

Hydrogen Permeance of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ Membranes According to Yttrium Content

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ABSTRACT

Porous ceramic membranes consisting of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ were developed for hydrogen permeation tests. Various amounts ($x = 0, 0.05, 0.1, 0.2$) of yttrium were doped to ceria to study the effect of yttrium doping on ceria membranes on various properties, including hydrogen permeability. $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ powder was synthesized by the sol-gel method. These membranes were fabricated by pressing and sintering at 1300°C for 6 h. As the amount of yttrium increased, the grain size of the membrane decreased. Hydrogen permeability was improved as the yttrium content increased. Selective permeability of hydrogen compared to CO is explained by electric conductivity. As the temperature rose, both the hydrogen perm-selectivity and electric conductivity on $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ improved.

Key words : Porous ceramic membrane, Hydrogen permeation tests, Sol-gel method, $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$

1. Introduction

Considering the world energy crisis, there is an increasing demand for hydrogen energy as an alternative to fossil fuel, not only in the petrochemical industry but also in renewable energy. Membranes composed of Pd alloys are known as superior classic hydrogen perm-selective membranes, but their high cost is a fatal hindrance to their wide application. Thus, cost-effective inorganic ceramic membranes have been widely studied. Among other materials, porous inorganic membranes have received attention due to their availability either at high operating temperatures or in organic vapors.¹⁾

Inorganic membranes based on proton-electron conductors have the advantage of being able to be applied to various areas such as hydrogen pumps, hydrogen sensors and electrolytes for fuel cells as well as to hydrogen separation membranes.²⁾ For producing proton conducting oxide, other ions with a radius similar to Ce^{4+} (ion radius 0.0870 nm) were added to Ce^{4+} . The ion conductivity of ceria with various dopants such as Ca^{2+} , Ba^{2+} , Y^{3+} , La^{3+} , Gd^{3+} , and Sm^{3+} has also been investigated. In particular, the Y^{3+} dopant, which has a size similar to ceria, could affect densification and grain growth of a ceria matrix. The most effective ratio of these added ions to the ceria has been reported as 10 mol%.³⁾

In this study, various levels of yttrium doped ceria ($\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$) membranes were fabricated for investigating the properties of hydrogen permeable membranes. Nano-sized $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ powder was prepared by a wet chemical sol-gel method using metal nitrates as precursors. The powder was

fabricated into membranes by pressing and sintering and using a binder. These membranes were compared and characterized by XRD, FE-SEM and BET surface analysis. The difference in permeation flux was compared between H_2 and CO gas at changing temperatures. To analyze the permeation flux, electric conductivity was measured in H_2 and air atmospheres.

2. Experimental Procedure

2.1. Powder preparation

The $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ powders ($x = 0, 0.05, 0.1, 0.2$) were prepared by the sol-gel method from their corresponding nitrate solutions. Cerium(III) nitrate hexahydrate ($(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$ Aldrich, 99%) and yttrium(III) nitrate hexahydrate ($(\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$ Aldrich, 99.8%) with the appropriate molar ratio were dissolved in solvent. The solution was heated and stirred at 80°C for 3 h. Then, nitric acid was added to this solution to make its pH value 1.5-2.0 and the solution was stirred at room temperature for 24 h. The gel powder was obtained after the solution was dried at 120°C for about 24 h and then the powder was calcined at 900°C for 2 h. It was followed by milling with a mortar. XRD was used to examine the phase composition of the resulting powders.

2.2. Membrane fabrication

For the membrane fabrication, calcined $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ powders were pressed into about 1 mm thick pellets with 14.5 mm diameter. The pellets were sintered at 1300°C for 6 h in air atmosphere.

2.3. Characterization

The crystal structure of the membrane was studied by X-ray diffraction (XRD) (Bruker D8, Focus, $\text{CuK}\alpha$, 40 Kv, 40 mA). The microstructures of the membranes were characterized using scanning

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electron microscope (FE-SEM) (JEOL-JMS 7500F). Brunner-Emmett-Teller (BET) (BELSORP-max, mini II) techniques were carried out by the adsorption-desorption of N_2 gas to investigate the porosity and the surface area of the membranes. The hydrogen permeability was tested from room temperature to 600°C and the pressure of injected hydrogen was 0.5 bar. Electrical conductivity was evaluated by the dc-four-probe-method using a Frequency Response Analyzer (Solatron, SI1260) and Potentiostat/Galvanostat (Solatron, SI1287) at oxidizing and reducing atmospheres.

