

Analysis of the Catalyst Layer of Polymer Electrolyte Fuel Cells

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Abstract

Comprehensive techniques for diagnosing the catalyst layer of a polymer electrolyte fuel cell were developed. The developed techniques consist of an electronic resistance estimation by a four-probe measurement of the catalyst layer with crack compensation by image analysis, a protonic conductivity estimation by ac impedance analysis based on a porous electrode model, and an estimation of gas diffusivity by comparing the limiting current density for the case of a helium-oxygen mixture as oxidant with that for the case of air as oxidant. The techniques were applied to in-house fabricated catalyst layers. It was found

that electronic conductivity is sufficiently large to minimize voltage loss, and this is also true of protonic conductivity if the content of the polymer electrolyte is sufficient. Gas diffusivity was smaller than that calculated from the molecular diffusion model. Slow Knudsen diffusion through narrow pores contributes 40% to the total diffusion. From the abovementioned comparison, an increase of power in the fuel cell is attributed to an enlargement of pores in the catalyst layer that reduces the contribution of Knudsen diffusion.

Keywords

Polymer electrolyte fuel cell, Catalyst layer, Electronic conductivity, Protonic conductivity, Gas diffusivity

1. Introduction

A fuel cell is a device that directly converts chemical energy into electric energy without being limited by the Carnot cycle. Since the 1980's, intense research has been carried out globally on polymer electrolyte fuel cells (PEFCs) for use as power sources in portable, stationary and mobile applications.¹⁾ Although the power density of PEFCs is comparable to that of internal combustion engines, further studies are actively underway.

Figure 1 is a schematic illustration of a PEFC. A polymer electrolyte membrane that conducts protons is sandwiched between two catalyst layers. In addition, two gas diffusion layers are laminated to form a membrane-electrode assembly (MEA). Hydrogen is supplied through flow fields to one side of the MEA, and the hydrogen is oxidized electrochemically in the catalyst layer. At the other side of the MEA, air is supplied and oxygen is reduced to generate water.

The catalyst layer, a porous electrode containing carbon-supported platinum mixed with polymer electrolyte (shown in **Fig. 2**), is where the electrochemical reaction occurs, and therefore, its material and structure have a major influence on the performance of the MEA. To facilitate the electrochemical reactions, three properties are considered sufficient: electronic conductivity, protonic conductivity and gas diffusivity. Although a normal fuel cell performance test is sufficient for

ascertaining overall performance, one cannot determine how each property contributes and it is therefore difficult to obtain information for improving cell performance. The purpose of this paper is to present techniques for separately measuring these three properties.

2. Measurement

2.1 Catalyst layer and MEA preparations

The catalyst ink was prepared by dispersing carbon supported platinum (Pt/C) in a mixture containing Nafion® solution (E.I. du Pont de Nemours and Co.), water, ethanol and propylene glycol. The ink was then spread on a PTFE sheet using a doctor blade and dried overnight in a vacuum oven to form a cast electrode. Two cast electrodes with active areas of 1 cm² each were transferred to opposite sides of a membrane by hot pressing. Single-sided ELAT® (E-TEK) gas diffusion layers were laminated when the cell was assembled.

2.2 Electronic conductivity

Although electronic conductivity, that is, the inverse of resistivity, should be measured in a direction perpendicular to the catalyst layer, this measurement is technically difficult because the probes for measuring resistance must be set accurately so as to sandwich the thin and soft catalyst layer. In addition, contact resistance between the probe and the catalyst layer cannot be eliminated when the two-probe method is used, and

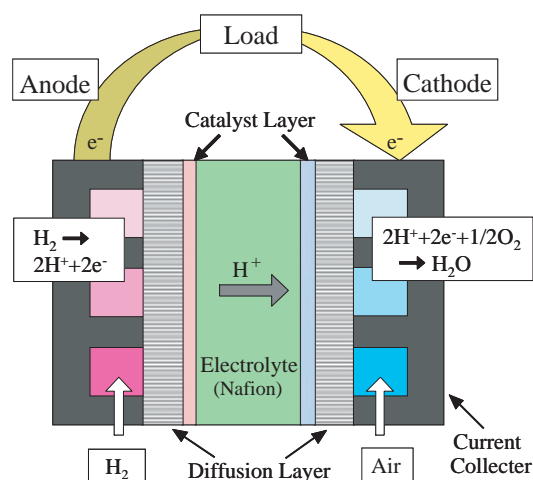


Fig. 1 Schematic image of a polymer electrolyte fuel cell.

