

The effect of surface coating on the oxygen permeation characteristics of zirconia

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Abstract

Yttria-stabilized-zirconia (YSZ) can be used as an oxygen permeating membrane at elevated temperature (>1400 °C) due to its chemical and mechanical stability. However, the permeation kinetics of zirconia has not been studied in detail, especially in low oxygen partial-pressure (P_{O_2}). In this study, the oxygen flux of YSZ was measured as a function of the temperature (1400–1600 °C) and P_{O_2} (1 to 1×10^{-3} , 2×10^{-3} to 2×10^{-7} and 3×10^{-12} to 2×10^{-8} atm). In high and middle P_{O_2} regions, the measured oxygen flux matched well the value estimated from the reported electrical conductivity. This observation shows that the oxygen permeation was mostly limited by the bulk diffusion as proved by the $P_{O_2}^{1/4}$ (high P_{O_2})- or $P_{O_2}^{-1/4}$ (middle P_{O_2})-dependence of oxygen flux. However, in low P_{O_2} region, the measured oxygen flux was about one order of magnitude smaller than the expected value from the electrical conductivity. In this region, the oxygen permeation was mostly limited by the surface oxygen-exchange kinetics in spite of very high temperature. Therefore, the coating of YSZ surface with porous layer was considered as one method to increase the oxygen flux. YSZ, GDC (Gd-doped Ceria), YSZ-GDC or LaCrO₃ were coated on both sides of YSZ and the flux was measured and compared with that without coating layer. The oxygen flux of GDC-coated YSZ drastically increased but the increase was not maintained for long time due to the reaction and the sintering of porous layer. LaCrO₃ was found to be the best coating material which maintains the porous layer and thus flux for extended time.

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1. Introduction

Various studies of oxygen permeation have been performed for the production of CO and H₂ (fuel gases) from methane, and the oxygen removal from steel melt.^{1,2} The perovskite-structured materials such as the doped LaCoO₃ or SrCoO₃ have been studied for the low temperature (<1000 °C) use due to their high mixed ionic and electronic conductivity. However, the doped ZrO₂ was only studied for the high temperature (>1000 °C) use due to their low electronic conductivity.^{3–5} The oxygen permeation studies of zirconia were mostly limited in relatively high oxygen partial pressure (P_{O_2}). The oxygen permeation study in low P_{O_2} is needed for the application such as the oxygen removal from

steel melt. In this study, the oxygen permeation using yttria-stabilized-zirconia (YSZ) was examined since YSZ has the required mechanical and chemical stability in low P_{O_2} .

The oxygen flux of Zr_{0.84}Y_{0.16}O_{2- δ} (8 mol% Y₂O₃-doped zirconia or YSZ in this study) was measured as a function of P_{O_2} and temperature in various P_{O_2} regions. The electronic conductivity of doped-ZrO₂ has been extracted from the measured permeation data in relatively high P_{O_2} .^{4,6} The oxygen fluxes of YSZ with various surface coatings were measured in low P_{O_2} region. The measured oxygen flux of YSZ with various coating layers was compared with that without coating.

2. Experimental procedure

Commercial Zr_{0.84}Y_{0.16}O_{2- δ} (99.9%, TOSOH, Japan) powder was pressed into pellet, followed by cold-isostatic

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Table 1
The P_{O_2} gradient used in permeation measurement

	Feed side P_{O_2} (P_1) (atm)	Permeate side P_{O_2} (P_2) (atm)	Gases
High P_{O_2}	1 to 1×10^{-3}	1×10^{-3}	He/ O_2
Middle P_{O_2}	2×10^{-3}	2×10^{-3} to 2×10^{-7}	He/ O_2 , CO/ CO_2
Low P_{O_2}	2×10^{-8} to 3×10^{-12}	3×10^{-12}	CO/ CO_2

