Characterization of Solid Oxide Fuel Cell Components by Gas Permeability Measurement*

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A binary gas permeation method is proposed to investigate gas transportation in the components of solid oxide fuel cells, in which the properties of porous media, such as pore diameter, porosity and the tortuosity factor, are obtained from the measured permeabilities of two different gases. It is also confirmed experimentally that permeabilities can be predicted with high accuracy for other gases as well as for nonisobaric binary gas diffusion systems. Moreover, we consider the airtightness of plasma-sprayed yttria-stabilized zirconia films and estimate the concentration polarization and distribution of total pressure in porous media at a high temperature.

Key Words: Fuel Cell, Diffusion, Porous Media, Gas Permeation, Solid Oxide Electrolyte, Concentration Polarization, Plasma Spray

1. Introduction

In recent years, there has been increased interest in solid oxide fuel cells (SOFC), which are also called third-generation fuel cells⁽¹⁾.

The structure of SOFC is schematically shown in Fig. 1: an oxygen-ion-conductive solid electrolyte and two porous electrode layers are formed on a porous support. Reactive gas species (hydrogen and oxygen) diffuse through the porous support and electrodes to the electrode/electrolyte interfaces, where the oxygen gas reacts with electrons to form oxygen ions. The oxygen ions go through the electrolyte to the anode, and reaction with hydrogen produces vapor and electrons, generating electric power in the outer circuit.

This type of fuel cell is composed of both porous and airtight solid layers. Basic performances of the fuel cell such as concentration polarization and limiting current depend on the gas transport properties of

the porous layers (support and electrodes). Evaluation of the electrolyte and interconnector layers is also important from the viewpoint of energy conversion efficiency, reliability and the selection of their product processes.

Gas permeability measurements have been carried out for the evaluation of the SOFC components from above standpoint⁽²⁾. However, more theoretical treatments are necessary to apply the results of measurements at room temperature to the high temperature region at approximately 1 000°C, where the

Fig. 1 Schematic of solid oxide fuel cell

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SOFC is generally operated.

In this paper, we propose a binary gas permeation method (BGP method) for the characterization of SOFC layers, where the properties of porous media are obtained from the measured permeabilities for two different gases, and gas transportation in porous media under various conditions is calculated using the obtained properties.

Firstly, we explain the principle and features of the BGP method and show the experimental results for two kinds of SOFC layers: porous supports and plasma-sprayed electrolytes. It is also shown that the results of the BGP method are applicable to nonisobaric gas diffusion systems.

Moreover, we evaluate the airtightness of plasma-sprayed electrolyte films of yttria-stabilized zirconia (YSZ) and show the calculated results of concentration polarization caused by the diffusion resistance of porous support tubes.

2. Binary Gas Permeation Method

2.1 Principle and features

The permeability K for a gas in a porous layer is expressed as Eq. (1) on the basis of the parallel pore model using Knudsen's empirical equation⁽³⁾ for gas

Fig. 2 Relation between viscosity and molecular weight for various gases

Fig. 3 Plot of permeability ratio (helium/propane) versus pore diameter

transport in a circular tube,

$$K = \frac{\epsilon}{\tau} \left(\frac{d^2}{32} \cdot \frac{1}{\mu} + \frac{d}{3} \cdot \sqrt{\frac{8RT}{\pi M}} \cdot \frac{f}{\bar{p}} \right). \quad (1)$$

The first term on the right-hand side represents the contribution from viscous flow, and the second, molecular flow, where R , T and $\bar{p}$ are the gas constant, temperature and mean pressure, respectively. The symbols μ and M are viscosity and molecular weight of the gas, and ϵ , τ and d are the porosity, tortuosity factor and pore diameter of the porous material, respectively. The coefficient f is defined as in Eq. (2), and varies from 0.806 to 1;

$$f = \frac{1 + (M/RT)^{1/2} (d\bar{p}/\mu)}{1.24 + (M/RT)^{1/2} (d\bar{p}/\mu)}. \quad (2)$$

The two parameters of the porous material, d and ϵ/τ , are the solutions of two simultaneous equations set up from the measurement of permeabilities for two different gases. The tortuosity factor τ is known when porosity ϵ is determined by a different method.

