Visualization of oxide ionic diffusion at cathode/interlayer/electrolyte interfaces in real flat-tube SOFC cells-stack

Teruhisa HORITA,¹ DoHyung CHO, Taro SHIMONOSUJI, Haruo KISHIMOTO, Katsuhiko YAMAJI, Manuel E. BRITO and Harumi YOKOKAWA
National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 5, 1–1–1, Higashi, Tsukuba, Ibaraki 305–8565, Japan

Local distribution of oxide ionic flows was visualized at the cathode/interlayer/electrolyte interfaces in real flat tube Solid Oxide Fuel Cells (SOFCs) stacks under operating condition. Isotope labeling (18O labeling) technique and secondary ion mass spectrometry (SIMS) analysis enabled us to visualize the trace of 18O diffusion through the (La,Sr)FeO3 cathode/ CeO2 interlayer/YSZ electrolyte interfaces in a “frozen state”. The difference of 18O intensity was observed at (La,Sr)FeO3 cathode as well as CeO2 interlayer among different cells. This difference can come from the surface 16O/18O exchange rates of (La,Sr)FeO3 cathode and the amounts of 18O2 supplied to cells. Local difference of 18O intensity suggested the local distribution of oxide ionic currents at different cells in the stack.

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1. Introduction

In Solid Oxide Fuel Cells (SOFCs), the ionization and incorporation of oxygen into solids (O2+4e−→ O22−) at cathode/interlayer/electrolyte interfaces are crucial reactions because the resistance of this reaction shows relatively large values.1)–3) To minimize the reaction resistance and to optimize the cathode/electrolyte interfaces, these reaction mechanisms should be precisely clarified. So far, a numbers of papers have been published regarding the cathode reaction mechanism by using conventional electrochemical measurements, such as DC polarizations and AC impedance.4)–7) Especially, a precise analysis of reaction mechanism has been made on mixed electronic-ionic conducting materials, La1−xFexSr1−xCo1−yFeyO3d (LSCF) on CeO2 based materials,8)–10) which are considered as the state of the art cathode/interlayer-electrolyte combination. Surface oxygen incorporation and bulk diffusion of oxide ions can be the rate-determining steps at the LSCF cathode when conventional electrochemical methods are used. The conventional current–voltage characteristics gave us the information on the oxygen reduction reaction mechanism at the examined interfaces, although the distribution of oxygen ionization active sites and diffusion of oxide ions were not directly determined. To visualize the distributions of active areas for oxygen ionization around the cathode/interlayer/electrolyte interfaces.

2. Experimental procedure

2.1 Samples

Figure 1 shows schematic diagrams of a flat tube SOFC cell-stack made by Kyocera Corporation [Fig 1(A)], a single cell configuration [Fig. 1(B)], and the motion of stable isotope oxygen-oxide ions (16O2 and 18O2) [Fig. 1(C)]. The size of labeling technique to observe the distribution of 18O intensity at different cells in the real flat-tube stacks and clarify the distribution of active areas for oxygen incorporation around the cathode/interlayer/electrolyte interfaces.

Fig. 1. (Color online) Schematic diagram showing flat tube three single cells stack (A), single cell configuration (B), and oxygen ionization and oxide ion (O22−) diffusion through the electrolyte under operation (C). Stable isotope oxygen (18O2) was flowed outside of the stack from the bottom of the cell and hydrogen fuel flow was inside of the holes of the flat tube.

¹ Corresponding author: T. Horita; E-mail: t.horita@aist.go.jp
a single cell is about 150 mm in length and 30 mm in width [in Fig. 1(A)]. In Fig. 1(B), schematic drawing of single cell is shown: Anode/substrate is a porous Ni-Y2O3 stabilized ZrO2 (YSZ) composite. A dense YSZ electrolyte film was fabricated on the porous anode support. Over the dense YSZ film, a reaction protective interlayer (CeO2 based oxide) and a porous (La, Sr)-Fe2O3 based cathode layer were fabricated. A dense interconnect (LaCrO3 based oxide) was deposited on a substrate for connecting to the next single cell. In this stack, three single cells are connected electrically in-series [Fig. 1(A)]. Stable isotope oxygen (^18O2, volume concentration of ^18O2 is higher than 92%) flows outside of the cells while hydrogen flows inside the holes of the flat tubes. The electricity is generated by the electrochemical reaction in each cell: the stack voltage is 3.33 V at open circuit (the average cell voltage is 1.11 V at open circuit) with a maximum power density of 0.49 W/cm² at 650°C. In Fig. 1(C), schematic drawing of isotopic oxygen ionization and motion are shown at the ^18O2/cathode/interlayer/electrolyte interfaces. Isotope oxide ions (^18O2−) diffuse through the interlayer-electrolyte due to the chemical potential gradient of oxygen (ΔμO2 = μO2 − μO) and the electrochemical potential gradient of oxide ions (ΔηO2− = ηO2− − η02−) under fuel cell operating conditions. The conducted oxide ions (^18O2−) react with hydrogen at the anode/electrolyte interfaces generating water and electrons. In this way, the electrochemical reaction proceeds as long as gases are supplied. The present study focuses on the visualization of oxygen ions at the real flat-tube type cathode/interlayer/electrolyte interfaces with different position in the stack. The normal operation temperature of this flat-tube stack is 750°C. However, the oxygen ions in the cells are seen to be relatively fast at this operation temperature and it gives homogeneous ^18O-distribution at a temperature of 750°C. To observe the distributions of ^18O in a frozen state, it is better to operate relatively low temperature. Therefore, the ^18O/^16O exchange was examined at 650°C in order to obtain a clearer distribution of ^18O images.

