

산소 분리를 위한 무공성 세라믹- 금속 복합 무기막

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Dense Ceramic-metal Composite Inorganic Membranes for Oxygen Separation

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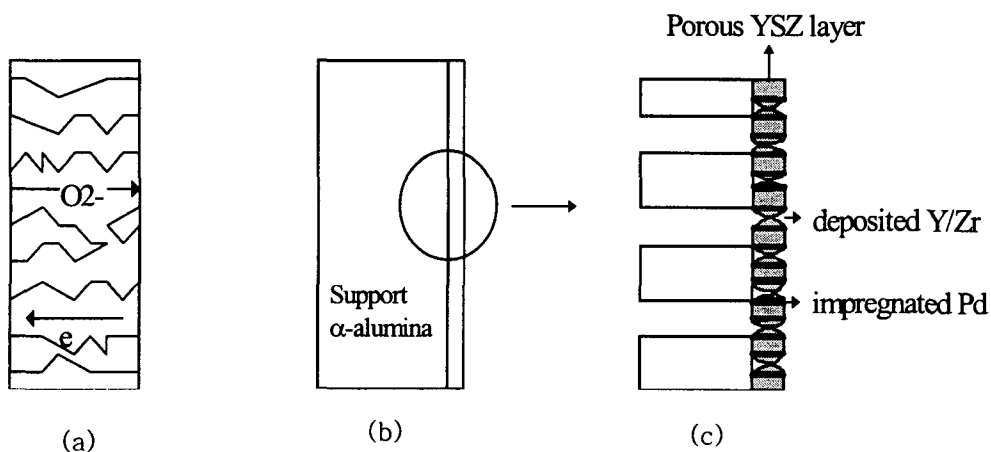
Dense oxygen ionic conducting materials can be used for oxygen separation membranes at high temperatures. However, they show relatively low permeation flux because of their large resistances. To reduce resistances and improve the oxygen permeation flux, thin dense yttria-stabilized-zirconia (YSZ)/Pd composite dual-phase membranes were fabricated by a new approach that combines the reservoir method and chemical vapor deposition (CVD). A thin porous YSZ layer was coated on a porous alumina support by dip-coating the YSZ suspension. A continuous Pd phase was formed inside pores of the YSZ layer by the reservoir method. The residual pores of the YSZ/Pd layer were plugged with yttria/zirconia by CVD to ensure the gas tightness of the membranes. The oxygen permeation fluxes through these composite membrane were 2.0×10^{-8} mol/cm² · s and 4.8×10^{-8} mol/cm² · s at 1050°C when air and oxygen were used as the permeate gases, respectively. These oxygen permeation values are about 1 order of magnitude higher than those of pure YSZ membranes prepared under similar conditions.

1. Introduction

Dense inorganic membranes made of oxygen ionic conducting solid oxide can be applied to high temperature oxygen separation. However, the dense oxygen semipermeable membranes prepared by conventional methods show relatively low permeation flux because of their large transport resistances, attributed to large thickness of the membrane and/or low electronic conductivity. To develop high oxygen semipermeable inorganic membranes, the large resistance of the membranes should be reduced. In general, two different approaches can be employed on the development of high oxygen flux semipermeable inorganic membranes: (1) increasing the electronic conductivity, and (2) reducing the membrane thickness[1,2].

Recently, dual-phase composite materials with improved conducting properties have been studied and used as membranes for oxygen separation[3-5]. The dual-phase membranes consist of two continuous phases: one phase with high oxygen ionic conductivity, and the other with high electronic conductivity, as shown in Figure 1(a). These dual-phase membranes showed much improved oxygen permeation flux, when both phases became continuous[3-5]. All the reported dual-phase membranes were prepared by bulk mixing of solid-state powders, resulting in thickness of 0.25-2 mm range[3-5]. In this study, a new approach combined with reservoir method and CVD was investigated to prepare thin ceramic-metal composite membranes.

Figure 1. (a) Symmetric dual-phase membrane (conventional membrane),
(b) thin composite (dual-phase) membrane, and (c) its structure[6]



2. Experimental

The following steps were used in sequence to fabricate thin YSZ/Pd composite (dual-phase) membranes.

(1) *Preparing porous YSZ membranes from suspension*

Stable YSZ suspension was prepared from commercially available YSZ powder (Tosoh, TZ-8Y). The YSZ powder and dilute nitric acid were mixed together (ball-milling) to stable YSZ suspension. The supported porous YSZ membranes were prepared by dip-coating the YSZ suspension on the polished α -alumina disks (diameter: 20 mm; thickness: 2 mm; pore diameter: 0.2 μ m; porosity: 50%). After drying at the controlled conditions (relative humidity: 40-50%; temperature: 40°C), they were calcined at 1000°C for 3 hr [7].

