PERMEATION CHARACTERISTICS OF YSZ FILMS DURING THE DEPOSITION ON A POROUS NiO/YSZ SUBSTRATE

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ABSTRACT
Films of YSZ have been deposited on a porous NiO/YSZ substrate by a slurry coating method. Evolution of gas permeation rate through the film during the deposition was measured at 600~1000°C using He, N₂, Ar and O₂. The viscous flow effect dominated the gas permeation through the porous NiO/YSZ substrate. As the YSZ layer was formed on the substrate, however, the gas permeation rate decreased and the permeation through the YSZ films became governed by Knudsen diffusion. The permeation rate through the porous YSZ films decreased with increasing temperature. As the film became denser, YSZ film became selective for O₂ permeation. The permeation rate of O₂ through the dense YSZ film increased with increasing temperature.

INTRODUCTION
Yttria-stabilized zirconia (YSZ) is widely used as an electrolyte material for SOFC. For practical application YSZ layer has to be made very thin and dense so that only oxide ion can permeate through the electrolyte without significant Ohmic loss. To get the high permeation rate and the sufficient mechanical strength, YSZ was deposited on a porous electrode in the form of thin film. Both vapor-phase and liquid-phase techniques have been developed for YSZ film deposition on a porous substrate. A vapor-phase technique based on CVD-EVD has been used at Westinghouse Electric Co. to make YSZ film on a porous air-electrode for tubular SOFC [1]. Plasma-spraying of YSZ on a porous anode has been carried out at Fuji Electric Co. to prepare a planar SOFC [2]. Liquid-phase slurry dipping method has been suggested as an economical alternative method to fabricate a tubular SOFC [3]. Recently electrophoretic deposition technique was considered for YSZ deposition [4]. All the techniques involve the gradual plugging of substrate pores by YSZ films. In this study, we investigated the permeation characteristic of
YSZ films during the deposition on a porous anode. YSZ films were prepared on a porous NiO/YSZ substrate with a slurry coating method and gas permeation rates through the films were measured at various temperature and pressure.

EXPERIMENTAL

Porous anode substrates were prepared using NiO (Junsei) and 8 mol% YSZ (Tosoh, TZ-8YS) powders. YSZ powder was sintered at 1400°C before mixing with NiO powder. A NiO/YSZ mixture containing 50 wt% NiO was ball-milled for 72 hours and then formed by uniaxial pressing to a disk of 1cm in diameter and 0.2 cm in thickness. The disk was sintered at 1200°C for 1 hour.

Films of YSZ were prepared on NiO/YSZ with a dip coating method using YSZ slurry containing 12wt% YSZ powder (Tosoh, TZ-8Y or TZ-8YS) in ethanol. The slurry was then coated on one side of the substrate by dipping. The film-coated anode was sintered at 1150°C for 1 hour. The dipping-sintering cycle was repeated until a desired electrolyte thickness was obtained. The sample was finally sintered at 1430°C for 4 hours. For comparison, dense YSZ films were prepared by the tape-casting of TZ-8YS slurry and sintered at 1400°C for 4 hours.

The permeation rate was measured with an apparatus depicted in Figure 1. The sample was placed on the top of an alumina tube and sealed by glass powder (GA-33, Nippon Electric Glass Co.). Before the permeation measurement, the sample was heated at 1200°C for 1 hour under air flow to soften and melt the glass for sealing.

The permeation rate was evaluated by a bubble flowmeter while the pressure difference between the compartments separated by the sample was maintained at 0 ~ 1 atm. Low permeation rates were measured by use of a pressure transducer (Baratron) connected to a recorder. In this case the outside of the sample was maintained at 1 atm under flow while the inside of the alumina tube was initially evacuated. After the inside volume of the alumina tube was isolated from the evacuation system, the increase in initial pressure was measured by the pressure transducer. The permeation rate was then determined, assuming the validity of ideal gas law. The permeation rate [cm³(STP)/min·cm²·atm] was defined as the flux of gas through the unit area of the sample when the pressure difference was 1 atm. In this study permeation rates of He, N₂, Ar and O₂ were measured separately. The morphology and thickness of the films were evaluated by a scanning electron microscopy (SEM).
RESULTS AND DISCUSSION

Permeation of N₂ at room temperature

Figure 2-a shows a decrease in permeation rate of N₂ through the YSZ film during the deposition. The permeation rate was measured at room temperature. During the deposition the film thickness increased as shown in Figure 2-b. The films prepared from TZ-8YS slurry became thick and dense faster than the films formed from TZ-8Y slurry. Since the N₂ permeation rates through the films having the same thickness (e.g. the film formed from TZ-8Y after 10th coating and the film formed from TZ-8YS after 2nd coating), were the same, the permeability (permeation rate for a unit thickness) for N₂ and thus pore structure of the films may be the same although the films were prepared from the different sources. The cross-section of YSZ film on a porous NiO/YSZ substrate after 10th coating of TZ-8Y slurry is shown in Figure 3.