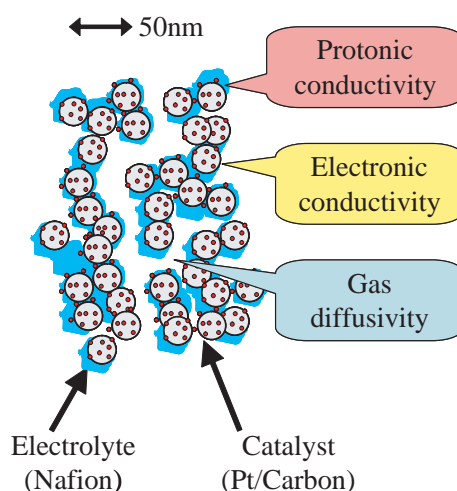


Fig. 2 Schematic illustration of a catalyst layer.

it is impossible to apply the four-probe method to such a thin layer.

An alternative is to measure the in-plane resistance. This approach is valid if the resistance can be regarded as isotropic. In this study, assuming isotropy, we applied this approach using the four-probe method. The resistance measurement was performed in accordance with JIS-K7194 using a high-frequency resistance meter (MCP-T600 Low Resistivity Meter, Dia Instruments Co., Ltd.).

Because catalyst layers often have cracks that seriously influence the measurements, we applied the following image-processing technique to compensate for their effects. The catalyst layer is digitally photographed using an optical microscope. The photo-image is converted to a bitmap containing only black and white pixels. An example of the images is shown in **Fig. 3**. The connectivity of the black area is evaluated using the bond percolation theory, assuming that the neighboring black pixels are connected. Connectivity is obtained as a dimensionless number between 0 (the region is divided) and 1 (the region is fully occupied). Then, bulk electronic conductivity, which is conductivity without cracks, is calculated by dividing the measured conductivity by the evaluated connectivity.

2.3 Protonic conductivity

The protonic conductivity can be estimated on the basis of the 1-D homogeneous model of the electrode, shown in **Fig. 4**. It is formulated as follows.²⁾ Assuming that the protonic resistance and the double layer capacitance are constant throughout the electrode thickness, and that the electronic resistance is negligible, the impedance of the electrode $Z = Z' + iZ''$ for an inert condition is

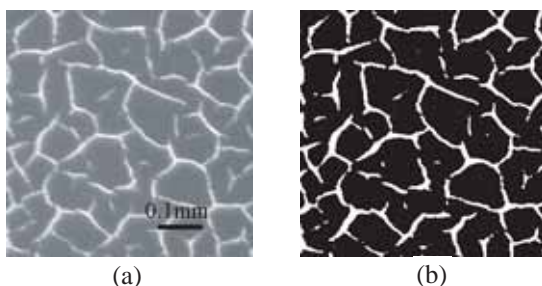


Fig. 3 (a) An example of the micrographs of cast electrodes and (b) its binary transform.

expressed as:

$$Z = \sqrt{\frac{R}{i\omega C}} \coth(l\sqrt{i\omega RC}) = Rl \frac{(\sinh x - \sin x) - i(\sinh x + \sin x)}{x(\cosh x - \cos x)}, \quad \dots \dots \dots (1)$$

where R is the resistance per unit length, C is the double layer capacitance per unit length, l is the thickness of the catalyst layer, ω is the angular frequency, i is the imaginary unit and $x = l\sqrt{2\omega RC}$. **Figure 5** shows the Nyquist plot of the impedance; the slope approaches $1(-dZ''/dZ' \rightarrow 1)$ for large ω , and the impedance exhibits the asymptotic behavior $Z' \rightarrow Rl/3$ and $-1/(\omega Z'') \rightarrow Cl$ when $\omega \rightarrow 0$.