3. Results and Discussion

XRD patterns of the $Ce_{1-x}Y_xO_{2-\delta}$ powders verifying the $Ce_{1-x}Y_xO_{2-\delta}$ structure are shown in Fig. 1. The figure indicates that the structure of these powders was crystallized to a single phase of a cubic fluorite structure and there is no phase transition in any of the membranes. The formulas of the samples are (a) CeO_2 (JCPDS file No. 03-065-2975) (b) $Ce_{0.9}Y_{0.1}O_{1.95}$ (JCPDS file No. 01-075-0174) (c) $Ce_{0.9}Y_{0.1}O_{1.95}$ (JCPDS file No. 01-075-0174) (d) $Ce_{0.8}Y_{0.2}O_{1.9}$ (JCPDS file No. 01-075-0175). At higher amounts of doped yttrium, the pattern has weaker peaks and the parameters of the unit cells are reduced from 5.4100 to 5.40400 Å.

The FE-SEM micrographs of $Ce_{1-x}Y_xO_{2-\delta}$ membranes fabricated with various amounts of yttrium are shown in Fig. 2. The inset diagrams of high magnification images show the distinct grain morphology of each membrane. As the content of yttrium dopant increased, the grain size appeared to be positively finer and more angular under the same sintering conditions. The average size of the grains, from 10 randomly selected grains for each $Ce_{1-x}Y_xO_{2-\delta}$, were 0.77, 0.49, 0.39, and 0.23 μm , respectively. Yttrium doping on the ceria greatly suppressed the grain growth during sintering. The tendency of decreasing grain size with yttrium doping content was also investigated by Ji-Guang Li *et al.*⁴⁾ This variation in grain size could influence porosity and active sites of the grain boundary. The low magnification images of the membrane surface show a porous morphology of the membranes. The pore size and pore volume values measured by the BET

technique are given in Table 1. The $Ce_{0.8}Y_{0.2}O_{2-\delta}$ membrane had the largest pore diameter and pore volume among the doped membranes.

The polarization resistance of the electrode was in inverse proportion to the quantity of triple-phase-boundary.⁵⁾ According to the triple-phase-boundary diffusion mechanism, hydrogen diffusion permeability through the membrane was predicted to be improved as yttrium content increased because of the increasing active site of triple phase boundary arising from the grain size reduction as shown in Fig. 2.

The result of the hydrogen permeation test is shown in Fig. 3. The permeability increased as the yttrium content increased. The $Ce_{0.8}Y_{0.2}O_{1.9}$ membrane had the highest flux and the value at the room temperature was $8.13 \times 10^{-6} \text{ mol/m}^2 \text{ s Pa}$. However, this value is remarkably large compared to the membranes with lower yttrium content. This result is related to the effect of the large pore size distribution and incompletely sintered pellets caused by small grains.

The hydrogen flux of all the membranes displayed a tendency to decrease with an increasing temperature. These membranes followed the Knudsen diffusion mechanism. CO gas permeability was measured to compare and evaluate the hydrogen selectivity of the membranes. The perm-selectivity of the H_2/CO gas was from 4.5 to 5.0 depending on the temperatures.

The electric conductivity in Fig. 4 shows the proportionate

Table 1. Pore Size and Pore Volume of $Ce_{1-x}Y_xO_{2-\delta}$ Membranes According to Yttrium Content

X (yttrium content) [mol]	Average Pore Diameter [nm]	Total Pore Volume [$\text{cm}^3 \text{ g}^{-1}$]
0	49.7	4.12×10^{-3}
0.05	25.6	4.02×10^{-3}
0.1	26.3	3.51×10^{-3}
0.2	38.4	4.70×10^{-3}

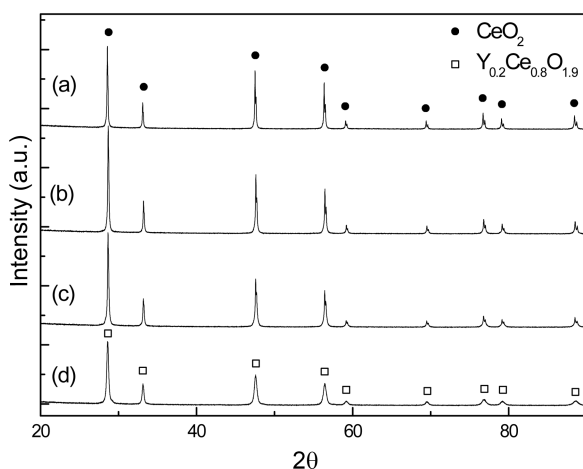


Fig. 1. XRD patterns of synthesized $Ce_{1-x}Y_xO_{2-\delta}$ powders calcined at 900°C according to yttrium content (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.2$ mol.

