupont) and isopropyl alcohol were mixed under sonication, sprayed on to the Nafion® 112 membrane, and dried at 50 °C for 3 h. The dried MEA was pressed for 2 min at 10 MPa and room temperature. The Pt loading at both the anode and cathode was 0.4 mg Pt cm^{-2} and the effective area of the MEA was 25 cm^2 (5 cm × 5 cm).

MEAs with a Ru catalyst layer. A 40 wt.% Ru/C (E-tek), a 5 wt.% Nafion® solution (Dupont) and isopropyl alcohol were mixed, and sprayed on to the anodic side of a Nafion® 112 membrane, as shown in Fig. 2. The Ru loading was set at 0.05 and 0.1 mg Ru cm^{-2}. A Pt/C catalyst for the anodic part was coated on to the Ru/C layer using the same method described above for the standard MEA.

2.2.2. Single-cell construction

The fuel gas was pure hydrogen and the oxidant gas was pure oxygen. The gases were humidified by passage through bubble-type humidifiers. The relative humidity of the inlet gases was controlled by adjusting the temperature of the humidifiers. The reactant gases were fed to both the anode and cathode using a mass-flow controller through a graphite plate with five serpentine channels, which was used as a bipolar plate. Carbon paper (10BC, SGL Carbon) with a thickness of 430 μm was placed on both sides of the MEA to distribute the gas uniformly on the catalyst layer. For gas sealing, a 300 μm thick

polytetrafluoroethylene (PTFE) sheet was placed between the MEA and bipolar plate. Finally, a stainless-steel end-plate was used to fix the cell structure.

2.2.3. Polarization measurements

The cell temperature was fixed to $70\,^{\circ}\mathrm{C}$ and all experiments were carried out at atmospheric pressure. The O_2/H_2 gas flow was maintained at a stoichiometric ratio of 1.5 at both the anode and the cathode. The temperature of the gas lines to the anode and the cathode were always set to $5\,^{\circ}\mathrm{C}$ above the cell temperature in order to prevent water condensation. The humidifier was set at 65 and $58\,^{\circ}\mathrm{C}$ for the anode and the cathode, respectively. Before measuring polarization curves, each MEA was operated for 12 h at $70\,^{\circ}\mathrm{C}$ and a current density of $1.0\,\mathrm{A\,cm^{-2}}$ for stabilization.

3. Results and discussion

3.1. PEMFC half-cell potential

Under open-circuit conditions, H_2O_2 is produced at the anode by O_2 cross-over. The H_2O_2 diffuses through the membrane to the cathode and becomes electrochemically oxidized at the cathode to cause an internal current because the cathode potential of the PEMFC under open-circuit conditions is about 0.9–1.0 V (versus SHE), which is much higher than that of H_2O_2 oxidation, i.e.:

$$H_2O_2 \leftrightarrow O_2 + 2H^+ + 2e^- \quad (0.68\ \text{V versus SHE}) \qquad (6)$$
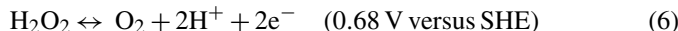
Therefore, the OCV of the PEMFC can be affected by both of H_2 cross-over and H_2O_2 diffusion from the anode side, if there is H_2O_2 production at the interface of a membrane and the anode catalyst layer.

The effect of H_2O_2 in the membrane on the anode and cathode potential of the PEMFC is shown in Fig. 3. The anode potential of the PEMFC is unaffected by H_2O_2 concentrations up to 100 ppm, which is due to the large exchange current density of the H_2 oxidation reaction. The exchange current density
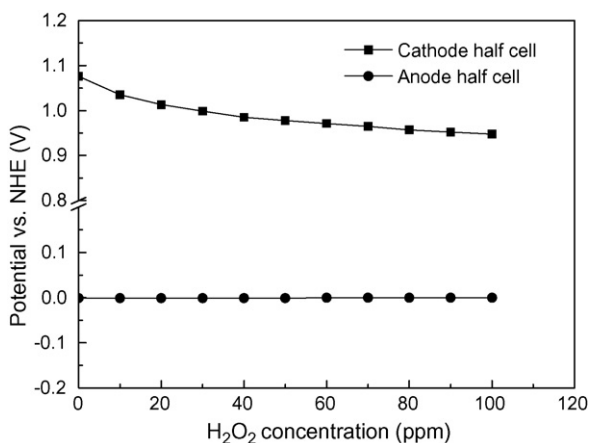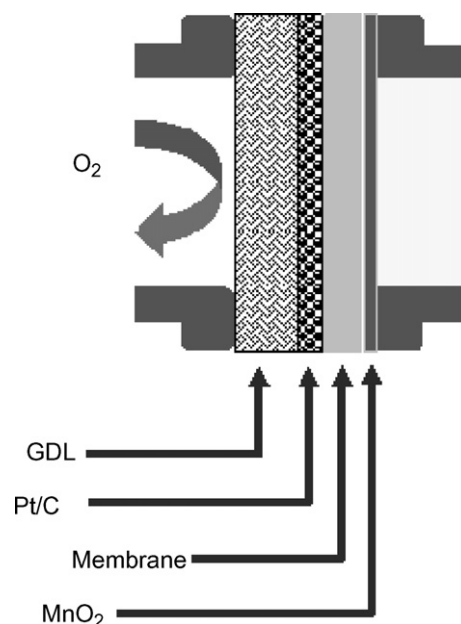

