ANALYSIS OF GAS TRANSPORT IN POROUS Ni-YSZ ANODES
BY TRANSIENT RESPONSE METHOD

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ABSTRACT

Chemical relaxation of fuel partial pressure (H2, CO, and/or CH4) is analyzed to quantify gas transport at 1000°C in porous Ni-YSZ electrodes of solid oxide fuel cells. Pore size of Ni-YSZ electrodes was mainly below 1µm, and thus both the bulk-gas diffusion and the Knudsen diffusion may have contributed to the gas transport. The diffusion kinetics of the fuels was influenced by the kind and the concentration of the fuel gas. These results indicate that the diffusion process of fuel gases in the electrode pores, a major source of the concentration polarization, may become sluggish for fuel gases with a larger molecular weight. For CH4 fuel, the response curve was affected by reforming reactions.

INTRODUCTION

Solid oxide fuel cell (SOFC) is promising for future power generation because of higher efficiency and clean environment (1). The performance of the fuel cells is often limited by internal resistances, leading to a larger voltage drop with increasing current flow. These internal resistances consist of the ohmic contribution due to the resistances in e.g. electrolytes and electrodes, and the nonohmic contribution arising e.g. from electrode reactions. The latter includes activation polarization and concentration polarization. The concentration polarization can be caused by a slow gas diffusion in microporous electrodes, and this effect may become significant especially under conditions with a lean fuel concentration and/or at a high fuel utilization (2,3). In addition, if hydrocarbons such as CH4 are directly used as fuels, the reforming reactions (e.g. CH4+2H2O<–>CO2+4H2) on the electrode surfaces and the shift reaction (CO+H2O<–>CO2+H2) also take place simultaneously. In this study, we apply the transient response method to detect voltage responses by abruptly varying the kind or the concentration of fuel gases. The voltage response curves are fitted to derive gas diffusion coefficients, which are compared to those derived from literature data.

EXPERIMENTAL

An anode-supported tubular-type cell (supplied by Saibu Gas Co., Ltd., Japan) was used in this study. The YSZ electrolyte with a thickness of 40 µm was prepared via a slurry-coating method on a porous Ni-YSZ support (initially with a diameter of 1.4 cm, a length of 13 cm, and a thickness of 0.2 cm). This tube was then cut into pieces with a width of 1cm. The cathode layer with a width of 4 mm was deposited using a paste
consisting of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powder and turpentine-oil, and then heat-treated at 1100°C for 5 hours.

The cell configuration is schematically shown in Fig. 1. Throughout the gas relaxation measurements, the cathode was exposed to the ambient atmosphere. Fuel gases such as $\text{H}_2$, $\text{CO}$, and/or $\text{CH}_4$ were supplied to the anode. $\text{N}_2$ gas was also simultaneously supplied with which the total gas flow was fixed to be 150 ml/min. A $\text{ZrO}_2$-based potentiometric sensor was placed near the cell to detect the oxygen partial pressure and thus the fuel composition. All measurements were carried out at 1000°C. The fuel composition was abruptly varied to apply stepwise concentration gradients of gases leading to gas diffusion. The diffusion coefficients of fuel gases can be derived by measuring a change in cell voltage. Owing to the very fast response of the neighboring YSZ potentiometric sensor at 1000°C, it can be inferred that the fuel gas with a different composition reached the electrode surface when the voltage of the YSZ sensor started to change, referring to $t=0$. The oxygen partial pressure was derived from the cell voltage via the Nernst equation.