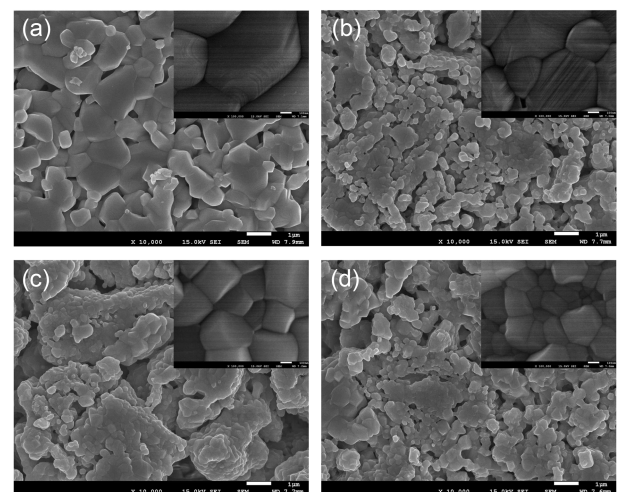


Fig. 2. FE-SEM micrographs of $Ce_{1-x}Y_xO_{2-\delta}$ membranes (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.2$ mol sintered at 1300°C for 6 h.

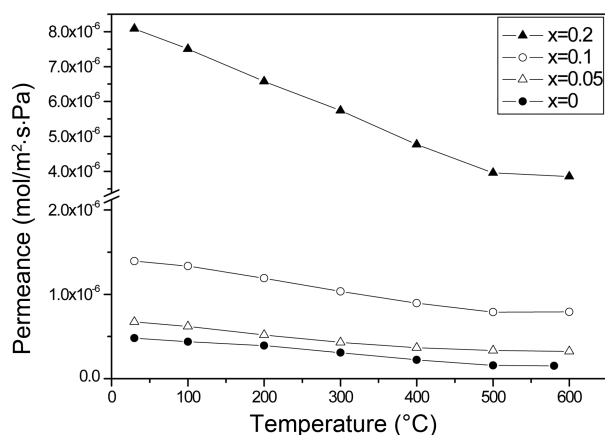


Fig. 3. Hydrogen permeance of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ membranes according to yttrium content.

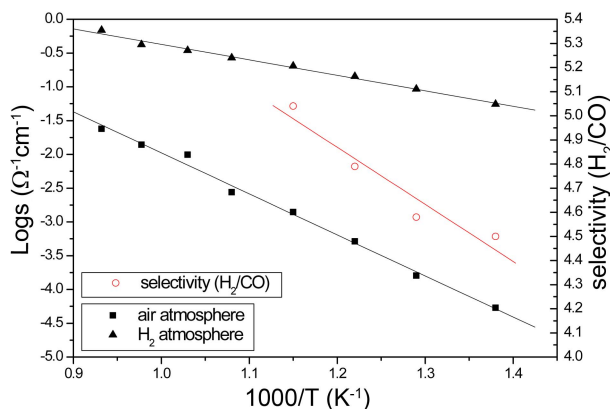


Fig. 4. Electrical conductivity and perm-selectivity of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ membrane.

relationship with H_2 gas selectivity. H_2 selectivity was improved as the temperatures rose. Thus, these phenomena could relate to increased electric conductivity data depending on the temperature. Moreover, the value of conductivity in the reduction H_2 atmosphere was larger than the values in the oxidation atmosphere.

4. Conclusions

$\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ membranes were fabricated as hydrogen permeation membranes and characterized according to the doped yttrium content. With higher yttrium content, there was reduced grain growth which was related to an increased value of hydrogen permeation. The hydrogen permeance of CeO_2 was $5.12 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ and of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ it was $8.13 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ at 28°C . Yttrium doping on a ceria matrix suppressed the grain growth and influenced the flux of the gas permeation.

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REFERENCES

1. A. K. Jain, N. K. Acharya, V. Kulshreshtha, K. Awasthi, M. Singh, and Y. K. Vijay, "Study of Hydrogen Transport through Porous Aluminum and Composite Membranes," *Int. J. Hydrogen Energy*, **33** [1] 346-49 (2008).
2. M. Heidari, A. Zamaniyan, A. Safe Kordi, E. G. Babakhani, and M. Amanipour, "Effect of Sintering Temperature on Microstructure and Hydrogen Permeation Properties of Perovskite Membrane," *J. Mater. Sci. Technol.*, **29** [2] 137-41 (2013).
3. S. M. Choi, S. M. Jeong, W. S. Seo, and H. L. Lee, "Single Cell Test for Proton Conducting Oxide Electrolytes Based on the $\text{BaCe}_{0.9}\text{M}_{0.1}\text{O}_{3-\delta}$ ($\text{M} = \text{La}, \text{Al}$) System (in Korean)," *J. Kor. Ceram. Soc.*, **45** [11] 694-700 (2008).
4. J. G. Li, Y. Wang, T. Ikegami, and T. Ishigaki, "Densification below 1000°C and Grain Growth Behaviors of Yttria Doped Ceria Ceramics," *Solid State Ionics*, **197** [21-26] 951-54 (2008).
5. N. U. Cho, S. C. Hwang, and I. S. Lee, "Single Cell Stacked Planar Type SOFC Assembled Using a Ag-Current Collector (in Korean)," *J. Kor. Ceram. Soc.*, **44** [12] 720-26 (2007).