(2) *Pd modification inside YSZ pores by reservoir method*

Pd was impregnated inside the supported porous YSZ membranes by the reservoir method [8]. The Pd solution was first prepared by dissolving Pd acetate (Alfa, Mw=673.46) in the mixture of acetone and HCl. The supported YSZ membranes were fully soaked inside the Pd solution, and then dried for 1 day in the hood. After that, they were calcined at 500°C for 2 hr under hydrogen flow [8]. During the calcination step, the Pd acetate changed to pure Pd. These soaking, drying, and calcination processes were repeated to get an appropriate amount of Pd inside the porous YSZ membranes.

(3) *Pore plugging of Pd modified YSZ membranes by CVD/EVD technique*

Thin gas-tight YSZ/Pd composite (dual-phase) membranes were prepared by plugging the residual pores of Pd-impregnated YSZ membranes by counter diffusion CVD (Figure 2). The metal precursors, $ZrCl_4$ and YCl_3 , were placed at the desired temperature zone, which was selected based on the equilibrium vapor pressure data. When reactor pressure and temperature were stabilized, the CVD experiment was started by introducing the oxygen-source stream into the CVD reactor. Both metal precursors and oxygen source were introduced from the other sides into the pores of Pd modified YSZ membranes, plugging the residual pores.

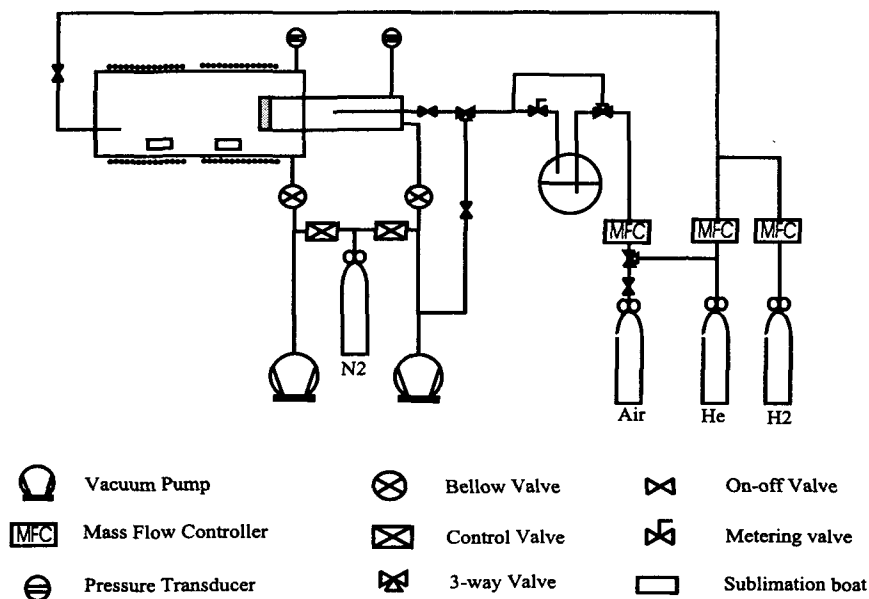


Figure 2. Schematic diagram of CVD reactor[6]

3. Results and Discussion

Stable YSZ suspension was prepared by ball-milling the commercially available YSZ powder in dilute nitric acid. After 7 days of ball-milling, the YSZ particle size was in the range of 50-100 nm. Crack-free supported YSZ membranes could be prepared by dip-coating the stable YSZ suspension on α -alumina supports. The YSZ layer thickness was about 5 mm after 1-time dip-coating and 10 mm after 2-time dip-coating, respectively. The pore diameter of dip-coated YSZ membranes was determined to be 100 nm with Mercury porosimeter, and 114 nm with He permeation measurement. The XRD result showed that they were in cubic fluorite structure[7].

The prepared porous YSZ membranes were modified with Pd by the reservoir method. The α -alumina/YSZ two-layer membranes were put in the Pd solution, followed by drying, which promoted the concentration of the metal cations inside the top layer of the membranes. During drying process, the Pd solution in the YSZ layer dried first, then the Pd solution inside the alumina layer filled the pores of the YSZ top layer by the capillary pressure that resulted from the difference in pore sizes. During the calcination, the Pd

precursor changed into pure metal Pd. Figure 3 shows the electrical conductivity data with the number of Pd loading. Up to 3-time Pd loading, the conductivity of Pd modified YSZ membrane showed similar value with that of pure YSZ membrane. However, the total electrical conductivity of the 4-time Pd loaded YSZ membrane is three orders of magnitude higher than that of pure and 3-time Pd loaded YSZ membranes. This indicates that the Pd phase became continuous after 4-time Pd loading. Based on these results, the 4-time Pd-loaded YSZ membranes were used as the substrates for CVD experiments.

