TEMPERATURE DISTRIBUTION IN TUBULAR SOLID OXIDE FUEL CELL

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ABSTRACT

The temperature distribution in tubular solid oxide fuel cell (SOFC) was calculated by using finite element method. In order to estimate the temperature distribution, the current distribution and the partial pressure distributions of hydrogen, water, and oxygen were obtained. From the temperature distribution in the tubular SOFC, it can be seen that the heat generated in SOFC flows from the electrolyte region to the porous yttria stabilized zirconia substrate and the hydrogen electrode. The half of heat generated in SOFC was transported to hydrogen gas chamber. If such heat is utilized for the reforming reaction of a hydrocarbon to hydrogen, the total energy conversion efficiency is improved from 70% to 90%. Therefore, the internal reforming fuel cell is attractive.

1. INTRODUCTION

Solid oxide fuel cells (SOFC) have been investigated and developed, because of their high energy conversion efficiency. These researches concentrated on the development of materials for electrodes and electrolytes and the construction of the cell [1]. Recently, the excellent design of SOFC has been achieved by using Electrochemical Vapor Deposition (EVD) [2]. In such a SOFC, the thin electrolyte was deposited on the conductive oxide cathode which was deposited on the porous calcia stabilized zirconia. In this study, the temperature distribution in such a solid oxide fuel cell was calculated by finite element method in order to offer the fundamental data for the development of the high energy conversion SOFC.

The maximum work generated by SOFC corresponds to AG of the hydrogen combustion. The energy of TAS cannot be utilized as electric energy in SOFC. Moreover, additional work caused by the overpotentials of hydrogen and oxygen electrodes and the ohmic loss of the electrolyte cannot be utilized as electric energy. In order to minimize such unutilized work, the thickness of electrolyte must be decreased and excellent oxygen and hydrogen electrodes must be developed.

On the other hand, the heat generated in SOFC may be utilized for
the reforming reaction of a hydrocarbon. The calculation of the temperature distribution in SOFC is important to determine the practical operation conditions.

2. CURRENT AND PARTIAL PRESSURES DISTRIBUTIONS IN TUBULAR SOFC

In this calculation, the heat generation elements and the heat absorption elements were considered as follows. In the case of the tubular solid oxide fuel cell, the heat is generated or absorbed by the following factors;

(1) Overpotentials of hydrogen and oxygen electrodes.
(2) Ohmic resistance of yttria stabilized zirconia.
(3) Ohmic resistance of electrodes.
(4) Entropy changes of hydrogen and oxygen electrodes.

The overpotentials of hydrogen and oxygen electrodes are dependent on the current. The relationship between the overpotentials and the current has been examined and suggested by many researchers [3,4,5]. In this study, the model cell was constructed by using LaCoO3 as a cathode, Ni cermet as an anode, and yttria stabilized zirconia as an electrolyte. The following equations were adopted in the calculation of the heat generation from the overpotentials [3]. The electrochemical parameters are listed in Table 1.

For hydrogen electrode, the overpotential ($\eta_{iA}$) is

$$\eta_{iA} = \frac{RT}{anF} \ln\left(\frac{I}{I_0}\right)$$ (1)

where I is current and $I_0$ is exchange current.

For oxygen electrode, if the activation and diffusion overpotential is assumed to be negligible, the overpotential ($\eta_{iC}$) is

$$\eta_{iC} = 0$$ (2)

The heat generation from the ohmic resistance of yttria stabilized zirconia is also dependent on the current. The ohmic resistance of electrodes is negligibly small. The relationship between the voltage loss in the electrolyte ($\Delta V$) and the current (I) obeys Ohm’s law.

$$\Delta V = I \times R$$ (3)

where R is the resistance of yttria stabilized zirconia. It can be measured by using the impedance method [6].

The heat generation from the thermodynamic entropy change
becomes larger with increasing temperature. The heat of $\Delta S$ has to be taken into account for the calculation of the temperature distribution. The total reaction in SOFC is the hydrogen combustion. $\Delta S$ is easily estimated from the thermodynamic consideration. However, in the electrochemical system, the total reaction is separated into cathode and anode reactions. The entropy change is also separated.

$$\Delta S = \Delta S_{\text{cathode}} + \Delta S_{\text{anode}} \quad (4)$$

The entropy changes at cathode and anode can be estimated from Seebeck coefficients of oxygen and hydrogen electrode reaction as reported in [7]. The entropy change of oxygen electrode reaction was estimated to be $-81.6 \text{ J K}^{-1} \text{ mol}^{-1}$ per two electrons under 0.21 atm oxygen partial pressure. The dependence of entropy change on partial pressure can be represented by the following equations.