**RESULTS**

**H$_2$ Gas as a Fuel**

Figure 2 shows the relaxation of the $\text{H}_2$ partial pressure for various fuel ($\text{H}_2$) concentrations measured by the transient response method. For the $\text{H}_2$-$\text{H}_2\text{O}$ fuel system, gas diffusion and electrode reactions are involved but without the reforming reactions and the shift reaction. As an initial condition, the low-concentration fuel gas, with 0.7% $\text{H}_2$ and 3% $\text{H}_2\text{O}$, diluted by $\text{N}_2$ gas was supplied to the anode. At $t=0$, the gas was exchanged to a fuel gas with a higher $\text{H}_2$ concentration ranging between 97 and 7% $\text{H}_2$, while the water vapor concentration was 3% $\text{H}_2\text{O}$, diluted by $\text{N}_2$ gas. The cell voltage associated with the $\text{H}_2$ partial pressure started to respond around $t=6$ sec. This initial delay corresponds to the time needed for gas molecules to diffuse from the electrode surface to the three-phase boundaries. This delay was not affected by the $\text{H}_2$ concentration of the fuel gas. This result indicates that the diffusion coefficient of $\text{H}_2$ molecules is independent of the $\text{H}_2$ concentration.

Since the $\text{H}_2\text{O}$ concentration remained constant upon the gas exchange, only the diffusion of $\text{H}_2$ and $\text{N}_2$ was involved. Although the $\text{H}_2\text{O}$ concentration must actually be changed by the gas exchange, this change was negligibly small. The gas transport in the porous anodes can thus be described as the ambipolar diffusion of $\text{H}_2$ gas and $\text{N}_2$ gas with no net volume change. Net transport of the $\text{H}_2$ gas and $\text{N}_2$ gas was to the three-phase boundaries and to the electrode surface, respectively. As the total gas pressure has to remain constant, the net flow of gas transport in both directions must be identical.

**CO Gas as a Fuel**

The transient response method was also applied to the CO-$\text{CO}_2$ gas mixtures. For SOFC, CO can also be used as a fuel (3), and oxidized at the three-phase boundaries to form $\text{CO}_2$ as a reaction product. The dependence of the CO concentration on the relaxation of the CO partial pressure was also measured. Similar to the case using
H₂-H₂O gas mixtures, the gradient in the CO partial pressure response curves became smaller with decreasing concentration deviation. The initial delay remained unchanged with CO concentration. The relaxation behavior for the CO-CO₂ gas mixtures was therefore similar to that for the H₂-H₂O gas mixtures.

Figure 3 shows the voltage relaxation for the gas mixture of H₂ and CO, which simulates the gas after reforming CH₄. Thus the influence of the reforming reactions can be excluded. To ensure gas equilibria, steam (H₂O) with a concentration of 3% was added. The initial gas composition was H₂: 0.7%, CO: 0.7%, and H₂O: 3%, diluted by N₂ gas. At t=0, the initial gas was exchanged to the one with a higher fuel concentration. The sum of the H₂ and CO concentration in the latter gas was 97%, and the ratio between H₂ and CO was varied. The cell voltage decreased with decreasing H₂ concentration, but the difference was small since the total fuel concentration was fixed. The response became slower with increasing CO concentration.

**CH₄ Gas as a Fuel**

The voltage response for the CH₄-H₂O gas mixture (i.e. direct internal reforming) was compared with that for the H₂-CO gas mixture (i.e. simulated external reforming) in Fig. 4. The gas transport processes could be more complicated as the reforming reactions are concentrated around anode top surfaces as well as in the porous anode. Even though the cell voltage was comparable, the response was much more sluggish for the CH₄-H₂O gas mixture than for the H₂-CO gas mixture, mainly due to the reforming reactions involved in the former case. The gas transport, dominated by the gas diffusion of molecules with a larger molar weight, is also important in case hydrocarbon fuels, such as CH₄, are used to produce H₂ and CO gas mixtures via direct reforming reactions. A higher performance is expected if the fuel contains more H₂ and less CO₂ It can also be expected that the slow-diffusing gas affects the polarization behavior leading to a high concentration polarization even though fast-diffusing gas (e.g. H₂ gas) is concentrated in the fuel (3).

