Thermoelectric Power in Ionic and Electronic Mixed Conductors

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In order to study the thermoelectric property of the oxide ionic and electronic mixed conductor of 10 mol% CaO-doped CeO₂ (CDC), a new type of thermocell was prepared, in which platinum electrodes were embedded in the tube-type sample to diminish the large temperature gradient over the electrodes due to the local heat radiation from heating furnace. Using this thermocell, reproducible data were obtained. The thermoelectric power measured in CDC under various oxygen atmospheres (P_{O₂}) from 1.0 to about 10⁻¹⁵ atm showed that the sign of Seebeck coefficients changed from minus to plus. This variation of Seebeck coefficients vs. P_{O₂} was well interpreted by considering that (1) the thermoelectric power could be a driving force to make actual and electrochemical oxygen transfer in the mixed conductor and (2) the electrode processes had limiting rates due to slow oxygen diffusion (or oxygen gas exhaustion at the cathode and evolution at the anode).

1 INTRODUCTION

Fuel pellets used in nuclear reactors are made of UO_{2+x} or the mixture of UO_{2+x} and PuO_{2+x}. These pellets are packed within zircaloy claddings and loaded into the reactor. It is widely known that the oxygen redistributes and the uniformity of the composition is lost in a fuel pellet while it is irradiated in a reactor^{1,2}. This redistribution is generally considered to be ascribed by thermal diffusion. In case of a mixed conductor, however, it can also be interpreted as the result of an electrochemical ion flow caused by the thermoelectric power³.

In order to verify this interpretation, it is necessary to know the thermoelectric power and the specific conductivities due to each conductive species in a mixed conductor. However, there are few experimental works as to the thermoelectric power measurements in mixed conductors. Furthermore, thermoelectric powers of ionic or mixed conductors were ordinarily measured

using a cylindrical thermocell as illustrated in Fig. 1. This type of cell has two oxygen electrodes on its flat surfaces and two thermocouples adjacent to the electrodes. When this cell is placed in a furnace, the heat flux from the furnace first heats the electrode and then the heat transfers to the conductor. This means that there exists a large temperature gradient over the electrode, and therefore, the temperature of the electrode cannot be determined accurately. Consequently, the data obtained by different workers would be poorly coincident in case of pure ionic conductors as well as mixed conductors.

Fig. 1 Schematic illustration of heat transfer in the ordinary type of samples.

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One of the purposes of this study is to surmount the difficulties in thermoelectric power measurements of ionic or mixed conductors from a viewpoint of the thermal engineering. Another purpose is to measure a thermoelectric power of a mixed conductor of 10 mol% CaO-doped CeO_2 (CDC) and to propose a mass transfer model that explains its oxygen pressure dependence.

2 EXPERIMENTAL

In order to avoid a large temperature gradient over the electrode, the electrodes may be fixed deep in the conductor with thermocouples, but this configuration cannot be applied to the electrode which should be reversible to oxygen in the atmosphere.

In this study, a tube-type thermocell was set up as shown in Fig. 2. Two Pt electrodes are placed on the inner wall of the tube-type conductor and two thermocouples are fixed within the conductor adjacent to each electrode from the outer surface. Radiant heat from the furnace cannot reach directly to the electrode. This means that the temperature gradient over the electrode is limited and the temperature of the electrode can be correctly measured.

In order to confirm the validity of this method, the thermoelectric power of 8 mol% Y_2O_3 -stabilized ZrO_2 (YSZ) was first measured. Then the thermoelectric power of 10 mol% CaO-doped CeO_2 (CDC) was measured with respect to several kinds of atmospheres to clarify how it depends on the partial pressure of oxygen (Po_2).

The YSZ used in this study was made by Nikkato Co., Ltd. Its length is 30 mm, and its outer and inner diameters are 7 mm and 5 mm, respectively. CDC used as a mixed conductor in

Fig. 2 Schematic illustration of heat transfer in the sample used in this study.