pressing at 200 MPa and then sintered at 1650 °C for 4 h in air. The sintered sample with 25 mm diameter was sliced into 1 mm-thick disk. For surface coating, YSZ–C (YSZ–carbon black, 10:1 weight ratio), YSZ–GDC (1:1 weight ratio) mixture, GDC and LaCrO₃ were used. GDC (Ce_{0.8}Gd_{0.2}O_{2–δ}) and LaCrO₃ were obtained by calcining the appropriate mixture of CeO₂ (99.9%, High Purity Chemicals, Japan) and Gd₂O₃ (99.9%, High Purity Chemicals, Japan), and La₂O₃ (99.9%, STREM, USA) and Cr₂O₃ (99%, Acros, USA) at 1200 °C for 2 h, respectively. Before calcination, the powders were ball-milled in ethyl alcohol with alumina ball for 12 h. The calcined powders were screen-printed on both surfaces of YSZ and heated at 1600 °C for 1 h in air. The coated layers of YSZ, YSZ–GDC mixture, GDC and LaCrO₃ were examined by X-ray diffraction. The microstructures, before and after permeation experiment, were examined with a scanning electron microscope. Energy dispersive spectroscopic (EDS) analysis was also performed.

The permeation measurement was accomplished in various P_{O_2} gradients as shown in Table 1. The configuration of permeation cell was reported elsewhere.⁷ Air leakage due to bad sealing was detected by monitoring nitrogen gas concentration with gas chromatograph (HP 4890D, USA). The amount of nitrogen gas was below 0.02% of sweep gas volume. The side-wall leakage of oxygen through the sample was estimated by the difference in the inlet and outlet P_{O_2} under no permeation condition, i.e., when the feed side P_{O_2} (P_1) and the permeate side P_{O_2} (P_2) was maintained at the same P_{O_2} . The average diameter of YSZ exposed to gas and that of coated layers were 19 and 17 mm, respectively.

3. Results and discussion

3.1. High and middle P_{O_2} region

Fig. 1 shows the measured oxygen flux of YSZ between 1400 and 1600 °C. The rate of oxygen permeation, in general, is essentially controlled by two factors. One factor is the bulk diffusion within the membrane and the other is the surface oxygen-exchange kinetics on either side of membrane. If the oxygen flux is limited by the bulk diffusion, the oxygen flux can be estimated by Eq. (1) according to the Wagner's theory.⁸

$$J_{O_2} = \frac{RT}{4F^2L} \sigma_h^0 [P_1^{1/4} - P_2^{1/4}] \quad (1)$$

where σ_h^0 is σ_h at $P_{O_2} = 1$ atm and L is membrane thickness.

In this graph, the two dotted lines indicate the oxygen flux estimated by using Eq. (1) with the reported electrical conductivity data of 9 YSZ (9 mol% Y₂O₃-doped ZrO₂).^{4,5} As shown, the measured data at 1600 °C match reasonably well with the estimated values. It means that the oxygen flux is mostly limited by the bulk diffusion. The p-type conductivity in $P_{O_2} = 1$ atm can be obtained by using Eq. (1) from the linear fitting. The obtained result is shown below:

$$\sigma_h^0 = 27 \exp\left(\frac{-1.40 \pm 0.11}{RT}\right) \quad (2)$$

In Fig. 2, the oxygen flux of YSZ was shown between 1500 and 1600 °C. In the same manner, a dashed line indicates the value estimated from the Wanger equation, assuming the oxygen transport is limited by n-type conductivity. In order to obtain the n-type conductivity, the following equation was used:⁸

$$\begin{aligned} J'_{O_2} &= J_{O_2} - \frac{RT}{4F^2L} \sigma_h^0 [P_1^{1/4} - P_2^{1/4}] \\ &= \frac{RT}{4F^2L} \sigma_e^0 [P_2^{-1/4} - P_1^{-1/4}] \end{aligned} \quad (3)$$

where σ_e^0 is σ_e at $P_{O_2} = 1$ atm.

