Methanol Permeation through Membrane Electrode Assembly under Proton Transmission

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This paper describes the phenomena of methanol permeation through a membrane electrode assembly (MEA) incorporating a proton exchange membrane (PEM) from anode to cathode under the proton transmission to clarify the methanol crossover, which diminishes the direct methanol fuel cell power. By using the MEA-installed single cell with a feed of a methanol-water solution to the anode and without any feed to the cathode, we measured (i) the hydrogen evolution rate and (ii) the methanol-water solution permeation rate, both observed at the cathode by single-cell electrolysis operation. As a result, when the current density of the electrolysis increased, the rates of hydrogen evolution and methanol-water permeation proportionally increased. Based on the observations, protons generated at the anode were transformed to hydrogen at cathode, accompanied by the generation of the methanol-water solution at the cathode. In addition, the methanol concentration of the methanol-water solution was found to be the same as that fed to the anode. According to these, protons solvated with methanol and water are transmitted through the PEM to generate the methanol-water solution at the cathode, which leads to a methanol crossover.

Key Words : DMFC, Methanol Permeation, Proton Transmission, Methanol Oxidation, Membrane Electrode Assembly

1 Introduction

The direct methanol fuel cell (DMFC) is one of the most promising power sources for practical applications because it feeds methanol fuel directly to the anode, which results in a small size and light weight.^{1,2)} For practical uses, improvement of electrocatalytic activity of the anode and reduction of methanol crossover needs to be achieved for the purpose of enhancing cell performance.

Methanol crossover is a phenomenon in which methanol fuel permeation from the anode to the cathode occurs, which causes a loss of methanol fuel and a suppression of DMFC power.³⁾ To control the DMFC power generation, an appropriate technique of measuring the methanol crossover is required. Techniques of measuring methanol crossover through the proton exchange membrane (PEM) include (i) CO₂ trace analysis by IR spectroscopy and gravimetric analysis,^{4,5)} (ii) electrochemical analysis,^{6,7)} (iii) gas chromatography analysis^{8,9)}, and (iv) electrochemical analysis combined with gas chromatography¹⁰⁾ or mass spectroscopy¹¹⁾ are used for the membrane electrode assembly (MEA). Recently, Dai *et al.* measured methanol crossover flux from the measurement of the CO₂ quantity at the anode by FTIR.¹²⁾ Jiang *et al.* measured the equivalent current of methanol crossover from the gravimetric CO₂ observed at the anode and cathode.¹³⁾

Methanol crossover consists of methanol fuel permeation to the cathode, and methanol oxidation occurs there, which decreases the cathode potential. Methanol

permeation comprises methanol diffusion and electroosmosis. Previously, we studied the methanol diffusion phenomenon in Nafion 117 membrane by using a microelectrode technique.¹⁴⁾ We have analyzed the electroosmosis phenomenon by a measurement of liquid generated at the cathode during a single-cell operation.

To clarify the methanol permeation in terms of electroosmosis, we used an electrolytic cell incorporating an MEA for DMFC use. For the electrolysis, methanol-water solution was fed to the anode and no reactant was fed to the cathode. Methanol-water solution permeation to the cathode was measured by using the setup under the condition of single-cell electrolysis.

2 Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. The MEA used in this study was prepared as follows. Nafion 112 (DuPont, thickness 50.8 μm) was used as a PEM. First, Nafion 112 membrane was immersed in 0.5 mol dm⁻³ H₂SO₄ overnight and then washed in Milli-Q water for three times. The pretreated Nafion was dried in a vacuum chamber at room temperature before the coating of the electrocatalyst layer. Next, electrocatalyst dispersions were made by using Pt-Ru/C (32.5 wt% Pt-16.9wt% Ru/C, Tanaka Kikinzoku Kogyo K. K.) for anode and Pt/C (46.8 wt% Pt/C, Tanaka Kikinzoku Kogyo K. K.) for cathode. The electrocatalyst powder and Nafion solution (Aldrich, 5 wt% Nafion) were mixed in a Pt/C(Pt-Ru/C):Nafion weight ratio of 6:1, and then diluted to 5 wt% solid content by adding a solution

Fig. 1 Schematic diagram of experimental apparatus.

of methanol:2-propanol:water in a weight ratio of 1:1:1. Each dispersion was coated on one side of the Nafion 112 by employing a conventional air-spray technique so that the weight of Pt(Pt-Ru) per unit area could be 1.0 mg cm^{-2} . The catalyst-coated membrane was dried at 140°C for 30 minutes in a vacuum oven. Subsequently, the membrane was sandwiched by a set of carbon papers (Toray, thickness 0.11 mm) as current collectors to install in the electrolytic cell shown in Fig. 1. The effective electrode area was 23 cm^2 .

The methanol-water solution was fed to the anode in the electrolytic cell. During the electrolysis of the methanol-water solution, nothing was fed to the cathode. In this apparatus, the cathode was maintained in a dry condition until the cell operation began. Unless otherwise stated, the methanol concentration fed to the anode was 16.5 mol dm^{-3} . The hydrogen evolution rate and methanol-water solution permeation rate were measured after 60 min at several current-density settings. The liquid generated at the cathode was collected in the water trap.