Fig. 4. Schematic diagram of half-cell using MnO_2 layer.

is much larger than that for the O_2 and H_2O_2 reduction reaction so that a small amount of internal current cannot affect the anode potential of the PEMFC. On the other hand, on the cathode side, H_2O_2 can be oxidized electrochemically, which can cause a decrease in the cathode potential. Therefore, the cathode potential of the PEMFC decreases with increasing H_2O_2 concentration. In order to confirm that the electrochemical oxidation of H_2O_2 is responsible for the decrease in the cathode potential, another half-cell was applied using a MnO_2 catalyst, as shown in Fig. 4. The electrochemical oxidation of H_2O_2 on the Pt catalyst is prevented by placing a mixture containing MnO_2 particles and Nafion® ionomer on the opposite side of the Pt/C catalyst layer to decompose the H_2O_2 and prevent migration through the membrane. Note, MnO_2 is a well-known catalyst for the catalytic decomposition of H_2O_2 [21–24]. Therefore, MnO_2 can decompose H_2O_2 chemically in advance of the electrochemical reaction with Pt/C. The results obtained from the half-cell with a MnO_2 layer show that the cathode potential is not affected by the H_2O_2 concentration in the absence of electrochemical oxidation of H_2O_2, as shown in Fig. 5. Therefore, it is reasonable that the decrease in the cathode potential in the half-cell is mainly due to the electrochemical oxidation of H_2O_2.

3.2. Ru/C addition to anode

H_2O_2 is formed as an intermediate during O_2 reduction on various precious metal catalysts. In particular, in the potential region of 0–0.2 V (versus NHE), the level of H_2O_2 production on the Pt catalyst is much higher than in the other potential range, i.e., 0.2–1.0 V versus SHE [14,16,17]. This is related to H_2 adsorption on the Pt surface. In the potential range of 0–0.2 V, the Pt surface is covered with hydrogen atoms through H_2 adsorption and dissociation so that there is an insufficient number of active
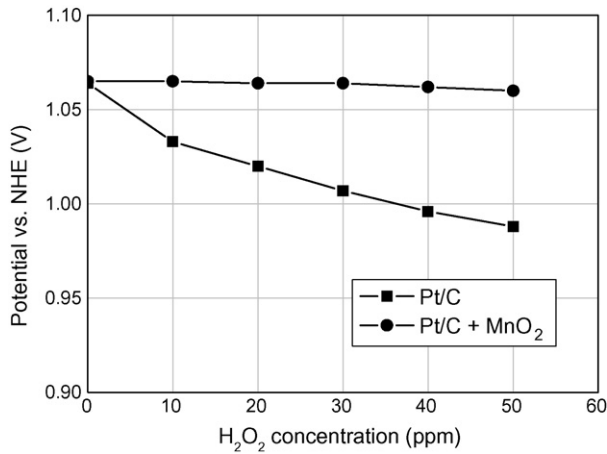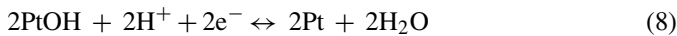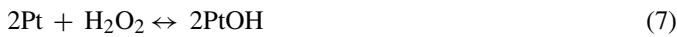

Fig. 3. Half-cell potential of anode and cathode as function of H_2O_2 concentration.