Fig. 3 Experimental apparatus of thermoelectric power measurements.

the subsequent study was prepared in our laboratory with a solid state reaction using powders of CeO_2 and CaCO_3 as starting materials. The shape of CDC is similar to that of YSZ although its outer diameter is 10 mm.

The apparatus for thermoelectric power measurement is presented in Fig. 3. After setting some temperature difference up to 50 K in the vertical direction around 1270 K by controlling two independent heaters, the electric motive force (EMF) between two electrodes and the temperature of each electrode were measured by a digital multimeter. In case of CDC, several kinds of atmospheric gases were used to study the Po_2 dependence of the thermoelectric power, which are pure oxygen ($\text{Po}_2 = 1.0$ atm), air ($\text{Po}_2 = 0.21$ atm), N_2 - O_2 mixture ($10^{-4} < \text{Po}_2 < 0.21$ atm), N_2 whose Po_2 was controlled using a YSZ oxygen pump ($10^{-15} < \text{Po}_2 < 10^{-4}$ atm). During the experiment, the Po_2 in the apparatus was measured by the oxygen sensor which was placed just below the conductor.

3 RESULTS AND DISCUSSION

The measured EMF's of the YSZ thermocell are presented in Fig. 4. The horizontal axis presents the temperature difference between two electrodes and the vertical one presents the EMF observed between them. The symbol $\circ$ denotes

Fig. 4 The EMF as a function of ΔT in YSZ.

the data obtained in pure oxygen atmosphere and Δ denotes the data obtained in air. The solid lines in this figure were determined using the least square method and the slopes of these lines present the Seebeck coefficients dE/dT (mV K^{-1}), which are -0.461 mV K^{-1} for $P_{\text{O}_2} = 1.0 \text{ atm}$ and -0.495 mV K^{-1} for $P_{\text{O}_2} = 0.21 \text{ atm}$. These values are very close to -0.462 mV K^{-1} and -0.495 mV K^{-1} obtained by Ratkje and Tomii through their specially careful experiment⁴⁾. In addition, the reproducibility of the measured values were highly improved by the thermocell in Fig. 2 instead of the ordinary type in Fig. 1. This means that the measuring method developed in this work is appropriate.

Next, the measured EMF's of the CDC

Fig. 5 The EMF as a function of ΔT in CDC.

thermocell are presented in Fig. 5. The symbols $\circ$, Δ , $\square$ denote the data for $P_{\text{O}_2} = 1.0 \text{ atm}$, 0.21 atm , $5 \times 10^{-12} \text{ atm}$, respectively. The measured results were so reproducible that the data in this figure are also considered to be reliable. When $P_{\text{O}_2} > 0.21 \text{ atm}$, the magnitude of Seebeck coefficients of the CDC thermocell is slightly smaller than those of the YSZ thermocell as shown in Fig. 5, but their P_{O_2} dependencies are similar to each other. When P_{O_2} is low enough, the sign of Seebeck coefficients of the CDC thermocell was reversed.

CDC is ionically conductive when P_{O_2} is high and electronically conductive when P_{O_2} is low. This means that the P_{O_2} dependence of the Seebeck coefficients may be based on the change of the conductive mechanism. In order to understand this P_{O_2} dependence of a mixed conductor, an equivalent circuit to simulate a thermocell of a mixed conductor will be considered. The equivalent circuit is illustrated in Fig. 6, where E_{obs} is the electric potential difference observed between two electrodes when the temperature difference between them is ΔT . E_i is the electromotive force generated ionically by temperature difference ΔT and E_e is that generated electronically. R_i and R_e are the ionic and electronic resistances, respectively. It should be noted here that the direction of E_i is opposite to that of E_e in Fig. 6. This is simply because the actually measured Seebeck coefficients have opposite signs.

