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Oxygen-permeating zirconia membrane: The effect of thickness and surface coating

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Abstract

The oxygen flux of yttria-stabilized-zirconia (YSZ) was measured as a function of membrane thickness and surface coating, under controlled P_{O_2} gradient (permeate side: $\sim 3 \times 10^{-12}$ atm; feed side: 2×10^{-12} to 2×10^{-8} atm) in reducing atmosphere at 1600 °C. The oxygen flux was determined by measuring the change of CO_2 content in CO gas stream of permeate side with gas chromatograph. In order to study the effect of surface-exchange kinetics, YSZ membranes with or without $LaCrO_3$ coating were used. The oxygen flux increased with decreasing YSZ thickness from 0.7 mm to 0.2 mm. The oxygen flux was controlled by both the bulk diffusion and surface exchange kinetics. Permeation experiment was possible for the membrane as thin as 200 μm by a new experiment setup. Characteristic membrane thickness (L_C) which divides the bulk diffusion and surface-exchange limits was calculated as 0.365 mm. Based on this study, the increased permeation flux is expected for YSZ with different coating layer.

Keywords: Permeation; Membrane; ZrO_2

1. Introduction

Recently, mixed ionic–electronic conductors (MIECs) draw a lot of attentions due to their applications in gas sensors, batteries, and fuel cells.[1,2] Special application is in the de-oxidation in steel melt, where the membrane requires high chemical and mechanical stability as well as high oxygen permeation at a high temperature in low oxygen partial pressure.[3] Stabilized-ZrO_2 membrane is used for this purpose due to its exceptionally high chemical and mechanical stabilities, despite lower expected permeation rate than perovskite materials (such as $LaCrO_3$, $SrCoO_3$, $LaAlO_3$) or ceria materials.[4–7]

In our previous experiment, we have found that the permeation of uncoated zirconia at a high temperature in low P_{O_2} is mostly limited by surface oxygen-exchange kinetics.[4] Oxygen permeation was increased by coating the membrane with variable materials. As a result of experiment using YSZ membrane with 1mm thickness, the highest oxygen flux was obtained with Gd-doped ceria (GDC) or $LaCrO_3$ coating. $LaCrO_3$-coated membrane was more stable than GDC-coated one although the flux was slightly lower.[4,8] Even though GDC is known as a mixed conductor with high catalytic activity, the YSZ membrane with GDC coating showed poor long-term performance due to its easy sinterability at a high temperature. In this study, in order to determine the contributions to permeation rate from bulk diffusion and surface-exchange kinetics with $LaCrO_3$ coating, the thickness of YSZ membranes was varied.[9,10] We expect to determine the characteristic thickness value of YSZ membrane with $LaCrO_3$ coating and whether we have to reduce the membrane thickness or change the coating material to increase the permeation rate.

2. Experimental procedure

In order to fabricate YSZ oxygen membrane, commercial $Zr_{0.84}Y_{0.16}O_{2-\delta}$ (99.9%, TOSOH, Japan) powder was used. The powder was pressed uniaxially at 0.5 MPa, followed by CIP (Cold-Isostatic Pressing at 200 MPa for 30 s). The samples with three different thicknesses (0.7 mm, 0.5 mm, and 0.2 mm) and a diameter of 25 mm were sintered at 1650 °C for 3 h in air. For surface coating of YSZ membrane, $LaCrO_3$ powder was prepared by mixing La_2O_3 and CrO_3 powder and calcining at 1200° for 2 h. The powder was screen-printed on both surfaces of YSZ membranes followed by sintering at 1600 °C for 1 h.

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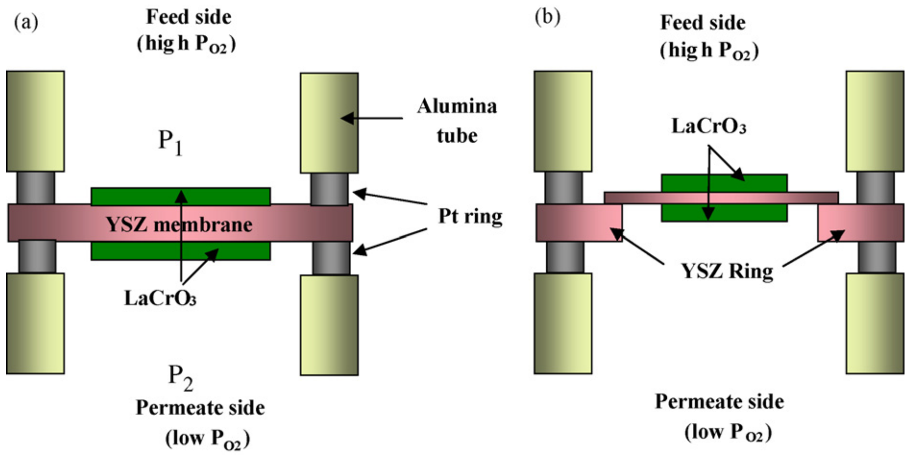

Fig. 1. Schematic experimental setup for permeation measurement of YSZ membrane: for (a) self-supporting, thick (≥0.5 mm) membranes and (b) a supported, thin (0.2 mm) sample.