As shown in this figure, the oxygen flux (J'_{O_2}) shows a linearity against x -axis in small P_{O_2} gradient. However, the data start to deviate from the linearity as the P_{O_2} gradient increases. By fitting the data with Eq. (3) in linear region (solid line), the n-type conductivity of YSZ at $P_{O_2} = 1$ atm

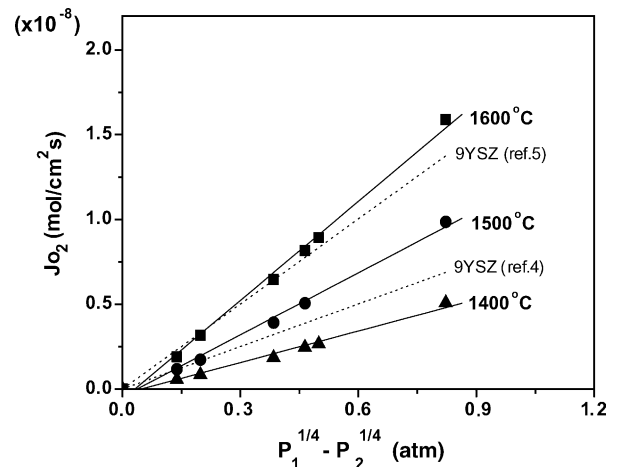


Fig. 1. The oxygen flux of YSZ membrane in high P_{O_2} ($P_2 \sim 1 \times 10^{-3}$ atm). The dotted lines indicate the estimated value for 9 mol% Y₂O₃-doped zirconia at 1600 °C from the published electrical-conductivity data.^{4,5} The solid lines are linearly fitted lines following Eq. (1) for 1400–1600 °C.

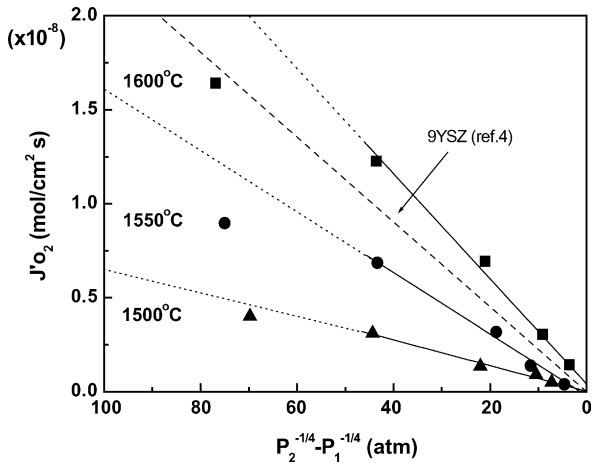


Fig. 2. The oxygen flux of YSZ membrane in middle P_{O_2} ($P_1 \sim 2 \times 10^{-3}$ atm). The dashed line indicates the estimated value for 9 mol% Y_2O_3 -doped zirconia at 1600 °C from the published electrical-conductivity data.⁴ The solid lines are linearly fitted lines using Eq. (3) for 1500–1600 °C.

was obtained.

$$\sigma_e^0 = 1.65 \times 10^6 \exp\left(\frac{-3.85 \pm 0.40}{RT}\right) \quad (4)$$

3.2. Low P_{O_2} region

In Fig. 3, the oxygen flux of YSZ was measured as a function of feed side P_{O_2} (P_1). A solid line indicates the oxygen flux estimated from Eq. (3) by using the obtained n-type conductivity and assuming bulk-diffusion limit. The measured oxygen flux of YSZ was much smaller than the estimated value. It means that the oxygen flux is heavily influenced by the surface-exchange kinetics. If the surface kinetics is rate determining, the oxygen flux can be written as Eq. (5).⁹

$$J_{O_2} = \frac{1}{1 + (2L_C/L)} \frac{RT}{4F^2L} \sigma_e^0 [P_2^{-1/4} - P_1^{-1/4}] \quad (5)$$

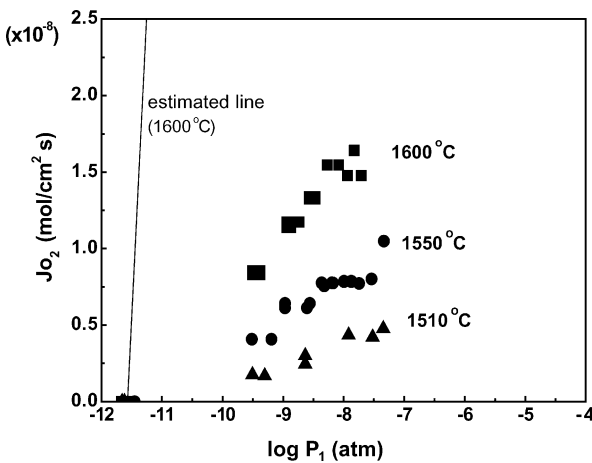


Fig. 3. The oxygen flux of YSZ membrane at high temperature (1510–1600 °C) and in low P_{O_2} ($P_2 \sim 3 \times 10^{-12}$ atm). The solid line indicates the flux estimated from the electrical conductivity by using Eq. (3).