In this equivalent circuit, if P_{O_2} is nearly equal to 1.0 atm , then $R_e \gg R_i$ which leads to $E_{\text{obs}} = E_i$. If P_{O_2} is less than 10^{-10} atm , $R_e \ll R_i$ which leads to $E_{\text{obs}} = E_e$. In general, the following equation is valid.

Fig. 6 Equivalent circuit of the thermocell in case the electrode process is reversible.

$$E_{\text{obs}} = (R_i E_e - R_e E_i) / (R_i + R_e) \quad (1)$$

R_e and R_i can be rewritten in the followings using the cell constant k , the ionic conductivity σ_i and the electronic conductivity σ_e .

$$R_i = k / \sigma_i \quad (2)$$

$$R_e = k / \sigma_e \quad (3),$$

where k was determined to be 8.28 cm^{-1} based on our experiment. σ_i and σ_e were determined as;

$$\sigma_i = 0.2 \text{ S cm}^{-1} \quad (4)$$

$$\sigma_e = 5.62 \times 10^{-4} \cdot \text{Po}_2^{-1/4} \text{ S cm}^{-1} \quad (5).$$

These are based on other workers' report⁵⁾ and on the assumption that σ_e of an n-type semiconductor such as CDC is proportional to $\text{Po}_2^{-1/4}$. Then equations (2) and (3) can be rewritten in the followings by substituting $k = 8.23 \text{ cm}^{-1}$ and equations (4) and (5) into them.

$$R_i = 41.4 \, \Omega \quad (6),$$

$$R_e = 1.47 \times 10^4 \cdot \text{Po}_2^{1/4} \, \Omega \quad (7).$$

On the other hand, a Seebeck coefficient of an ionic conductor such as YSZ can be expressed as⁴⁾;

$$\begin{aligned} dE/dT = (1/F) \{ & (1/2) S_{\text{O}_2^{2-}} + S_{\text{Pt}}^* \\ & - (1/4) (S_{\text{O}_2^0} - R \ln \text{Po}_2) \} \end{aligned} \quad (8)$$

Thus, the electric motive force generated ionically by temperature difference ΔT can be written as;

$$\begin{aligned} E_i = \{ & (-1/F) \{ (1/2) S_{\text{O}_2^{2-}} + S_{\text{Pt}}^* - (1/4) S_{\text{O}_2^0} \\ & - (R/4F) \ln \text{Po}_2 \} \Delta T \\ = & \{ 0.306 \times 10^{-3} - (R/4F) \ln \text{Po}_2 \} \Delta T \end{aligned} \quad (9),$$

where F is Faraday constant and S_{Pt}^* and $S_{\text{O}_2^{2-}}$ are a transported entropy of an electron in a Pt electrode and that of an oxide ion in a conductor. $S_{\text{O}_2^0}$ is a standard molar entropy of oxygen in the gas phase.

Since $-(1/F) \{ (1/2) S_{\text{O}_2^{2-}} + S_{\text{Pt}}^* - (1/4) S_{\text{O}_2^0} \}$ in

equation (9) denotes the Seebeck coefficient of a CDC thermocell for $\text{Po}_2 = 1.0 \text{ atm}$, it was determined as $-0.306 \times 10^{-3} \text{ V}$ based on our experiment.

E_e was determined as;

$$E_e = 0.5 \times 10^{-3} \Delta T \quad (10).$$

This is based on our data obtained under low oxygen pressure and on the assumption that it does not depend on Po_2 .

By substituting equations (6), (7), (9) and (10) into equation (1), the observable electromotive force E_{obs} can be calculated. The Po_2 dependence of the thermoelectric power calculated in this way is presented by a broken line in Fig. 7, where the horizontal axis denotes the partial pressure of oxygen, Po_2 , and the vertical one presents the Seebeck coefficient, dE/dT ($= E_{\text{obs}}/dT$). Experimentally measured data are also presented in the same figure.

Fig. 7 Po_2 dependence of the thermoelectric power measured in CDC.

Fig. 8 Equivalent circuit of the thermocell in case the electrode process is not fully reversible.