As for the selection of the two gases, accurate calculation requires that one gas have large viscosity and small molecular weight, while the other has the inverse tendency. Figure 2 shows the relation between viscosity and molecular weight for several gases⁽⁴⁾. We chose the combination of helium (He) and propane (C_3H_8) for the binary gases from the above criterion. The solid circles in Fig. 2 denote the gases used in this study: hydrogen (H_2), nitrogen (N_2) and methane (CH_4).

The permeability ratio of helium to propane varies within a wide range, 0.412 and 3.32 being the two extremes, corresponding to the pore diameters, as shown in Fig. 3; this range ensures the accurate calculation of pore diameter from the measured permeability ratio. Furthermore, the range of pore diameters obtained by this method is approximately 0.1 to 10 μm , which is adequate for the characterization of SOFC materials.

2.2 Samples, experimental apparatus and method

Two porous support tubes and two plasma-sprayed YSZ films on porous support were examined in this study;

- (1) Alumina porous support tube : 3.05 mm thick
- (2) Calcia-stabilized zirconia porous support tube : 3.19 mm thick
- (3) YSZ film sprayed at atmospheric pressure : 0.225 mm thick
- (4) YSZ film sprayed at low pressure : 0.065 mm thick

They are abbreviated as Alumina, CSZ, ATM and LPC, respectively.

The apparatus for gas permeability measurement

is schematically shown in Fig. 4; a tubular sample was set in a glass vessel, and a single gas was supplied to the inside of the sample to permeate through the sample wall into the glass vessel. After the vessel was filled with supplied gas, the pressure difference Δp through the wall and flow rate Q were measured. The temperature and pressure difference were maintained at $25 \pm 1^\circ\text{C}$ and below 500 Pa, respectively. The permeability K is obtained from Eq. (3),

$$K = QL / (A \Delta p), \quad (3)$$

where A and L are the permeation cross section area

Fig. 4 Apparatus for gas permeability measurement

Fig. 5 Comparison of pore diameters by binary gas permeation (BGP) method with those of the mercury intrusion method for (a) alumina and (b) CSZ porous support tubes

and thickness of the sample, respectively. In the case of sprayed films, the flow resistance of the support tube was appropriately subtracted.

2.3 Calculation of properties of porous media

The properties of the four samples obtained by the BGP method are shown in Table 1. The porosities of the porous support tubes were obtained by the liquid displacement method⁽⁵⁾.

The pore diameters obtained using the BGP method for two support tubes are compared in Fig. 5 with the distributions measured by the mercury intrusion method; the pore diameter for porous alumina (a) lies between the values of the two peaks in the distribution chart, while the diameter for CSZ (b) is in agreement with the value for the single peak. The term "bubbling" in Fig. 6 denotes the maximum pore diameter obtained from Eq. (4), using the minimum bubbling pressure difference $\Delta p_{\min}$ when the inside of a completely wet sample in water is pressurized by gas⁽⁵⁾,

Table 1 Results of binary gas permeation method for four samples

Property		Pore diameter d μm	Tortuosity τ	Porosity ϵ
porous tube	Alumina	4.22	0.257	3.51
	CSZ	2.18	0.265	3.15
YSZ-sprayed film	ATM	2.28	$\epsilon/\tau = 0.00364$	
	LPC	0.452	$\epsilon/\tau = 0.00446$

Fig. 6 Comparison of calculated and measured permeabilities of alumina and CSZ porous support tubes for hydrogen, nitrogen and methane

$$d_{\max} = 4\sigma/\Delta p_{\min}, \quad (4)$$

where σ is the surface tension of water.

A fairly good agreement of pore diameters measured by the two different methods may indicate the appropriateness of the BGP method for these conditions.

2.4 Calculation of permeabilities for other gases

The permeabilities for other gases can be calculated from Eq.(1), using values of d and ε/τ derived from the BGP method. The measured permeabilities of four porous samples for hydrogen, nitrogen and methane are in good agreement with the calculated values as shown in Fig. 6, where the differences are about one percent for the support tubes and less than a few percent for the sprayed films.