2.2 Electrochemical performance of three cells stack

The electrochemical performance of three cells stack was examined in H2-air atmospheres at temperatures of 873–1023 K (650–750°C). The current–voltage (J–E) characteristics and current power (J–P) characteristics are measured as a function of current. Hydrogen (H2) and air flows are controlled by the mass flow controller at flow rates of 100 to 500 ml/min. The oxygen utilization was also measured by changing the flow rates of air under a constant H2 flow at temperatures of 650, 700 and 750°C. The oxygen utilization was changed from 10 to about 40%.

2.3 Isotope oxygen exchange (^16O/^18O exchange) technique

An isotopic oxygen exchange technique (^16O/^18O exchange) has been applied to determine the surface reactivity and diffusion properties of oxygen in solids, especially in oxide ion conducting ceramics.15–24 In Fig. 2, a schematic diagram of the ^16O incorporation and diffusion at ^16O2−/cathode/interlayer/electrolyte interfaces is shown. In ^16O2 atmosphere, dissociative adsorption of ^16O occurs on the surface of the cathode or the interlayer. Then, an exchange reaction occurs between adsorbed ^16O2− and ^18O in the lattice of cathode and/or at the interlayer with electronic charge transfer according to the following reaction sequence:24–26

\[
\text{18O}_2(\text{g}) \rightarrow 2\text{18O}_{\text{ad}} \quad \text{(oxygen adsorption and dissociation) (1)}
\]

\[
\text{18O}_{\text{ad}} + 2e^- \rightarrow 18\text{O}^2- \quad \text{(charge transfer) (2)}
\]

\[
18\text{O}^2- \rightarrow 16\text{O}^2- \quad \text{(isotopic exchange on solid surface region) (3)}
\]

The driving force of the isotopic exchange reaction is the gradient of isotopic oxygen concentration between the gas phase and the solids. In the present study, in addition to the ^16O/^18O exchange, the fuel cell reaction promotes the ^18O incorporation into the cathode-electrolyte through the electrochemical reaction [promotion of reaction of (2) as indicated by thick arrows in Fig. 2 (bottom)]. In such a condition, diffusion of ^18O is enhanced by the electrochemical pumping of ^18O2− through the electrolyte. The current density (J) is directly related to the number of oxide ions [n(^18O2−)] passing through the electrolyte in the following equation: n(^18O2−) = J/2F [F is the Faraday constant and n(^18O2−) = 1.295 umol⋅cm⁻² in this condition]. The duration time of ^18O introduction was 300 s under a constant current flow of 0.25 A/cm² at a temperature of 650°C.

2.4 Secondary ion mass spectrometry (SIMS) analysis

An imaging analysis of ^18O was made by secondary ion mass spectrometry (SIMS) using a sector type dynamic SIMS (AMETEK-CAMECA ims-5f). The primary ion beam was positive Cs⁺ and the negative secondary ions (^18O−, ^16O−, M^16O−, where M indicates metal) were collected in an area of 50 × 50 μm².11–14 In this report, we describe ^18O and ^16O for the detected secondary ions of ^18O− and ^16O−. The samples were mounted in an epoxy and the cross sectional cathode/interlayer/electrolyte samples were polished and coated with gold. The SIMS images were taken during electronic shower by E-gun in order to avoid the charge-up during the measurements. Secondary ion images were measured by scanning the focused ion beam of Cs⁺ at the cross-sectional samples. The beam diameter of Cs⁺ primary ion was about 200 nm (0.2 μm). Thus, the secondary ion images can be detected with a resolution of sub-micrometer level.
3. Results and discussion