Fig. 5. Half-cell potential of cathode using MnO_2 layer.

sites for H_2O_2 reduction, which is initiated by H_2O_2 adsorption to form initially PtOH by the following reaction [25]:

$$2Pt + H_2O_2 \leftrightarrow 2PtOH \tag{7}$$

$$2PtOH + 2H^+ + 2e^- \leftrightarrow 2Pt + 2H_2O \tag{8}$$

Reduction of H_2O_2 on the Pt catalyst in 1.0 M H_2SO_4 solution with 100 ppm H_2O_2 at 25 °C is shown in Fig. 6(a). The
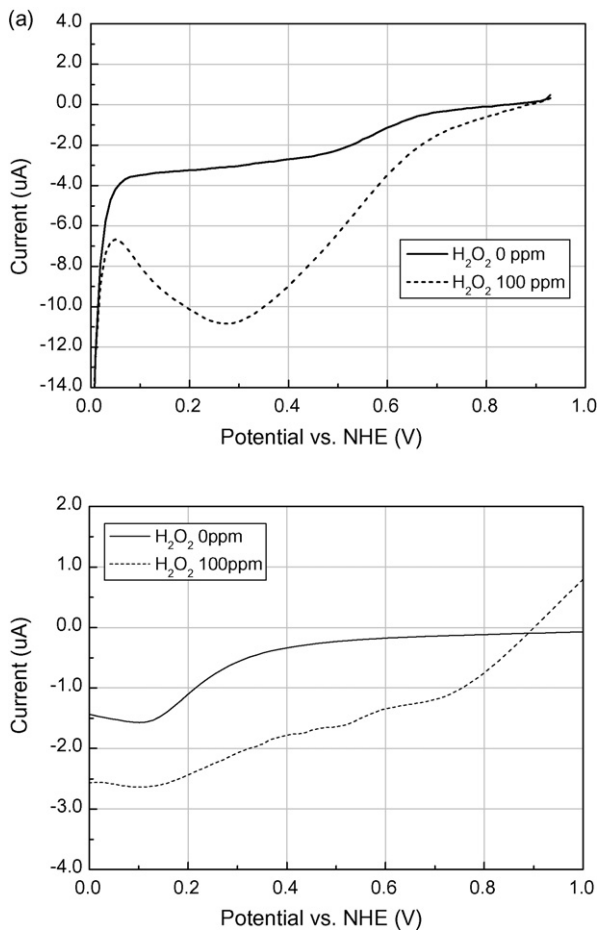

Fig. 6. Linear sweeps for H_2O_2 reduction using (a) Pt/C and (b) Ru/C.
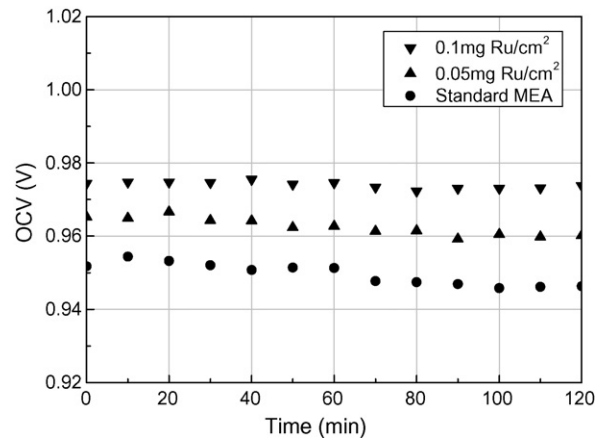

Fig. 7. Open-circuit voltages of three different MEAs at 70 °C.

H_2O_2 reduction reaction is suppressed severely at a potential of 0–0.2 V (versus SHE) so that the reduction current is decreased dramatically. In the case of the Ru catalyst, however, H_2 adsorption does not occur on the surface of the Ru catalyst so that the dissociation and reduction of H_2O_2 is easier than that than on the Pt catalyst [26–29]. As shown in Fig. 6(b), there is no dramatic decrease in the reduction current between 0 and 0.2 V versus SHE in the case of the Ru catalyst.

During open-circuit conditions, the H_2O_2 concentration in the membrane increases due to O_2 cross-over. If the anode catalyst layer of the PEMFC consists of Ru/C, there is less H_2O_2 in the membrane at open-circuit. On the other hand, the Ru catalyst is much less active for H_2 oxidation than the Pt catalyst so that it is difficult to use Ru/C for the anode catalyst layer instead of Pt/C. Nevertheless, considering that the amount of O_2 cross-over is small, a very thin layer of Ru/C might reduce the O_2 in advance of Pt/C. This means that all of the O_2 that crosses over from the cathode to the anode can be reduced on the Ru catalyst and produce less H_2O_2.