3. Extension to the Binary Gas Diffusion System

An interdiffusion of more than two gases occurs in the porous components of SOFC. In this section, we investigate experimentally whether the properties obtained by the BGP method can be used in a binary gas diffusion system.

3.1 Experimental apparatus and method

The experimental apparatus for the binary gas system is shown in Fig. 7, where one gas (Gas 2 ; flowing gas) permeates a porous sample tube to the space filled with the other gas (Gas 1 ; backing gas). The flow rate of the backing gas was adjusted to be more than 100 times that of the flowing gas.

3.2 Mathematical model and equations

Figure 8 shows the mathematical model for the nonisobaric binary gas diffusion system shown in Fig. 7, where Gas 2 permeates from $z=L$ to $z=0$ at which the total pressure p_0 is 0.1013 MPa and the mole fraction of Gas 1 is unity ($x_{10}=1$). Under these boundary conditions, at $z=0$ and a given molar flux of Gas 2 J_2 , the total pressure p_L and mole fraction (x_{1L}, x_{2L}) at $z=L$ are calculated.

The system is described by two differential equations (5) and (6) for total pressure p and mole fraction x of Gas 1 or 2⁽⁶⁾

$$\frac{dp}{dz} = -\frac{(J - \beta J_1)RT}{D_2[1 + (x_1/D_1 + x_2/D_2)Bp/\mu]}, \quad (5)$$

$$\frac{dx_1}{dz} = \frac{RT}{aDp} \left\{ -J_1 + x_1 a J + \frac{(J - \beta J_1)[aDx_1 + x_1(1-a)Bp/\mu]}{D_2[1 + (x_1/D_1 + x_2/D_2)Bp/\mu]} \right\}, \quad (6)$$

where

$$J = J_1 + J_2, \quad (7)$$

$$a = D_1/(D_1 + D), \quad (8)$$

$$\beta = 1 - D_2/D_1, \quad (9)$$

$$B = (\varepsilon/\tau)(d^2/32), \quad (10)$$

$$D_i = d/3(8RT/\pi M_i)^{1/2}, \quad (11)$$

$$\Delta p = p_L - p_0. \quad (12)$$

Each value at $z=L$ is obtained with the numerical integration of these equations by the Runge-Kutta method, and the pressure difference Δp for the given flow rate of Gas 2 is obtained from Eq.(12).

In the calculation, the binary diffusion coefficient D and viscosity of gases are given as the Chapman-Enskog first approximation, and the viscosity of mixed gas is taken from the Wilke's equation⁽⁷⁾. The Knudsen diffusion coefficient D_i of each gas is obtained from Eq.(11). The diffusion coefficients D and D_i in Eqs.(5) and (6) are effective values multiplied by ε/τ . In the calculation of d and ε/τ by the BGP method, the f value in Eq.(1) was set to unity corresponding to the equations for the binary gas system.

3.3 Results and discussion

The experimental and calculated results for the alumina and CSZ porous tubes are compared in Fig. 9 for several combinations of flowing and backing gases. Solid curves indicate the calculated results using values of d and ε/τ determined by the BGP method. Broken lines are the experimental results for the single gas system. The flow rate is in proportion to pressure differences for the single gas system, while in the case of the binary gas system, the relation between flow rate and pressure difference is nonlinear and

Fig. 7 Experimental apparatus for the binary gas diffusion system

Fig. 8 Mathematical model and conditions for binary gas diffusion experiment

permeability differs considerably from the single gas system. The experimental results are in good agreement with calculated values, which permits us to apply the results of the BGP method to the nonisobaric binary gas diffusion system as observed in porous layers of SOFC.

4. Applications

4.1 Evaluation of YSZ plasma-sprayed films

It is shown in Fig. 6 that the permeability of YSZ

Fig. 9 Comparison of calculated and measured permeabilities for the binary gas diffusion system for (a) alumina and (b) calcia-stabilized zirconia porous support tubes

film sprayed at low pressure (LPC) is approximately one order smaller than that of YSZ film sprayed at atmospheric pressure (ATM). The pore diameter of LPC film is considerably smaller than that of ATM film, while the value of ϵ/τ of LPC film is larger than that of ATM film, as shown in Table 1. This fact indicates that LPC film is superior to ATM film, due to its smaller pore size rather than its pore volume. The scanning electron microscope (SEM) photographs of YSZ films are shown in Fig. 10. The trace of original particles is observed in ATM film, while it seems for LPC film that the YSZ particles were crushed by the collision and, thus, the pore diameter became smaller. It is also concluded that the relative density, which is usually used for the characterization of sprayed films, is inadequate as an index of airtightness of solid electrolyte layers of SOFC.