$LaCrO_3$ phase on YSZ surface was confirmed by X-ray diffraction. The microstructure was examined with a scanning electron microscope (SEM). The oxygen permeation was measured in various oxygen-partial pressure (P_{O_2}) gradients using gas chromatography (HP4890D, USA) and zirconia oxygen sensor. The permeate-side (low-P_{O_2} side) was fixed at $\sim 3 \times 10^{-12}$ atm. The feed side (high-P_{O_2} side) varied from $\sim 3 \times 10^{-12}$ to $\sim 1 \times 10^{-8}$ atm.

The amount of permeated oxygen was determined by measuring the P_{O_2} change in permeate side. The leakage was tested by using He/O_2 gas. The amount of nitrogen gas was below 0.01% of sweep gas volume (100 ml/min). The side-wall leakage of oxygen was estimated by the difference in the inlet and outlet P_{O_2} of each side under no permeation condition. The effect of side-wall leakage was negligible compared to total oxygen permeation flux across sample. The detailed description of measurement setup was described elsewhere.[3,11]

Although membranes thicker than 0.5 mm were self-supporting as shown in Fig. 1a, the membrane of 0.2 mm thickness easily cracked in self-supporting mode. Thus a new method was developed for a membrane with 0.2 mm thickness. The 0.2-mm-thick YSZ membrane was mounted on 1-mm-thick YSZ ring by sintering two pieces together. Two alumina tubes then pushed against the YSZ ring with Pt rings. With this new configuration, it was possible to measure the oxygen flux of membrane as thin as 0.2 mm.

The average diameter of membrane samples exposed to gas was ∼18 mm for 0.7 mm, 0.5 mm and ∼12 mm for 0.2 mm thick YSZ membrane, respectively.

3. Results and discussion

Fig. 2a shows permeate side's and Fig. 2b feed side's microstructure after permeation experiment for 0.5-mm-thick membrane. The thickness of coating layer ($LaCrO_3$) of 0.7 mm, 0.5 mm samples at feed side was ∼35 μm, and that of 0.2-mm-thick samples was about ∼20 μm. The reason for the different thicknesses lies in difficulty in handling 0.2-mm-thick sample during the screen-printing. Although the thickness of $LaCrO_3$ coating layer was different, they showed a similar microstructure. The permeate side was denser than the feed side. This means that the sintering of $LaCrO_3$ is easier in a low P_{O_2} atmosphere.[4] The surface-exchange kinetics or rate may be lower in permeate side due to the dense microstructure.

The rate of oxygen permeation in general, is decided by both the bulk diffusion of membrane and by surface oxygen-exchange kinetics. When the bulk diffusion is determining the rates, the flux is given by Wagner equation[12]:

$$J_{O_2} = -\frac{1}{4^2 F^2 L} \frac{\sigma_{el}\sigma_{ion}}{\sigma_{el} + \sigma_{ion}} \nabla \mu_{O_2} \tag{1a}$$

where L is the sample thickness, F the Faraday constant, σ_{el} the electronic conductivity, σ_{ion} the ionic conductivity and $\nabla \mu_{O_2}$ is

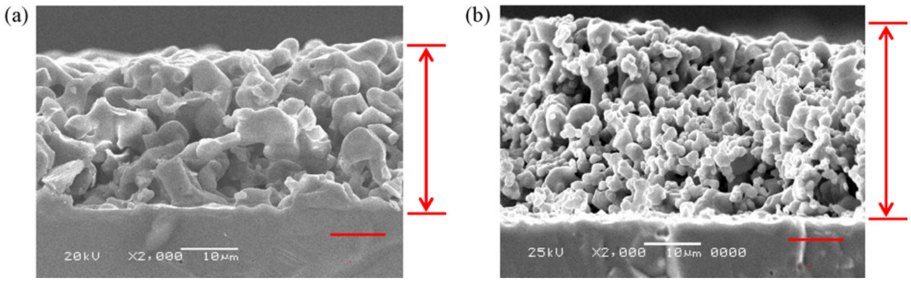

Fig. 2. SEM micrograph of coated-$LaCrO_3$ layer on YSZ membrane after permeation experiment at 1600 °C/24 h: (a) permeate side (low-P_{O_2} side) and (b) feed side (high-P_{O_2} side). The permeate side is more dense and grains are larger.