3.1 Electrochemical performance of flat tube SOFC cell-stack

Figure 3 shows current–voltage (J-E) [top, Fig. 3(A)] and current–power (J-P) characteristics [bottom, Fig. 3(B)] of three cells stack at different operating temperatures. The J-E characteristics show a significant decrease of voltages with decreasing temperatures. Same trends are observed at the J-P curves that the peaks of power densities are decreased with decreasing temperatures. The maximum power densities of 3 cells stack are 0.49, 0.59, and 0.66 W/cm$^2$ for the temperatures of 650, 700, and 750°C, respectively. These J-E and J-P characteristics are measured at constant H$_2$ flow of 500 ml/min and at air flow of 500 ml/min. There were sufficient amounts of H$_2$ and air (oxygen) flow in the power generation tests. That is, the J-E and J-P characteristics were measured at relatively low fuel and oxygen utilization conditions. In order to evaluate the stack performance more exactly, effects of oxygen utilization should be clarified under power generation condition.

We examined the effects of the oxygen utilization ($U_{ox}$) on the performance of the stack: that is, the dependence of oxygen flow on the stack performance. Figure 4 shows the effects of oxygen utilization on the voltage drops of the stack. The voltage of stack shows monotonically decreases with increasing the oxygen utilization. With an increase of $U_{ox}$ from 10 to 35% (with decreasing air flow rates), the voltage decreases from 1.9 to 1.3 V. This indicates the shortage of oxygen supply with increasing the oxygen utilization (when decreasing the flow rate of air to control the oxygen utilization). In these plots, temperature effects also show a significant factor for evaluating the stack performance. Especially, the stack voltage drops distinctly between 750 and 700°C.

3.2 SIMS images of $^{18}$O at different positions in the three cells stack

Figure 5 shows a schematic drawing of three cells stack from top view [Fig. 5(A)] and the corresponding SIMS $^{18}$O images around the cathode/interlayer/electrolyte interfaces [Fig. 5(B)]. The images are taken at the bottom parts of each cell. The $^{18}$O images show relatively high $^{18}$O signal counts at the cathode/interlayer interfaces and gradual decrease of signal intensities at the electrolyte. There is the highest $^{18}$O signal intensity around the interlayer for all examined samples. This indicates that the oxygen ionization and incorporation are most active around the interlayer. There are some differences of $^{18}$O signal intensities in the images at different positions. The Cell 3 shows the brighter $^{18}$O images at cathode and interface, which suggests the higher $^{18}$O signal counts in the samples. To analyze the $^{18}$O images more precisely, line analysis was made at the interfaces.

Figure 6 shows line analysis of SIMS images of $^{18}$O at the corresponding parts. The Y-axis of these profiles shows the following ratio of signal intensities of $^{18}$O and $^{16}$O:

$$R_{^{18}O}(x) = \frac{I_{^{18}O}(x)}{I_{^{18}O}(x) + I_{^{16}O}(x)}$$

where, $I_{^{18}O}(x)$ and $I_{^{16}O}(x)$ indicate the SIMS signal intensities of $^{18}$O and $^{16}$O, at the position of x, respectively. The line analyses of $^{18}$O show peaks around the CeO$_2$-interlayer for all
the examined samples. The $R_{18O}$ shows different values with different cell positions: Cell 3 shows the highest $R_{18O}$ value about 0.2, while Cell 1 shows about 0.1 at the peak values. Also, the $R_{18O}$ at the cathode shows different values with different cells. The difference of $R_{18O}$ values at different cells will be discussed in the later section.

### 3.3 Active sites for oxygen ionization and surface reaction at cathode

The SIMS image and the line analysis of $^{18}$O suggest the active sites for $^{18}$O incorporation into solids at the cathode/interlayer/ electrolyte interfaces: a peak formation of $^{18}$O at the cathode shows different values with different cells. The $R_{18O}$ values at cathode and peaks at the interlayer are different from the cell positions. Here, we consider the difference of $R_{18O}$ values at the cathode by taking into accounts the surface oxygen exchange rates and diffusion coefficient.