where 2 in front of L_C reflects the symmetry of surface-exchange kinetics at both sides of membrane and L_C is the characteristic membrane thickness. The oxygen flux should increase by reducing the thickness of the membrane until it is less than L_C . L_C is the thickness of transition from the bulk-diffusion limited to surface-exchange limited transport^{10,11}. In the case of $L < L_C$, the increase in the permeation rate is expected by coating the membrane with the porous layer. The surface-exchange kinetics is normally enhanced by increasing the effective surface area.

The temperature dependence of the measured oxygen flux of YSZ was shown in Fig. 4. Since the oxygen permeation is an activated process, it is given by:

$$J_{O_2} = J_0 \exp\left(-\frac{E_a}{kT}\right) \quad (6)$$

where E_a is the apparent activation energy. In high P_{O_2} ($P_1 \sim 1$ atm and $P_2 \sim 1 \times 10^{-3}$ atm) and middle P_{O_2} ($P_1 \sim 2 \times 10^{-3}$ atm and $P_2 \sim 2 \times 10^{-6}$ atm), the apparent activation energy of permeation (1.47 and 3.50 eV, respectively) is similar with that of electrical conductivity (1.40 and 3.85 eV, respectively). However, in low P_{O_2} , apparent activation energy of permeation (4.73 or 4.94 eV) is larger than that of electronic conduction (3.85 eV). Additionally, the oxygen flux in low P_{O_2} is lower than that in high P_{O_2} although the mixed conductivity is much higher. It implies again that the oxygen flux is heavily influenced by the surface-exchange kinetics.

Therefore, the improvement of surface exchange kinetics is needed in low P_{O_2} to maximize the oxygen flux. In Fig. 5, the oxygen flux of YSZ with YSZ, YSZ–GDC mixture, GDC and $LaCrO_3$ coating were shown as a function of feed side P_{O_2} (P_1) at 1600 °C. The solid and dotted lines indicate the estimated oxygen flux of YSZ from the electrical conductivity using Eq. (3) for $P_2 \sim 3 \times 10^{-12}$ atm and $\sim 6 \times 10^{-12}$ atm, respectively. The permeate side P_{O_2} (P_2) is slightly different among samples due to the difference in side

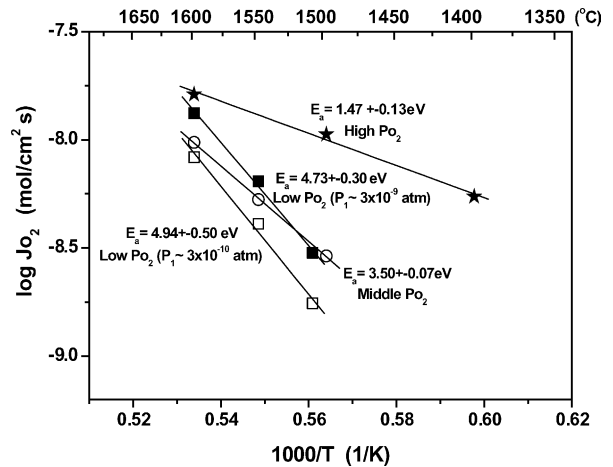


Fig. 4. Temperature dependence of the oxygen flux of YSZ membrane in various P_{O_2} gradients. The high, middle, and low P_{O_2} regions were defined in the text.