In case of external reforming, chemical transport in the anode includes the shift reaction but no reforming reaction is involved. Therefore no volume change is associated. In case of internal reforming, it becomes complicated, since gas transport, shift reaction, and reforming reactions as well as electrochemical reactions around the three-phase boundaries all contribute to overall electrochemical processes at the anode side. Furthermore, the conversion rates of such reactions are also affected by other parameters e.g. the amount of catalysts, so that the analysis based only on gas diffusion may no longer be valid.

**DISCUSSION**

The electrode reactions at the Ni-YSZ cermet anodes are considered to take place at or around three-phase boundaries among electrolyte, electrode, and gas phase. Therefore, on the anode side, fuel gases must be transported from the electrode surface to the three-phase boundaries. Simultaneously, the products formed by electrode reactions at the three-phase boundaries have to be removed to the electrode surface. In this study, we will derive gas diffusion coefficients either by the calculation based on gas diffusion.
theories or by fitting the voltage response curves with a relaxation model.

**Calculation of Gas Diffusion Coefficients in Porous Anodes**

We calculated the gas diffusion coefficients of mixed gases in a porous electrode in the following way. As possible fuel gases, H$_2$-H$_2$O, CO-CO$_2$, CH$_4$-H$_2$O mixtures were considered. First, the diffusion coefficient of a mixed gas, $D_{12}$, consisting of a molecule 1 and 2 may be given after Fuller (4):

$$D_{12} = \frac{10^{-3} T^{1.75}}{p (v_1^{1/3} + v_2^{1/3})^2} \cdot \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}$$

where $T$ is temperature in Kelvin, $v$ is the characteristic volume, $p$ is the total pressure (atm), and $M$ is the molar weight of gas species 1 and 2. Note that, in this study, H$_2$ and H$_2$O gases were diluted by N$_2$ gas, so that one actually has to deal with a mixed gas with 3 components. For simplicity, however, we assumed that multiple-component gas diffusion can be well described as an ambipolar diffusion of most slowly diffusing species in each direction (5).

The relation above is valid under the condition that the gas diffusion is rate-limiting by the collision of gas molecules in a space with a quasi-infinite volume. This condition is fulfilled only if the average mean free path is much longer than the pore radius. If this condition is no longer valid, i.e. pore radius is much smaller, the collisions of gas molecules with pore surfaces are rate-determining for the gas transport. In such a situation, the gas diffusion is rather described as Knudsen diffusion, i.e.,

$$D_k = \frac{4}{3} r_e \cdot \sqrt{\frac{2RT}{\pi M}} = 9700 r_e \cdot \sqrt{\frac{T}{M}}$$

where $r_e$ is the pore radius. In our anodes, the pore radius measured by a Hg-porosimeter, 27.75 nm, was used for further analysis. The molar weight was considered to correspond to that of N$_2$ with the largest molar weight among H$_2$, H$_2$O, and N$_2$ gases. This consideration is based on the assumption previously mentioned that the apparent diffusion coefficient is rate-limited by the most slowly diffusing molecule, i.e. the one with the largest molecular weight.

In general, both the bulk-gas diffusion and the Knudsen diffusion can contribute simultaneously. The latter is generally nonnegligible, if the pore radius is less than 1μm (6). For the mixed situation, we therefore derived an effective gas diffusion coefficient from both contributions as:

$$D = \frac{1}{1/D_{12} + 1/D_k}$$

where $D_k$ denotes the Knudsen diffusion coefficient of a gas component A with the largest molecular weight. This relation can be applied for simple pores with a cylindrical
Derivation of Gas Diffusion Coefficients from Voltage Responses

The gas diffusion coefficient can also be derived from the voltage response results of this study. The gas diffusion model for electrodes applied in this study is based on the Fick’s second law of diffusion, as the diffusion rate, corresponding to the gradient of the voltage response curve, is related to the concentration gradient of the fuel species (7). It holds that:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$  \[4\]

where $c$ refers to concentration, $t$ is time, and $x$ is length in the diffusion direction (x-axis). Pore volume was then divided into smaller pieces with a width of $\Delta x$. At a given position $x$ and time $t$, the concentration $c(i, t)$ can be described as (7):

$$\frac{c(i, t + \Delta t) - c(i, t)}{\Delta t} = \frac{D}{\Delta x} \left( \frac{c(i+1, t) - c(i, t)}{\Delta x} - \frac{c(i, t) - c(i-1, t)}{\Delta x} \right)$$  \[5\]

A fitting procedure was applied using the above relation. The values $\Delta t$ and $\Delta x$ were optimized.