The difference of $R_{18O}$ values at the cathode comes from the difference in the amounts of ionized $^{18}$O to $^{16}$O$^-$ at the surface of (La,Sr)FeO$_3$ (LSF) cathode grains. It has been reported that the $^{16}$O diffusion coefficient ($D^{16}$) and surface oxygen exchange rate ($k$) of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ are $5 \times 10^{-7}$ and $1.5 \times 10^{-6}$ cm$^2$s$^{-1}$ ($0.015 \mu$m s$^{-1}$) at 923K, respectively.$^{21}$ Using these values, the estimated $^{18}$O diffusion profiles are calculated from the diffusion equation of Fick’s second law (assuming the surface reaction). The calculated diffusion profiles of $^{18}$O are shown as lines at cathode in Fig. 6. These lines are diffusion profiles of $^{18}$O in La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$-d as $D^{18} = 5 \times 10^{-7}$ cm$^2$s$^{-1}$ with changing the $k$ values ($k = 0.015, 0.025,$ and $0.080 \mu$m s$^{-1}$). Since the grain size of (La,Sr)FeO$_3$ cathode in the real stack are smaller than 1 $\mu$m in diameter, the diffused $^{18}$O can penetrate though one grain of (La,Sr)FeO$_3$ and the diffusion length during $^{18}$O/$^{16}$O exchange is too longer than the thickness of several grains. Therefore, the $R_{18O}$ values should be almost the same values with the surface. The $R_{18O}$ values of (La,Sr)FeO$_3$ cathode in this study show relatively large values ($R_{18O} = 0.06$–$0.18$) than the calculated ones from the literature ($R_{18O} = 0.04$). This can be explained by two possibilities: one is the increase of oxygen vacancy contents in the real (La,Sr)FeO$_3$ cathode and the other is the enhancements of surface reaction rates under fuel cell reaction. Especially, under fuel cell reaction, the oxygen partial pressure at the (La,Sr)FeO$_3$/CeO$_2$ contacts can be lowered than the normal air (0.21 atm) by the cathodic polarization. The decrease of oxygen chemical potential at the (La,Sr)FeO$_3$/CeO$_2$ interfaces increases the oxygen vacancy concentration at (La,Sr)-O$_3$ cathode near the interfaces. The increase of oxygen vacancy concentration at the interface will affect the surface $^{18}$O/$^{16}$O exchange rates due to the increase of the number of exchange sites. The increase of $R_{18O}$ values with different cells indicates the local change for oxygen ionization and diffusion among different cells. The cathode at the Cell 3 shows relatively large $k$ and $R_{18O}$ values, which suggests the enhancement of surface $^{18}$O/$^{16}$O exchange rates under fuel cell reaction.

Under constant current flow in this experiment ($j = 0.25$ A cm$^{-2}$), the $^{18}$O$^-$ flux through the electrolyte should be the same for three cells. However, there may be an inhomogeneity of $^{18}$O$^-$ flux according to the distribution of $^{18}$O at the reaction areas under operating condition. We have already reported that the difference of $^{18}$O intensity in single cell between bottom and top positions. The bottom shows the higher $^{18}$O intensity because $^{18}$O$_2$ flows from bottom to top, which causes the lower concentration of $^{18}$O at the top.$^{13}$ Local distribution change of $^{18}$O concentration images in this stack can be considered by two factors [in Fig. 5(b)]. One is the concentration change of $^{18}$O$_2$ gas in the stack due to consumption of oxygen in the stack. A depletion of oxygen will cause the decrease of cell performance due to increase of oxygen utilization locally as shown in Fig. 4. Second factor is the inhomogeneity of $^{18}$O-diffusion in the cell-stacks. The $^{18}$O-diffusion at the cells can be different due to the inhomogeneity of cell components and materials at the interfaces. From the $^{18}$O distribution in the real cell-stack, it was the first time to observe the distribution of $^{18}$O in the real flat tube cell-stack. There is a local distribution of oxide ionic flows in the real flat tube cells even in a constant oxide ionic flow.

### 4. Conclusion

The use of isotopic oxygen exchange technique under fuel cell operated condition enabled us to visualize the local distribution of oxide ionic flows in the real flat-tube SOFC stack. Local distribution of oxide ionic flows was visualized by isotope labeling ($^{18}$O labeling) technique and secondary ion mass spectrometry (SIMS) analysis at (La,Sr)FeO$_3$ cathode/CeO$_2$ interlayer/YSZ electrolyte interfaces with three cells stack in a “frozen state”. The secondary ion intensities of $^{18}$O show difference of $^{18}$O distributions with different cells in the stack. The difference of $^{18}$O intensity ratio was observed at (La,Sr)FeO$_3$ cathode as well as CeO$_2$ interlayer. This difference can come from the surface $^{18}$O/$^{16}$O exchange rates (La,Sr)FeO$_3$ cathode and the amounts of $^{18}$O$_2$ supplied to cells. Local difference of $^{18}$O intensity suggested the distribution of local ionic current at different cells although the constant current density was set under operating conditions.

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