the P_{O_2} gradient. Assuming the transport of YSZ is limited by n-type conductivity in low P_{O_2}, Eq. (1a) becomes[13]:

$$J_{O_2} = \frac{RT}{4F^2L}\sigma_{el}^{o}[P_2^{-1/4} - P_1^{-1/4}] \tag{1b}$$

where σ_{el}^{o} is σ_{el} at $P_{O_2} = 1$ atm, P_2 the feed-side P_{O_2} and P_1 is the permeate-side P_{O_2}. When both the bulk diffusion and surface-exchange kinetics are limited, and P_{O_2} gradient is small, the Wagner equation is modified as[12]

$$J_{O_2} = -\frac{1}{1+(2L_C/L)}\frac{t_{el}t_{ion}\sigma_{total}}{4^2F^2}\frac{\Delta\mu_{O_2}}{L} \tag{2a}$$

where L_C is the characteristic membrane thickness, t_{el} the electronic transport number and t_{ion} is the ionic transport number. Under similar assumptions used for Eq. (1b), the flux becomes:

$$J_{O_2} = -\frac{1}{1+(2L_C/L)}\frac{RT}{4F^2L}\sigma_{ion}\left[\ln\frac{1}{\sigma_{ion}+\sigma_e^o P_{O_2}^{-1/4}}\right]_{P_1}^{P_2} \tag{2b}$$

where L_C is the D_a/K_s, D_a the ambi-polar diffusion coefficient and K_s is the surface-exchange coefficient. In this equation, if the P_{O_2} gradient is fixed, the oxygen flux increases with decreasing L_C or L.

Fig. 3 shows the oxygen permeation flux of YSZ as a function of thickness with or without $LaCrO_3$ coating. The oxygen flux increases with decreasing membrane thickness for either uncoated or $LaCrO_3$-coated samples. However, a large difference is shown for the $LaCrO_3$ coated samples. This implies that the uncoated YSZ is more surface-exchange limited than the coated YSZ. Thus $LaCrO_3$ is an effective coating material that enhances oxygen permeation. This also means that L_C is decreasing with $LaCrO_3$ coating.

In Eq. (2), there are two variables that change the flux under fixed P_{O_2} gradient: membrane thickness (L) and L_C. With fixed P_{O_2} gradient ($P_2 = 1 \times 10^{-9}$ atm, $P_1 = 6.3 \times 10^{-12}$ atm, arrows in Fig. 3), it is possible to estimate the L_C value by fitting the experimental data with Eq. (2). After simple modification of Eq. (2) by using the fixed value as "Const":

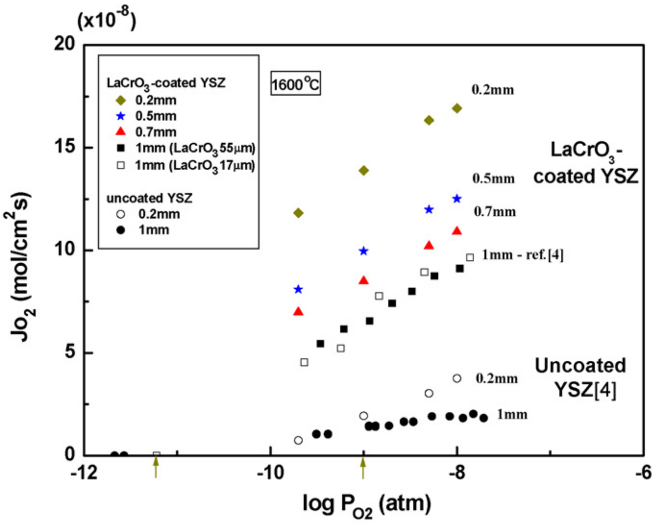

Fig. 3. Oxygen-permeation fluxes with and without $LaCrO_3$ coating under various P_{O_2} gradient at 1600 °C ($P_2 = 6.3 \times 10^{-12}$ to 2×10^{-8} atm and $P_1 = \sim 3 \times 10^{-12}$ atm). Large increase in oxygen flux was apparent for $LaCrO_3$-coating and with decreasing sample thickness.