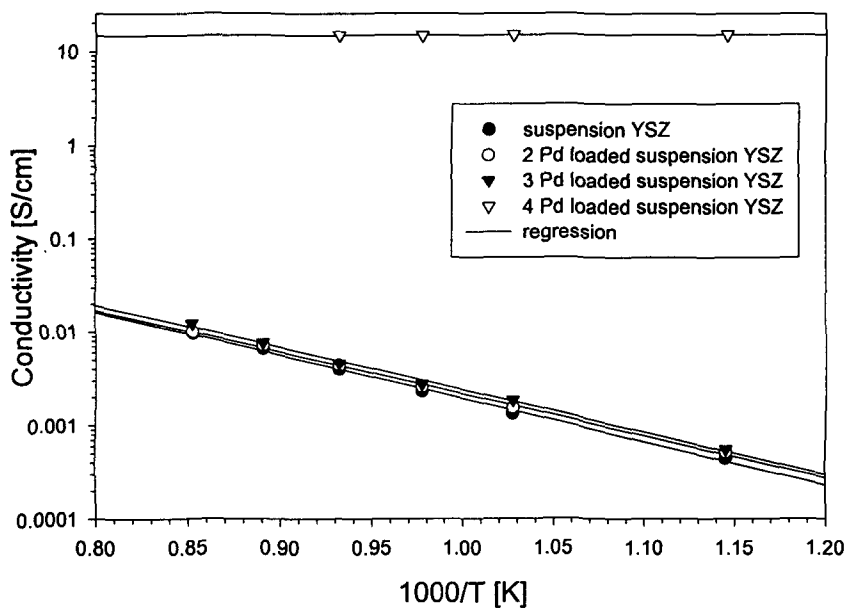


Figure 3. Electrical conductivity with the number of Pd loading

Yttria/zirconia (YZ) was deposited inside and/or on top of the Pd-loaded YSZ membranes by the CVD process to prepare thin YSZ/Pd composite (dual-phase) membranes. The unique feature of the counter

diffusion CVD process is the formation of the YZ deposit inside the pores of the Pd-loaded YSZ membranes, in contrast to other deposition techniques that result in the formation of a film on the substrate surface. The progress of the CVD stage results in significant pore narrowing until all the pores are completely closed. After this pore closure, direct contact of the precursors is no longer possible. However, film growth may continue since the oxygen precursor permeates through the YZ deposit or YSZ and meets metal precursors at the opposite side of the film, resulting in further reactions and solid film growth.

SEM images and EDS dot mappings (Al, Pd and Zr) of the cross section of thin composite membrane show that Pd is concentrated inside the YSZ layer (10 nm), leaving some Pd traces in the α -alumina support[6]. It also shows a fairly uniform distribution of palladium in the YSZ top layer, indicating the effectiveness of reservoir method on Pd loading inside YSZ layer. XRD patterns of thin composite membranes clearly indicate the presence of cubic phase YSZ and pure metal Pd.

Oxygen permeation fluxes through the YSZ/Pd composite (dual-phase) membranes were measured in the temperature range of 900–1050°C. The oxygen permeation fluxes through these membranes are in the range of 2.2×10^{-9} – 2.0×10^{-8} mol/cm²·s and 5.2×10^{-9} – 4.8×10^{-8} mol/cm²·s when air and oxygen are used as the permeate gases, respectively. The oxygen-permeation fluxes of pure YSZ membranes prepared by CVD are compared with those of the YSZ/Pd composite membranes. These pure YSZ membranes were on the same YSZ substrate and prepared under identical CVD conditions, except that no Pd was coated. Therefore, the dense layer of the YSZ membranes should be similar to that of the YSZ/Pd dual-phase membranes. The oxygen-permeation flux was about 10 times higher than that of pure YSZ membranes. The activation energies calculated from Arrhenius plots of oxygen permeation were 193 kJ/mol for YSZ/Pd composite membranes and 124 kJ/mol for pure YSZ membranes, respectively. This difference can be explained in terms of relative importance of various mass transfer steps for oxygen permeation and microstructure of the membranes.

4. Conclusions

Gas-tight thin YSZ/Pd composite (dual-phase) membranes can be fabricated by a technique that combines liquid-phase coating and CVD methods. Oxygen permeation fluxes through the YSZ/Pd composite (dual-phase) membranes were investigated *in-situ* in the CVD reactor, which avoided possible high-temperature sealing problems. The oxygen-permeation fluxes through these YSZ/Pd composite (dual-phase) membranes are in the 2×10^{-9} – 5×10^{-8} mol/cm² · s range, about one order of magnitude higher than pure YSZ membranes prepared in similar conditions. The apparent activation energies for oxygen permeation in the 900–1050 °C temperature range are 193 kJ/mol for the YSZ/Pd composite (dual-phase) membranes and 124 kJ/mol for pure YSZ membranes.

5. References

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