In this study, we measured the ac impedance of the MEA using the same catalyst layers on both sides of the membrane in an inert atmosphere to avoid complexity. Humidified nitrogen was supplied to

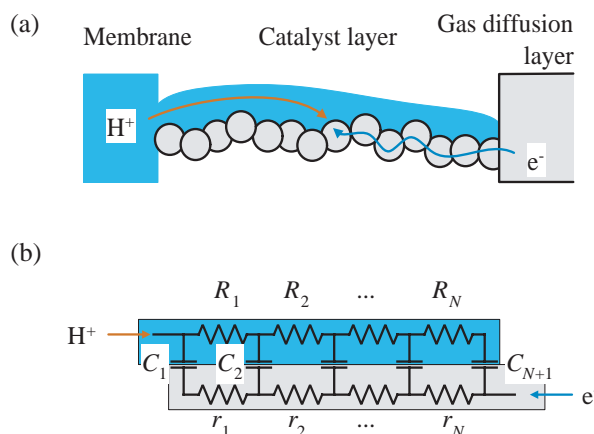


Fig. 4 The 1-D homogeneous model of the catalyst layer. (a) An illustration of the whole thickness of the catalyst layer. (b) An equivalent circuit of (a) described by the distributed constant circuit. R_i 's and r_i 's are the protonic and electronic resistance, respectively. C_i 's are the double layer capacitance.

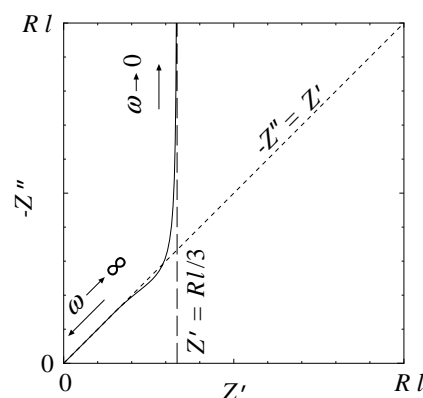


Fig. 5 Nyquist plot for the impedance of Eq. (1).

both compartments of the cell for more than an hour prior to the impedance measurement and throughout the experiment. The measurement was carried out from 100 kHz to 100 mHz with a perturbation amplitude of 10 mV at room temperature using an LCR meter (3522 LCR HiTESTER, HIOKI E. E. Corp.).

2.4 Gas diffusivity

The limiting current density in a current-voltage characteristic is usually interpreted as an oxygen-transport limitation. It is not easy, however, to determine where oxygen transport is limited in the oxygen path. Operating the cell using a helium-oxygen mixture (heliox) instead of air will lead to another limiting current density reflecting a change in the diffusivity of the oxygen. If the change deviates from the value calculated from the molecular diffusion model, which neglects the effect of the pore wall, the result implies some degree of interaction with the wall. Assuming that the limiting current density is proportional to the oxygen flux, which is described by Fick's law,³⁾ the ratio of the limiting current density I_L is expressed by the ratio of the overall diffusion coefficients D :

$$\frac{D_{\text{heliox}}}{D_{\text{nitrox}}} = \frac{I_{L, \text{heliox}}}{I_{L, \text{nitrox}}} \equiv G, \dots\dots\dots (2)$$

which is called the helium gain.

In this study, the fuel cell was operated using nitrox (nitrogen-oxygen mixture) or heliox containing 5 mol% of oxygen in a dry base. This concentration was chosen to make the mass transfer limitation conspicuous. Gases were supplied at a constant flow rate equivalent to 20A/cm². This large flow rate was chosen to minimize the effect of water flooding. The gas was humidified with a bubbler; the temperatures of the water were maintained at 85 °C and 75 °C for hydrogen and the oxidant gas, respectively, while the cell temperature was set at 80 °C. These temperatures were chosen to avoid a large ohmic drop caused by the dehydration of the polymer electrolyte. The pressure of the gas was set to 0.2MPa absolute. Under these conditions, the molecular diffusion model using binary diffusion coefficients^{4, 5)} yields a helium gain G of 2.6. Current-voltage characteristics were obtained using a $\pm 2\text{V}/20\text{A}$ discharge unit (Hokuto Denko Corp.) that can measure the high frequency resistance of the

electrolyte simultaneously.