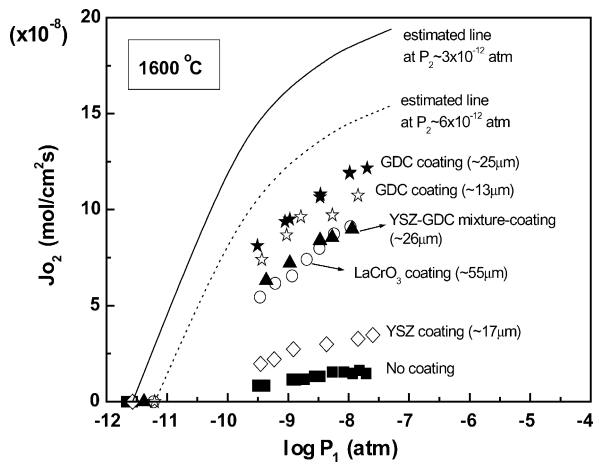


Fig. 5. The oxygen flux of YSZ membranes with YSZ, YSZ–GDC mixture, GDC and LaCrO_3 coatings at 1600°C in low P_{O_2} .

leakage. All the observed data were measured within ~ 3 h of CO/CO_2 gas flow at 1600°C . For all coatings, the oxygen flux of YSZ membrane increased from that of uncoated YSZ. Especially, the oxygen flux of GDC-coated YSZ showed the highest increase. In other words, the ceria coating is more effective than zirconia or LaCrO_3 coating. The observation indicates that the increase in the surface-exchange kinetics of the membrane can be improved by coating with more catalytic layer. The factors improving the surface-exchange kinetics is known to be related with surface adsorption and desorption rate, mixed conductivity, surface area/unit volume, porosity and thickness of porous coated layer.^{12,13} As shown in Fig. 6, YSZ–GDC layer, before and after permeation experiment, is more dense and thus the surface area of YSZ–GDC layer is smaller than that of YSZ layer. However the flux of YSZ–GDC coated sample is higher than that of YSZ coated samples. Thus, YSZ–GDC mixture must have a good catalytic activity. GDC alone is also expected as a good catalyst since YSZ with GDC layer shows the highest flux among all samples. The oxygen flux of the membrane with the coating layer of YSZ, YSZ–GDC mixture, GDC ($13\ \mu\text{m}$), GDC ($25\ \mu\text{m}$) and LaCrO_3 increased nearly 2, 7, 8, 9 and 6 times, respectively. However, this increase due to coating was not maintained for long time except for LaCrO_3 coating due to the reaction of the layer with YSZ membrane and the sintering of the porous layer as shown in Fig. 7.

The oxygen flux of YSZ with coating layer drastically decreased after 5–7 h except for LaCrO_3 layer. The decrease was associated with the sintering of the layer with time. The microstructure of LaCrO_3 layer remained porous during experiment. Cr evaporated from LaCrO_3 layer and the Cr deficiency was found up to $10\ \mu\text{m}$ from surface after experiment as observed by EDS line profile. After exposure to reducing gases, the oxygen flux of YSZ membrane with YSZ, YSZ–GDC, or GDC coating reduced to that of uncoated-YSZ. Since the sintering accompanies the reduc-