In Fig.1, the cathode-exhaust gas was sampled with an auto sampler, for analysis by gas chromatography (GC-8A, Shimadzu Corporation). A Molecular Sieve 5A glass column (Honma Riken) was used for the analysis. The volume of the liquid generated at the cathode was measured by a volumetric cylinder. The liquid generated at the cathode was sampled with a microsyringe and then injected into a gas chromatograph (GC-8A, Shimadzu Corporation) to be analyzed. A Greensorb F glass column (Chromato Research Ltd.) was used for the analysis. Gas chromatography data was then processed with an integrator (Chromatopak C-6RA, Shimadzu Corporation). The gas evaluation rate at the cathode was measured by a gas flow meter.

3 Results and discussion

Electrode reactions in the electrolytic cell shown in Fig. 1 are expected to be as follows: for the anode reaction,

and for the cathode reaction,

When the electrolysis is performed, gaseous evolution and liquid generated at the cathode are simultaneously observed. From the gas chromatography analysis, we know that the gas is pure hydrogen and the liquid is a methanol-water solution.

The relationship between the current density of the electrolysis and the hydrogen evolution rate is shown in Fig. 2(a), and the relationship between the current density and liquid generation rate is shown in Fig. 2(b). During the electrolysis, the methanol-water feed rate was controlled at $30 \text{ cm}^3 \text{ min}^{-1}$; and, the observed cell voltage was 0.75 V at 0.087 A cm^{-2} and 1.46 V at 1.30 A cm^{-2} .

In Fig. 2(a), the solid line indicates a theoretical hydrogen evolution rate calculated based on Eq. (2) in combination with Faraday's first law of electrolysis. The observed hydrogen evolution rate agrees well with the theoretical rate. This indicates that the proton generated at the anode, according to Eq. (1), transmits through the PEM of the MEA and is finally transformed to hydrogen at the cathode.

In Fig. 2(b), the methanol-water solution generation rate linearly increases with an increase in the current density. Initially, the cathode was dried, so there was no reactant. The methanol-water solution generated at the cathode is considered to be the result of methanol-water permeation from the anode.

As shown in Fig. 2, both the hydrogen evolution rate and methanol-water solution generation rate depend directly on the current density of the electrolysis. From these results, the methanol-water solution generated at the cathode is accompanied by proton transmission in the PEM.

Methanol and water permeation rates were analyzed by gas chromatography, and the data is shown in Fig. 3(a). Linear plots are shown in the graph indicating that

Fig. 2 Dependence of (a) hydrogen evolution rate and (b) methanol-water solution generation rate on current density of electrolysis. In (a), circles indicate measurements of hydrogen evolution rate.

the molar ratio of water:methanol is not changed by the electrolysis current density. By using the data of the hydrogen evolution rate, V_{H_2} , given in Fig. 2(a), and that of the water permeation rate or the methanol permeation rate, V_{liq} , represented in Fig. 3(a), the number of water or methanol molecules that are accompanied by one proton transmission, as calculated by Eq. (3), are shown in Fig. 3(b):

$$N_{liq} = (V_{liq} \times \rho_{liq} / M_{liq}) \times (22.4 \times 2 / V_{H_2}) \quad (3)$$

in which ρ_{liq} indicates the density of water or methanol and M_{liq} indicates the molecular weight of water or methanol.

From Fig. 3(b), we can observe that for each proton transmitted through the PEM there are 2.9-3.8 and 2.3-3.0 water and methanol molecules permeated through the PEM, respectively, in the case when the current density is larger than 0.2 A cm^{-2} . We think that in the case when the current density is smaller than 0.2 A cm^{-2} , the number of water and methanol molecules increases according to the error in the hydrogen evolution rate.

As shown in Fig. 4, the relationship between the methanol concentration of methanol-water solution fed to the anode and that generated at the cathode is obtained at the current density of 0.09 A cm^{-2} . As is apparent from the figure, the two concentrations agree well. According to the result, protons generated at the anode are solvated by the methanol-water solution fuel according to their molar ratio, and then direct permeation through the PEM occurs. As a result, the methanol-water solution is generated at the cathode. This is thought to be a methanol-crossover mechanism caused by the transmission of fuel-solvated protons. Further investigation will be needed for understanding the detailed mechanism of the methanol crossover.

4 Conclusion

To analyze the methanol crossover mechanism, methanol and water permeation from the anode to cath-

Fig. 3 Dependence of (a) methanol and water permeation rate on current density, and (b) permeation of methanol and water molecules per one proton depending on current density.

Fig. 4 Dependence of methanol concentration in methanol-water solution permeated from anode to cathode in single cell in which anode was fed methanol-water solution.

ode through the PEM was studied under the proton transmission. By using the MEA-installed single cell with a feed of methanol-water solution to the anode and without any feed to the cathode, we measured (i) the hydrogen evolution rate and (ii) methanol-water solution permeation rate, both observed at the cathode by a single-cell operation. As a result, when the current density of the electrolysis increased, both rates of hydrogen evolution and methanol-water permeation proportionally increased. Based on the observations, we believe protons generated at the anode were transformed to hydrogen at the cathode, accompanied by the generation of methanol-water solution at the cathode. In addition, the methanol concentration of the methanol-water solution generated at the cathode is found to be the same as that fed to the anode. According to these, protons solvated with methanol and water permeate through the PEM, and a water-methanol solution is generated at the cathode, which leads to a methanol crossover. In the future, we plan to study the methanol crossover mechanism by employing different type of the PEM varying the thickness and ion exchange capacity.

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