3. Results

3.1 Electronic conductivity

Figure 6 shows the estimated electronic conductivity plotted as a function of the volume fraction of the Pt/C. The electronic conductivity is found to be on the order of 0.1 to 1 S/cm, although the data are scattered. Considering the thickness of the catalyst layer (about 10 μm), electronic ohmic loss would be regarded as negligible (20 mV at 1 A/cm² at most).

3.2 Protonic conductivity

Figure 7 shows the obtained Nyquist plot which consists of a gentle slope ($\cong 45^\circ$) in the high frequency region and a steep slope in the low frequency region. This result agrees well with Eq. (1). The ionic conductivity and the double layer capacitance were estimated by a curve fitting. **Figure 8** shows the estimated protonic conductivity and the double layer capacitance of three electrodes. Because the derived conductivities are much smaller than the electronic conductivity, the assumption that electronic resistance is negligible is justified. The conductivity increases with an increasing volume fraction of Nafion. This indicates that catalyst layers with a higher volume fraction have a thicker Nafion layer covering the Pt/C particle and/or a larger number of protonic channels. In contrast, the double

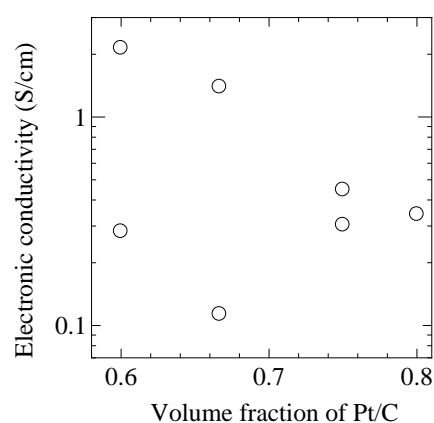


Fig. 6 Electronic conductivity vs. volume fraction of Pt/C. The volume fraction of Pt/C was defined by dividing the volume of Pt/C by the total volume of Pt/C and Nafion. Data for connectivity lower than 0.2 were omitted because the crack compensation appeared erroneous.

layer capacitance is almost constant. This implies that the Pt/C is almost fully covered with Nafion even at the smallest Nafion content.

3.3 Gas diffusivity

The measured current-voltage characteristics are shown in **Fig. 9**. Rapid voltage drops are observed for both nitrox and heliox, indicating the mass transport limitation of oxygen. The limiting current densities are 0.9 and 1.4 A/cm² for nitrox and heliox, respectively. The resultant helium gain, 1.6, is significantly smaller than 2.6, which is the

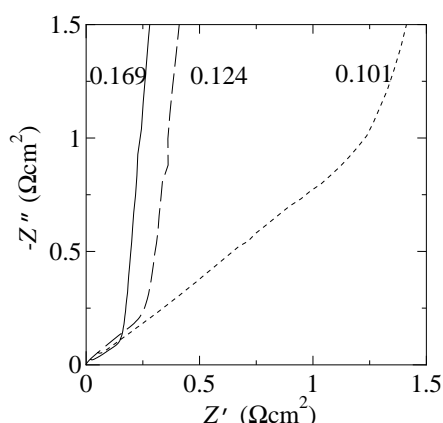


Fig. 7 Nyquist plots for three different catalyst layers with different loading of Nafion. Numbers in the figure are the volume fraction of Nafion. The volume fraction of Nafion is defined by dividing the volume of Nafion by the total volume of the catalyst layer including void.

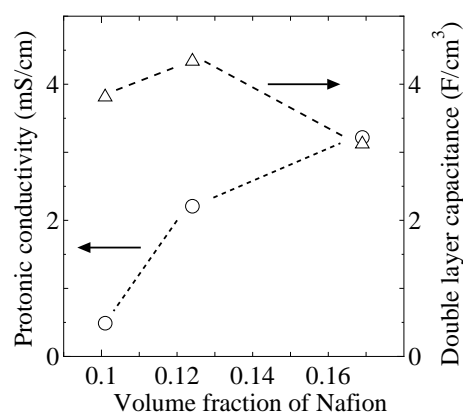


Fig. 8 Ionic conductivity (circle) and double layer capacitance per unit volume (triangle) vs. volume fraction of Nafion. The lines are provided to guide the eyes.

prediction of the molecular diffusion model. This indicates oxygen transport is limited not only by molecular diffusion but also by other processes. The most probable process is Knudsen diffusion, which is significant in pores smaller than 100 nm in diameter for this operating condition. Because pores of this size exist only in the catalyst layer, it is the location of the catalyst layer that is influenced by this diffusion process.