Figure 5 shows the voltage response curves fitted by assuming a gas diffusion coefficient of $D=0.17 \text{ cm}^2/\text{s}$. The calculated values (see Table 1) and the values by fitting with the experimental results agreed well. It also suggests that the diffusion coefficient is actually independent of concentration. The gradient in the voltage relaxation curve for H$_2$ fuel became smaller with decreasing concentration deviation (gradient) upon gas exchange, which can be easily understood via the Fick’s second law of diffusion. The agreement of the experimental results with the calculated value indicates that the gas diffusion coefficients derived via this simple pore diffusion model correspond to the gas diffusion coefficients in the anodes studied. This model can well describe the gas transport for the H$_2$- H$_2$O gas mixture.

The same simulation procedure was also applied to the CO-CO$_2$ gas system. The voltage relaxation curve could be fitted using a gas diffusion coefficient of $D=0.14 \text{ cm}^2/\text{s}$. One again finds the agreement between the calculated values and the values obtained by the fitting. The gas diffusion coefficients derived via this pore model were comparable with those derived previously from limiting current density (7). It can therefore be concluded that the model applied here is suitable and valid for porous SOFC anodes.

It is also of interest to apply the model to other gas systems including the CH$_4$-H$_2$O gas mixture. However, the application of this model was difficult, since, first of all, the voltage response can not be directly transformed into a partial pressure of a specific gas component in a mixed gas with several gas compositions. A quantitative analysis based on gas diffusion could not be well applied. We have therefore tried to estimate an apparent diffusion coefficient from the voltage response. Equation 4 indicates that the...
time dependence of the concentration is coupled with the concentration gradient via a diffusion coefficient. Furthermore, the initial gradient of the relaxation curve is proportional to the diffusion coefficient, provided that the concentration gradient is identical. The concentration gradient is related to the voltage change before and after the abrupt gas exchange. Based on these relations, apparent diffusion coefficients were derived. The results are compiled in Table 2. The diffusion coefficients calculated via the single pore model are also shown. Table 2 well indicates that the coefficients derived via these two models are identical for the H$_2$-H$_2$O, CO-CO$_2$, and H$_2$-CO-H$_2$O systems. However, it was not the case for the CH$_4$-H$_2$O system, as a much lower apparent diffusion coefficient was obtained via the simple pore model.

The behavior for the H$_2$-CO gas mixtures and for the H$_2$ or CO gas was identical. The difference, if any, should arise from the shift reaction or the reforming reactions. It is considered that the shift reaction is very fast under conditions studied and no volume change is involved. Therefore the shift reaction does not influence the analysis based solely on gas diffusion. On the other hand, the reforming reactions are nonnegligible, as the experimental values were much lower than those calculated if CH$_4$ is used as a fuel (see Table 2). This can be explained since reforming reactions, in addition to the gas diffusion in the porous anodes, became significant, leading to a much smaller apparent diffusion coefficient. As the reforming reactions take place on the pore surfaces, anode microstructure is an important factor affecting anodic polarization.

**SUMMARY**

Gas transport in porous SOFC anodes at 1000°C studied by the transient response method could be well explained via a diffusion model in porous anodes, except for the case in which methane was directly used as a fuel. This deviation arises from the sluggish reforming reactions. For other fuel systems including H$_2$-H$_2$O, CO-CO$_2$, and their mixtures, the gas diffusion model for porous anodes can well be applied, where the slowest diffusing gas species with a larger molecular weight dominates the gas diffusion. The concentration relaxation results suggest that concentration polarization, in addition to activation polarization, can be a major source of the anodic polarization under the experimental conditions studied.