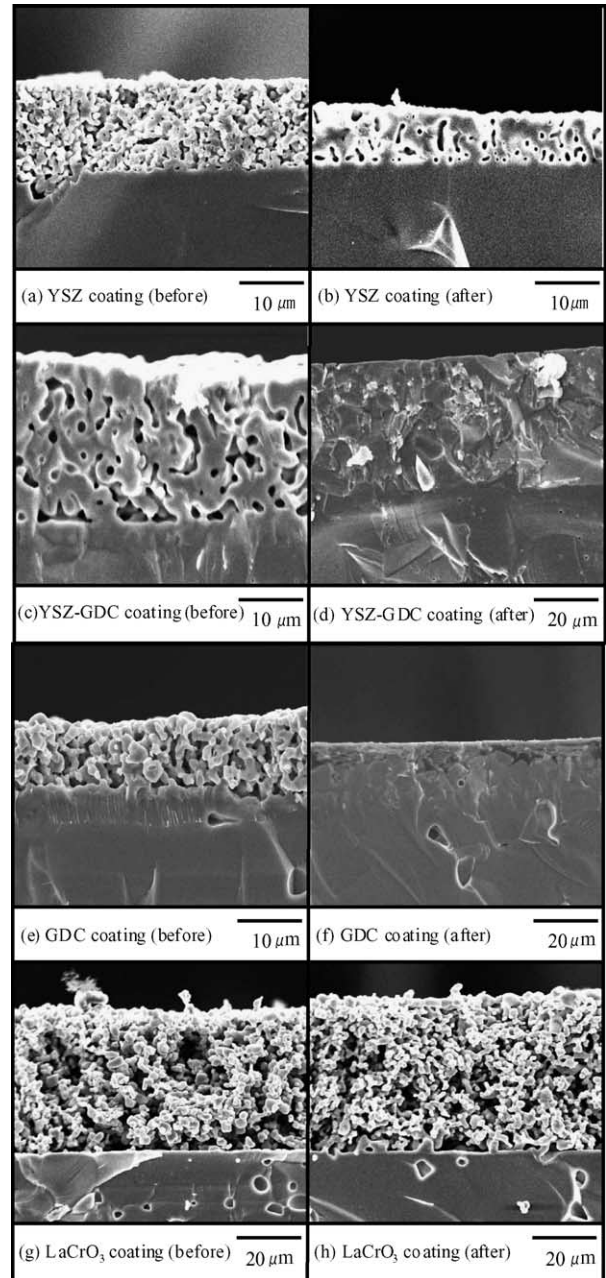


Fig. 6. Microstructure of coated membranes of feed side before (left column) and after (right column) permeation experiment. Note the scale is not the same for all photos.

tion, it is believed that the oxygen flux is again mostly controlled by surface-exchange kinetics. For YSZ coating, the decrease is clearly due to the decrease in the reactive surface area by the sintering of porous layers. For YSZ–GDC mixture and GDC coating, the decrease may also be due to the reaction with YSZ membrane. The reaction of GDC layer with YSZ membrane was proved by XRD, SEM-image, and EDS line profile. The thickness of reaction zone of $13\ \mu\text{m}$ -thick GDC coating was about $25\text{--}30\ \mu\text{m}$, and unknown peaks and YSZ–GDC solid-solution peaks

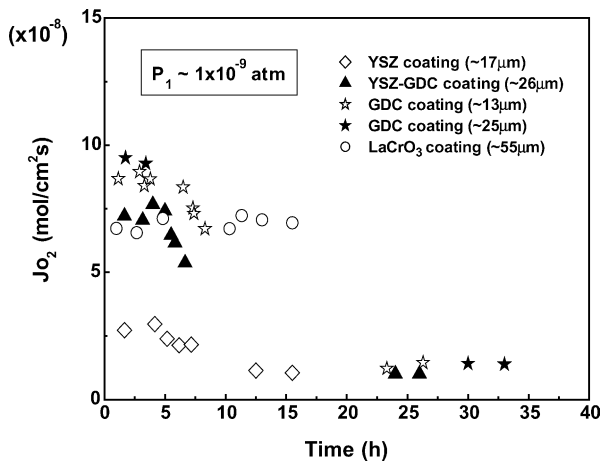


Fig. 7. The time dependent oxygen flux of YSZ membrane with YSZ, YSZ–GDC mixture, GDC and LaCrO₃ coatings at 1600 °C in low P_{O_2} .

were detected in both sides of YSZ membrane after experiment.

4. Conclusions

The oxygen flux of YSZ membrane was measured as a function of the temperature (1400–1600 °C) and P_{O_2} (1 to 1×10^{-3} , 2×10^{-3} to 2×10^{-7} , and 3×10^{-12} to 2×10^{-8} atm). In high and middle P_{O_2} regions, the hole and electron conductivity (σ_h^0 , σ_e^0) were obtained since in this regions the oxygen flux was mostly limited by the bulk diffusion. However, in low P_{O_2} region, the measured oxygen flux was much smaller than the estimated value from the electrical conductivity. It shows that the oxygen permeation was mostly limited by the surface-exchange kinetics. The coating of YSZ membrane with YSZ, YSZ–GDC mixture, GDC and LaCrO₃ layers increased the oxygen flux by increasing the effective surface area. Especially, the oxygen flux of YSZ membrane with YSZ–GDC mixture, GDC and LaCrO₃ coatings drastically (six to nine times) increased. However, the increased flux was not maintained for long time except for LaCrO₃ due to the reaction and the sintering of porous layer. Therefore, the porous LaCrO₃-coating is the most effective layer for long time use in low P_{O_2} .

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