Figure 4 shows the effect of pressure difference on the permeation rate. Permeation rate of N₂ through a porous NiO/YSZ support increased with increasing pressure difference, indicating that viscous flow effect dominated during the gas permeation. However, the permeation rate (calculated at ΔP = 1 atm) through the YSZ films prepared from TZ-8Y slurry after 4th coating slightly depends on the applied pressure, suggesting that permeation became governed by Knudsen diffusion.

Gas permeation at high temperature

Permeation rates of He, N₂ and Ar through the YSZ film were measured at 600~1000°C. Figure 5 shows the gas permeation rate at various temperatures through the sample prepared from TZ-8Y slurry after 4th coating. At this stage of film deposition the YSZ film is still porous as shown in Figure 2. Gas permeation rate decreased with increasing temperature. Permeation rate of He is higher than the rate of N₂ or Ar. Permeation ratios of He to N₂ and He to Ar were about 2.5 and 3.0, respectively, at all temperatures. The ideal separation factors estimated assuming Knudsen diffusion for He/N₂ and He/Ar are 2.6 and 3.0, respectively, which are close to the experimental results.

Figure 6 shows the gas permeation rate through the sample prepared from TZ-8YS slurry after 5th coating. As the YSZ films became denser by repeating the coating, the gas permeation rate decreased rapidly to 0. Even though the permeation rate decreased by 3 orders of magnitude compared with the result shown in Fig. 5, the general trend was the same as mentioned for porous YSZ films. At this stage of film deposition, gas may permeate through very small pores or pinholes unplugged yet by the deposition. One thing to be noted is that
permeation rate of air through the films at this stage was higher than the rate of \( N_2 \), indicating that the film became selective for \( O_2 \) permeation.

**Permeation rate of \( O_2 \) through the dense YSZ films**

Figure 7 shows an increase in permeation rate of oxygen through a dense YSZ film with increasing temperatures ranging from 900 to 1200°C. The permeation rate was measured from a 160\( \mu \)m thick YSZ film tape-casted from TZ-8YS slurry; no electrode or lead wire was used. The increasing permeation rate with temperature suggests an activation of oxygen permeation. Since the permeation rates of other gases, such as \( N_2 \) or He, through the YSZ film was negligible (2 orders of magnitude lower than the rate of \( O_2 \) at 1200°C), it is most likely that the selective permeation of oxygen through the film may have been due to the electronic conductivity of the film at high temperatures. The oxygen permeation rate at 1000°C through the dense YSZ film, however, was 100 times lower than the rate through the YSZ film formed by the slurry coating method (see Fig. 6), indicating that the conductivity of YSZ with electronic charge carrier is extremely low. Electronic conductivity in YSZ film at high temperatures has been reported by Kleitz et al. [5]. Furthermore, some attempts have been made to use the stabilized zirconia as an oxygen semipermeable membrane for the thermal decomposition of \( H_2O \) [6] and \( CO_2 \) [7,8]. Further works are under progress to quantitatively investigate the \( O_2 \) permeation and the electronic conductivity phenomena occurring at high temperatures.

**CONCLUSIONS**

Films of YSZ have been deposited on a porous NiO/YSZ substrate by a slurry coating method. The gas permeation through the porous NiO/YSZ substrate was dominated by the viscous flow effect. As the YSZ layer was formed on the substrate, the gas permeation rate decreased and the gas permeation became governed by Knudsen diffusion. The permeation rate of \( N_2 \), He and Ar through the porous YSZ films decreased with increasing temperature. As the film became denser by repeating the coating, YSZ films became selective for \( O_2 \) permeation. The permeation rate of \( O_2 \) through the dense YSZ film increased with increasing temperature.

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Fig. 1. A system for gas permeation measurement.
Fig. 2. Evolution of permeation rate (a) and film thickness (b) during the YSZ deposition on NiO/YSZ substrate.

Fig. 3. SEM micrograph of the cross-section of YSZ film on NiO/YSZ substrate.
Fig. 4. Permeation rate of N2 versus pressure difference at room temperature.

Fig. 5. Permeation rate of gases at high temperature through YSZ films formed on a NiO/YSZ substrate using TZ-8Y slurry after 4th coating.
Fig. 6. Permeation rate of gases at high temperature through YSZ films formed on a NiO/YSZ substrate using TZ-8YS slurry after 5th coating.

Fig. 7. Permeation rate of O$_2$ at high temperature through the dense YSZ films.