**Total reaction**

$$\begin{align*}
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} \\
(5)
\end{align*}$$

For hydrogen electrode,

$$\Delta S_{\text{anode}} = (S_{\text{H}_2\text{O}} - R \int_1^{P_{\text{H}_2\text{O}}} \ln P \, dP) - (S_{\text{H}_2} - R \int_1^{P_{\text{H}_2}} \ln P \, dP) - S_{\text{O}_2}^* \quad (6)$$

For oxygen electrode,

$$\Delta S_{\text{cathode}} = S_{\text{O}_2}^* - \frac{1}{2} (S_{\text{O}_2} - R \int_1^{P_{\text{O}_2}} \ln P \, dP) \quad (7)$$

where $S_{\text{O}_2}^*$ is transported entropy of $\text{O}^{2-}$ ion. The entropy changes of hydrogen and oxygen electrodes under various partial pressures can be calculated from equations (6) and (7).

Thus $\Delta S_{\text{cathode}}$ changes with the partial pressure of oxygen and $\Delta S_{\text{anode}}$ changes with the partial pressure of hydrogen and water in solid oxide fuel cell. In other words, the heat generation depends on the partial pressure of hydrogen, water and oxygen. Therefore, the partial pressure distribution has to be estimated in order to calculate the temperature distribution in the tubular SOFC.

The current distribution was calculated by using a model, as shown in Fig.1. The SOFC was divided into $n$ elements. The current passed through each element is represented by $I_n$. The total current ($I$) is given by the sum of each element current ($I_n$).
\[ I = I_1 + I_2 + \cdots + I_i + \cdots + I_n \quad (8) \]

If the electrode or bus bars have excellent electronic conductivities, the cell voltage of each element is equal to total cell voltage (V).

\[ V = V_1 = V_2 = \cdots = V_n \quad (9) \]

For element 1, the relationship between \( V_1 \) and \( I_1 \) is represented by the following equation,

\[ V_1 = E_e - \eta_i - R I_1 \quad (10) \]

where \( \eta_i \) is given by equation (11) and \( E_e \) is determined from the partial pressures of hydrogen, water, and oxygen according to the Nernst equation.

\[ \eta_i = \eta_{i_a} + \eta_{i_c} \quad (11) \]

\[ E_e = E_0 - \frac{RT}{nF} \ln \left( \frac{P_0}{P_0 P_{\text{H}_2} O_{\text{H}_2}} \right) \quad (12) \]

For other elements, the same relationship can be established. The hydrogen and air flow horizontally through the chambers in the cell at constant rate, where the flow rate of air is the same as that of hydrogen. The partial pressures of oxygen and hydrogen at the entrances of chambers are higher than that at the exits, because oxygen and hydrogen are consumed by the electrode reactions. The partial pressure in element 2 is given by the following equation,

\[ P_{\text{H}_2, 2} = \frac{U_{\text{H}_2, 1} - \frac{2F}{2F}}{U_{\text{H}_2, 1} + U_{\text{H}_2, 0, 1}} \quad (13) \]

The air and water partial pressures are given by similar equations.

\[ P_{0_{2, 2}} = \frac{0.21 U_{\text{air}, 1} - \frac{F}{4F}}{U_{\text{air}, 1} - \frac{I_1}{4F}} \quad (14) \]
\[
\begin{align*}
\left\{ \begin{array}{c}
P_{H_2O,2} = \frac{I_1}{2F} + \frac{U_{H_2O,1}}{U_{H_2O,1} + U_{H_2,1}} \\
\end{array} \right.
\end{align*}
\]

where \(U_{i,1}\) is the molar flux of species \(i\) at the entrance of SOFC (mol s\(^{-1}\)) and is calculated from the flow rate. In this way, the partial pressures in element 2 can be obtained. As a result, \(E_e\) can also be determined. From \(E_e\) and \(V\), \(I_2\) can be calculated by using equation (10). Such a procedure is repeated \(n\) times. Finally, the current distribution and the partial pressure distribution can be calculated.

Fig. 4 shows the current distribution in SOFC at various flow rates of hydrogen. The average current density is 200 mA cm\(^{-2}\). The partial current near the entrance of SOFC is larger than that near the exit. The distribution depends on the flow rate and current. The distribution becomes larger with decreasing flow rate. Fig. 5 shows the partial pressure distributions in SOFC at 5 cm s\(^{-1}\) (0.0376 mol s\(^{-1}\)) flow rate of hydrogen and air. The hydrogen partial pressure gradually decreases along the Z axis from the entrance to the exit. Under these conditions, 90% of hydrogen introduced in SOFC is consumed by the electrode reaction. The oxygen partial pressure also decreases. The partial pressure distribution of hydrogen is larger than that of oxygen. Thus the flow rate influences the distributions of current and the partial pressures.