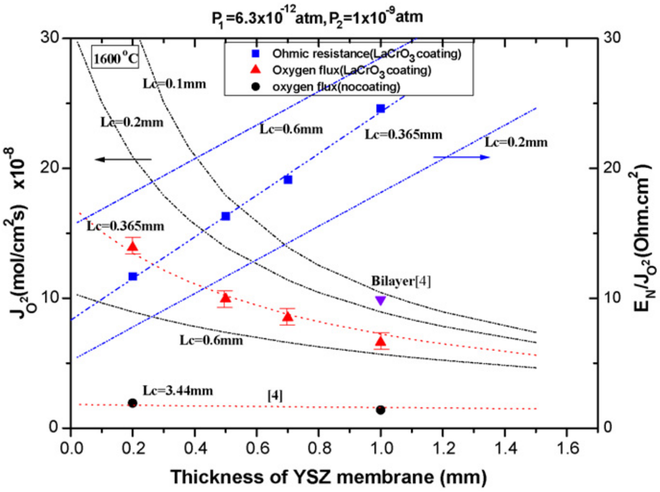

Fig. 4. Oxygen flux as a function of membrane thickness was shown for uncoated (circles) and $LaCrO_3$-coated YSZ (triangles), respectively. The characteristic membrane thickness (L_C) was obtained by curve fitting of oxygen flux under fixed P_{O_2} gradient at 1600 °C ($P_2 = 6.3 \times 10^{-12}$ atm and $P_1 = 1 \times 10^{-9}$ atm, arrows in Fig. 3). Interfacial polarization resistance (R_P) (squares) was also obtained. The expected oxygen fluxes for other L_C values, and R_P values for three different L_C values were calculated and shown for comparison.

$$J_{O_2} = -\frac{1}{1+(2L_C/L)}\frac{1}{L}\text{Const} = -\frac{\text{Const}}{L+2L_C} \tag{2c}$$

where Const is the constant under fixed P_{O_2} gradient for YSZ at 1600 °C.

After least squares fitting by using Eq. (2d), Fig. 4 was obtained:

$$\left(J'_{O_2\,\text{exp}} - \frac{\text{Const}}{L+2L_C}\right)^2_{\text{sum}} = \text{minimum} \tag{2d}$$

Here, $J'_{O_2\,\text{exp}}$ is the experimental permeation data. Since the surface-exchange kinetics does not vary with sample thickness, the interfacial polarization resistance can also be calculated when L approaches zero.[9] Since Nernst potential (E_N) is fixed under fixed P_{O_2} gradient and given by

$$E_N = \frac{RT}{4F}\ln\left(\frac{P''_{O_2}}{P'_{O_2}}\right) \tag{3}$$

The interfacial polarization resistance (R_P) was calculated by using:

$$R_P = \left(\frac{E_N}{J_{O_2}}\right)_{L\to 0} \tag{4}$$

and represents the resistance due to the slow surface kinetics excluding the bulk contribution. The obtained L_C value of YSZ membrane coated with $LaCrO_3$ was ~0.365 mm (±0.013 mm), and R_P was ~8.32 Ω cm^2. The expected oxygen fluxes for other L_C values, and R_P values for three different L_C values were calculated and shown for comparison. As the thickness of membrane decreases from 1 mm to 0.2 mm, oxygen flux rapidly increased.

However, for a given value of L_C (0.365 ± 0.013 mm), the flux is expected to increase only up to $\sim 1.7 \times 10^{-7}$ mol/cm^{2}s for negligible sample thickness due to the surface-kinetics limitation. Large increase in oxygen flux is expected for thin sample only if L_C value becomes smaller with more effective surface coating. YSZ coated with $LaCrO_3$/Ceria bilayer is an example as shown in Fig. 4.[4]

4. Conclusions

The oxygen flux of YSZ membranes with and without $LaCrO_3$ coating was measured as a function of the membrane thickness (0.7 mm, 0.5 mm, and 0.2 mm) and the variation of oxygen partial pressure ($P_2 = \sim 2 \times 10^{-12}$ to $\sim 2 \times 10^{-8}$ atm and $P_1 = \sim 3 \times 10^{-12}$ atm). A new experiment setup, utilizing supporting ring for thin disk-shape sample, made permeation measurement possible for a sample as thin as 0.2 mm (200 μm). The permeation was controlled by both the bulk diffusion and surface oxygen-exchange kinetics. The characteristic membrane thickness, which divides the bulk diffusion and the surface-exchange limit, was estimated by the modified Wagner equation. Although the large increase in oxygen flux was shown with $LaCrO_3$ coating, the further increased flux is expected for a sample with a better coating material that increases surface-exchange kinetics.

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