The contribution of Knudsen diffusion is estimated as follows. The overall diffusion resistance, defined as the inverse of the diffusion coefficient of oxygen, is assumed to be expressed as the sum of the resistances of the different diffusion mechanisms as:

$$D_{\alpha}^{-1} = xD_K^{-1} + (1-x)D_{M,\alpha}^{-1}, \quad \alpha = \text{nitrox or heliox}, \quad \dots \dots \dots (3)$$

where D_{α} is the diffusion coefficient of oxygen in a mixture α , used in Eq. (2). D_K and $D_{M,\alpha}$ are the Knudsen and the molecular diffusion coefficients of oxygen, respectively, and x is a parameter ranging from 0 to 1. From Eqs. (2) and (3), the helium gain G is expressed as:

$$G = \frac{D_{\text{heliox}}}{D_{\text{nitrox}}} = \frac{x D_K^{-1} + (1-x) D_{M,\text{nitrox}}^{-1}}{x D_K^{-1} + (1-x) D_{M,\text{heliox}}^{-1}},$$

or

$$\frac{x}{1-x} \frac{D_K^{-1}}{D_{M,\text{nitrox}}^{-1}} = \frac{1 - \frac{G}{D_{M,\text{heliox}}/D_{M,\text{nitrox}}}}{G-1}.$$

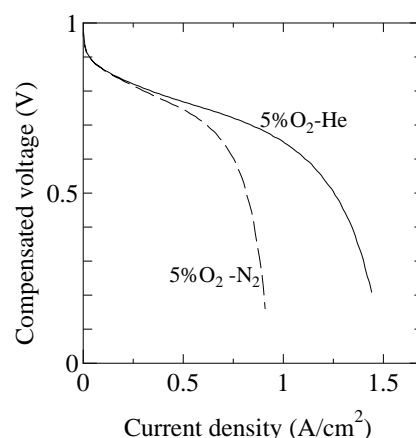


Fig. 9 Influence of the cathode gas composition on current-voltage characteristics. The compensated voltage is given by $E + IR$, where E is the cell voltage, I is the current and R is the resistance of the electrolyte.

Therefore, the contribution of Knudsen diffusion to the overall diffusion:

$$\frac{x D_K^{-1}}{x D_K^{-1} + (1-x) D_{M, nitrox}^{-1}} = \frac{\frac{x}{1-x} \frac{D_K^{-1}}{D_{M, nitrox}^{-1}}}{\frac{x}{1-x} \frac{D_K^{-1}}{D_{M, nitrox}^{-1}} + 1} = \frac{1 - \frac{G}{D_{M, heliox}/D_{M, nitrox}}}{\left(1 - \frac{1}{D_{M, heliox}/D_{M, nitrox}}\right) G},$$

is obtained as 0.4.

4. Discussion

The analysis results show that the obtained catalyst layers have high electronic conductivity and that the protonic conductivity can be high if the Nafion content is sufficient. Thus, electron and proton transport in the catalyst layers do not appear to bring about significant loss. However, oxygen transport is found to be limited significantly in the catalyst layer. Improving gas diffusivity in the catalyst layer by changing the material or preparation process could reduce transportation loss and lead to a high-power MEA.

5. Conclusions

The present work has demonstrated diagnostic techniques for evaluating electronic conductivity, protonic conductivity and gas diffusivity in the catalyst layer. Although the electronic conductivity measurement using the four-probe method requires further improvement, it could estimate the order of conductivity which, practically, is sufficiently high. The protonic conductivity measurement using the ac impedance method showed a reasonable dependence on Nafion loading. The gas diffusivity measurement using helium gain revealed the contribution of Knudsen diffusion in the catalyst layer. From these measurements, we found that gas diffusion in the catalyst layer limits cell performance.

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