In this way, the partial pressure distributions of hydrogen, oxygen, and water and the current distribution in SOFC were obtained. From these results, the heat generation at each element can be estimated. The temperature distribution in SOFC can be calculated by using finite element method.

3. TEMPERATURE DISTRIBUTION IN TUBULAR SOFC

Fig. 6 shows the model of the tubular SOFC and the initial and boundary conditions of the calculation. At the interface between the oxygen chamber and the porous yttria stabilized zirconia, the thermal boundary is assumed. Thermal conductivity at the interface is calculated from \(\rho\) (density), \(\mu\) (viscosity), \(C_p\) (heat capacity), \(k\) (heat conductivity), \(u\) (velocity), and \(D\) (diameter or length), as summarized in Table 2. The hydrogen and oxygen flow along the Z axis from the entrance to the exit. The hydrogen electrode is made from nickel cermet and its thickness is 500 \(\mu\)m. The oxygen electrode is made from LaCoO\(_3\) and its thickness is 500 \(\mu\)m. The electrolyte is yttria stabilized zirconia and its thickness is 500 \(\mu\)m. Thermal conductivities of these materials are listed in Table 3.
Thus, all parameters used in the calculation of the temperature distribution in the tubular SOFC can be estimated. Therefore the calculation by finite element method was carried out. Fig. 7 shows the temperature distribution in the electrolyte along the Z axis. The temperature at the entrance is lower than that at the exit. From the current distribution, it is expected that the heat generated at the entrance is larger than that at the exit. This fact indicates that the heat generated near the entrance of SOFC is transported to the hydrogen gas and oxygen gas and the temperatures in hydrogen and oxygen chambers increase. As a result, the temperature in electrolyte near the exit also increases. The temperature distribution in SOFC strongly depends on the flow rate, and the uniform temperature distribution can be obtained at 30 cm s⁻¹, where the flow rate of air is the same as that of hydrogen gas. With increasing flow rate, the amount of heat transported to gas decreases; as a result the temperature difference between the entrance and the exit becomes small.

Fig. 8 shows the temperature distribution along the R axis near the entrance of SOFC. The highest temperature is observed at the cathode region. The temperatures at the porous yttria stabilized zirconia and the nickel cermet electrode are lower than that at the electrolyte. The heat is transported from the electrolyte to hydrogen gas and oxygen gas. The temperature gradient is largest at the electrolyte region.

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Table 1  Electrochemical Parameters used in the calculation of the current distribution.

| Electrochemical parameters |  
|---------------------------|
| \( I_0 \)             | 9.8 A m\(^{-2}\)  
| \( \alpha_n \)         | 1.8\(^*\)  
| \( \sigma^{**} \)       | 0.1 S cm\(^{-1}\)  

\(^*\): from reference [8].  
\(^{**}\): \( \sigma = (1/\alpha)(L/S) \); \( L \): thickness of YSZ element, \( S \): surface area of YSZ element.

Table 2  Physical parameters of hydrogen and air at 1273 K.

| \( \rho/g \text{ cm}^{-3} \) | \( \mu/\text{g cm}^{-1} \text{ s}^{-1} \) | \( C_p/J \text{ g}^{-1} \text{ K}^{-1} \) | \( k/J \text{ cm}^{-1} \text{ s}^{-1} \text{ K}^{-1} \) |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Air                         | 0.276                       | 6x10\(^{-5}\)               | 1.1x10\(^3\)               | 0.2                         |
| \( \text{H}_2 \)            | 0.019                       | 3x10\(^{-5}\)               | 1.4x10\(^4\)               | 0.1                         |

Table 3  Heat conductivities of the materials in SOFC.

| material        | \( k/J \text{ cm}^{-1} \text{ s}^{-1} \text{ K}^{-1} \) |
|-----------------|-----------------------------------------------------|
| YSZ             | 0.027                                               |
| porous YSZ      | 0.011                                               |
| \( \text{LaCoO}_3 \) | 0.022                                               |
| \( \text{Ni cermet} \) | 0.11                                               |
Fig. 1  Schematic illustration of tubular SOFC.

Fig. 2  Model for calculation of current and partial pressure distributions.
Fig. 3  Equivalent circuit of model in Fig. 2.

Fig. 4  Current distribution in tubular SOFC.
Fig. 5 Partial pressure distribution in tubular SOFC.

Fig. 6 Model for calculation of temperature distribution and initial and boundary conditions.
Fig. 7 Temperature distribution in YSZ along the Z axis at various flow rates.

Fig. 8 Temperature distribution along the R axis near the entrance of SOFC at 10 cm s\(^{-1}\).