4.2 Estimation of concentration polarization and pressure gradient in porous layers

Porous supports in SOFC prevent gas transport to the electrode, so that the voltage of the fuel cell is lower than that expected from the concentration of supplied gas (concentration polarization). In this section, we estimate the concentration polarization and

(a) atmospheric pressure

(b) low pressure

Fig. 10 Scanning electron microscope photographs of yttria-stabilized zirconia films (top view) plasma-sprayed at (a) atmospheric pressure and (b) low pressure

total pressure gradient caused by the support tubes examined above.

The calculation was carried out for two cases, i.e., the support tube is at the anode side (Case 1) or the cathode side (Case 2). The mathematical model and conditions are shown in Fig. 11. Total pressure in the gas stream is assumed to be atmospheric pressure for both cases. In Case 1, equimolar binary diffusion occurs between hydrogen and vapor, while the unidirectional diffusion of oxygen in nitrogen occurs in case 2. Both cases are nonisobaric diffusion, and the equations are similar to those in section 3. A given current density i is converted into molar flux of the reactive gas J_i from Faraday's law,

$$J_{H_2} = -J_{H_2O} = i/(2F), \quad (13)$$

$$J_{O_2} = i/(4F), \quad (14)$$

where F is the Faraday constant.

Concentration polarizations is obtained for each case by the following equations, substituting the calculated partial pressures at the electrode ($z=L$),

$$\eta_a = \frac{RT}{2F} \ln \frac{p_{H_2}/p_{H_{2,L}}}{p_{H_2O}/p_{H_{2O,L}}} \quad (15)$$

Fig. 11 Mathematical model and conditions for the calculation of concentration polarization

Fig. 12 Calculated results of concentration polarization

$$\eta_c = \frac{RT}{4F} \ln \frac{p_{O_2}}{p_{O_{2,L}}} \quad (16)$$

where η_a and η_c are concentration polarizations for Cases 1 and 2, respectively, and suffix L denotes $z=L$.

The calculated results of the concentration polarization are shown in Fig. 12. There is a clear difference between Cases 1 and 2, which may be due to the difference in diffusion velocity between hydrogen and oxygen. The difference between alumina and CSZ is very small, and the low limiting currents in both cases signify the necessity of further improvement of porosity, thickness and pore diameter of the support tubes.

Figure 13 shows the calculated ratio of total pressure at the electrode to stream pressure (atmospheric pressure). A large difference between alumina and CSZ is observed in spite of the similarity of concentration polarization. The pressure difference through the porous support increases in proportion to current density, and pressure at the electrode is higher in Case 1 and lower in Case 2 than atmospheric pressure. These results may be used to set to the criterion for the airtightness of the electrolyte, as well as to decide the pressure setting of supplied gases to fuel cells.

5. Conclusions

(1) The binary gas permeation (BGP) method is proposed for the characterization of solid oxide fuel cell components. In this method, the properties of porous media are obtained from permeability measurements for binary gases (helium and propane). It was confirmed experimentally that the results of the BGP method are applicable to the prediction of permeabilities for other gases and mass transfer characteristics in the nonisobaric binary gas diffusion systems.

(2) We applied this method to the evaluation of plasma-sprayed yttria-stabilized zirconia (YSZ) electrolyte films. It has been shown that YSZ film sprayed

Fig. 13 Calculated results of total pressure at electrode

at low pressure is superior to atmospheric-sprayed film because of its smaller pore diameter, and that measurement of relative density is insufficient for the evaluation of airtightness of electrolyte films.

(3) The estimation of concentration polarization caused by two porous support tubes was examined in this study and the necessity of the improvement of porous tubes was noted. It has also been shown that a large pressure gradient appears in the porous support when the fuel cell operates, which may be important in considering the criterion for airtightness of the electrolyte.

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