The OCVs of single cells using three different MEAs are shown in Fig. 7. Each OCV was measured for 2 h after operation at a current density of 1 A cm^{-2} for 10 h and stabilization at open-circuit for 1 h to obtain an equilibrium state in the cell. There is an increase in OCV with the Ru/C layer at the anode. Both MEAs with 0.05 and 0.1 mg Ru cm^{-2} have higher OCVs
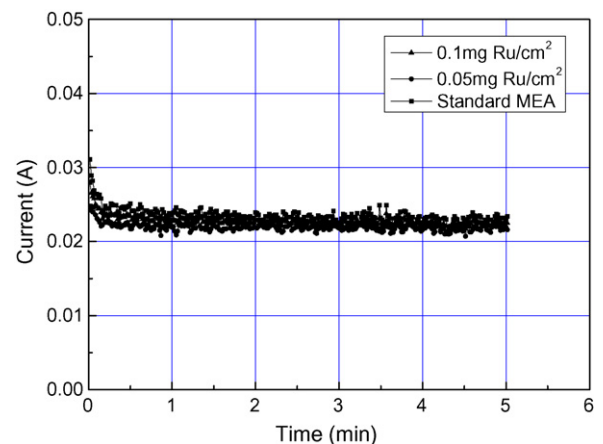

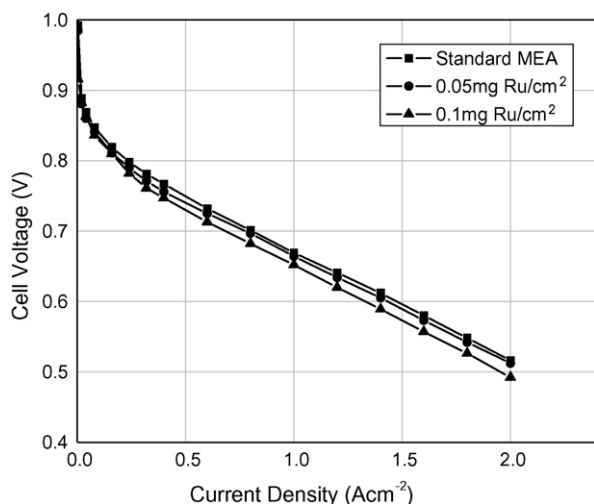Fig. 8. H_2 cross-over of three different MEAs at 70 °C.

Fig. 9. Polarization curves of three different MEAs at 70 °C.

than that of the MEA without a Ru/C layer. If the amount of H_2 cross-over is maintained at a similar level, and other effects such as the cell temperature and humidification are not changed, the OCV of the each MEA should have almost the same value. The data in Fig. 8 indicate that there is almost no difference in the amount of H_2 cross-over in all three MEAs. Therefore, there must be other reactions that can affect the OCV. The electrochemical oxidation of H_2O_2 at the cathode can be considered to be one of the reactions that can cause an internal current in the cell such as H_2 cross-over. In other words, the H_2O_2 concentration in the membrane is lower in the MEA with a Ru/C layer at the anode than in the MEA without a Ru/C layer. Consequently, these results correspond to the fact that less H_2O_2 is produced on the Ru catalyst than on the Pt catalyst. Too much addition of Ru/C may, however, provide resistance against ion conductivity because H^+ ions produced at the Pt/C layer during operation need to pass through the Ru/C layer, as shown in Fig. 9.

4. Conclusions

This study has examined the effect of H_2O_2 on the OCV of a PEMFC and the reduction of H_2O_2 concentration in the membrane using a Ru/C catalyst at the anode.

A half-cell was constructed using 1.0 M H_2SO_4 as an electrolyte. The cathode potential of the PEMFC decreased with increasing H_2O_2 concentration. This test showed that the electrochemical oxidation of H_2O_2 at the cathode is one of the possible reactions that causes an internal current in the cell such as H_2 cross-over.

A Ru/C layer, which is placed between a membrane and the anode catalyst layer, helps to reduce the H_2O_2 concentration in the membrane. There is an increase in cell OCV, which means that the H_2O_2 concentration in the membrane is lower in the MEA with a Ru/C layer at the anode than that of a MEA with no such layer.

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