When CDC is ionically conductive, or $P_{O_2} > 10^{-4}$ atm, the calculated values are in good coincidence with the experimental ones. However, when CDC is electronically conductive, or $P_{O_2} < 10^{-4}$ atm, the coincidence between them is poor. This incoincidence is considered to be resulted from the assumption that the charge transfer processes are fully reversible in spite of the fact that the mass transfer of oxygen can be a limiting process when P_{O_2} is very low.

Then an improved equivalent circuit is presented in Fig. 8 where another resistance R_t caused by the above limiting process is introduced. During thermoelectric power measurement, the following reactions are progressing at two electrodes.

These reactions make the oxygen concentration at the interface between Pt and CDC of the anode side higher and that of the cathode side lower than that in the surrounding atmosphere. R_t resulted from these concentration gradients can be expressed as

$$R_t = \{(RT/4F)\ln(Co_2[\text{anode}]/Co_2[\text{cathode}])\}/j \quad (13)$$

where j is the current flowing in the circuit. When the oxygen concentration at the cathode interface is written as $Co_2[i]$, the concentration at the anode interface can be written as $Co_2[b] + \{Co_2[b] - Co_2[i]\}$, where $Co_2[b]$ presents the oxygen concentration in the atmosphere. Then the equation (13) can be rewritten as;

$$R_t = (RT/4Fj)\ln\{(Co_2[b] + Co_2[b] - Co_2[i])/Co_2[i]\} \quad (14).$$

On the other hand, when the diffusion coefficient of oxygen in the atmosphere is expressed as D , oxygen concentration at the cathode interface, $Co_2[i]$, can be expressed as;

$$\varepsilon D(Co_2[b] - Co_2[i])/L = j / 4FS \quad (15),$$

if the concentration gradient was established only in the thickness of the porous Pt electrode. ε , L and S in equation (15) are the void fraction, the thickness, and the area of the electrode. Here, D was determined to be $2.63 \text{ cm}^2 \text{ s}^{-1}$ at 1273 K using the equation developed by Fuller⁶.

After eliminating $Co_2[i]$ in equation (14) by using equation (15), the equation (14) is substituted into equation (16) together with equations (6), (7), (9) and (10) to calculate j .

$$j = (E_c + E_i)/(R_c + R_i + R_t) \quad (16)$$

Then the electromotive force can be calculated using equation (17) with j that was numerically obtained from equation (16).

$$E_{\text{obs}} = E_c - R_c j \quad (17)$$

The calculated results are presented in Fig. 7 by solid lines for various values of $\varepsilon S/L = 0.1, 1, 10, 100 \text{ cm}$. The area S and the thickness of the electrode L on the experimental cell are approximately 0.08 cm^2 and 0.02 cm , which means that $\varepsilon S/L$ is estimated to be about 2 cm . Since the measured data are located between two solid lines of $\varepsilon S/L = 1 \text{ cm}$ and $\varepsilon S/L = 10 \text{ cm}$, the model developed above is considered to be valid in case of a CDC thermocell. The abrupt change of the Seebeck coefficient around $P_{O_2} = 10^{-4} \text{ atm}$ corresponds to the fact that the oxygen concentration at the cathode interface is nearly equal to 0.

The results of this study strongly indicates that the thermoelectric power of mixed conductors depends not only on material properties but also on the geometry of the electrode, which may make it difficult to obtain the same Seebeck coefficient among different workers or among different thermocells.

4 CONCLUSIONS

1. A new method was proposed for thermoelectric power measurement of ionic or mixed conductors from a viewpoint of the thermal engineering, and the validity of this method was experimentally confirmed.
2. It was made clear that the behavior of a CDC thermocell at high P_{O_2} atmosphere is completely

different from that at low Po_2 atmosphere.

3. A model, or an equivalent circuit, to simulate a thermocell of a mixed conductor has been proposed and the validity of this model has been experimentally confirmed.

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