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Table 1. Estimated diffusion coefficients ($D_{12}$, $D_K$, and $D$) at 1273 K

|          | $D_{12}$ $\text{cm}^2/\text{s}$ | $D_K$ $\text{cm}^2/\text{s}$ | $D$ $\text{cm}^2/\text{s}$ |
|----------|-----------------|-----------------|-----------------|
| H$_2$-H$_2$O | 3.03            | 0.182           | 0.172           |
| CO-CO$_2$   | 2.07            | 0.145           | 0.136           |
| CH$_4$-H$_2$O | 1.63            | 0.182           | 0.164           |

Table 2. The experimental values derived from the voltage response curves and the calculated values of gas diffusion coefficients for various fuels in porous anodes. For the calculation, no reforming reaction was taken into account.

|          | H$_2$-H$_2$O | CO-CO$_2$ | H$_2$-CO$_2$-H$_2$O | CH$_4$-H$_2$O |
|----------|-------------|-----------|---------------------|--------------|
| Experimental value $\text{cm}^2/\text{s}$ | 0.17 | 0.14 | 0.14 | 0.028 |
| Calculated value $\text{cm}^2/\text{s}$ | 0.17 | 0.14 | 0.14 | 0.16 |

Pt lead

Anode : Ni-YSZ [NiO:YSZ=4:6]
Electrolyte : (ZrO$_2$)$_{0.85}$(YO$_1.5$)$_{0.15}$ [YSZ]
Cathode : La$_{0.6}$Sr$_{0.4}$MnO$_3$ [LSM]
Spacer

O$_2$ Sensor
Glass ring
Mullite tube

Fig. 1. Schematic drawing of a fuel cell cross section.

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Fig. 2. Time dependence of partial pressure of H$_2$ for various concentrations at 1273 K. (Cell: H$_2$-H$_2$O, Ni-YSZ/YSZ/ La$_{0.6}$Sr$_{0.4}$MnO$_3$, air. t<0 : H$_2$, 0.7%; H$_2$O, 3%; N$_2$, balance, t>0 : H$_2$O, 3%; N$_2$, balance, Flow rate: 150ml/min.)

Fig. 3. Time dependence of terminal voltage for various concentrations at 1273 K. (Cell: H$_2$-CO-H$_2$O, Ni-YSZ/YSZ/ La$_{0.6}$Sr$_{0.4}$MnO$_3$, air. t<0 : H$_2$, 0.7%; CO, 0.7%; H$_2$O, 3%; N$_2$, balance. t>0 : H$_2$O, 3%. Flow rate: 150ml/min.)
Fig. 4. Time dependence of terminal voltage for various fuels at 1273 K. (Cell: CH₄-H₂O or H₂-CO-H₂O, Ni-YSZ/YSZ/ La₀.₆Sr₀.₄MnO₃, air. t<0 : CH₄, 0.7%; H₂O, 3%; N₂, balance, or H₂, 0.7%; CO, 0.7%; H₂O, 3%; N₂, balance. t>0 : CH₄, 13%; H₂O, 40%; N₂, balance, or H₂, 13%; CO, 13%; H₂O, 3%; N₂, balance. Flow rate: 150ml/min.)

Fig. 5. Time dependence of partial pressure of H₂ for various concentrations at 1273 K. (Cell: H₂-H₂O, Ni-YSZ/YSZ/ La₀.₆Sr₀.₄MnO₃, air. t<0 : H₂, 0.7%; H₂O, 3%; N₂, balance. t>0 : H₂O, 3%; N₂, balance. Flow rate: 150ml/min. Lines: values estimated using diffusion coefficient of 0.17 cm²/s. Plots: experimental value.)