Preparation and Permeation of $La_2Ce_2O_7$ Membrane

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ABSTRACT

$La_2Ce_2O_7$ and CeO_2 membranes were fabricated from the corresponding powders derived from sol-gel process with polyvinyl alcohol binder. These powders and membranes were characterized by XRD, BET, and FE-SEM analysis. Hydrogen and CO gas permeation experiments were performed using Sievert's type equipment. Both fluxes on these membranes were found to decrease with increase of the temperature. This phenomenon was followed by the surface and Knudsen diffusion mechanism. The hydrogen permeability of the $La_2Ce_2O_7$ membrane was found to be 7.27×10^{-5} mol/m^{2}sPa, with perm-selectivity of 7.24 at 303 K.

Key words : $La_2Ce_2O_7$ and CeO_2 membranes, Hydrogen permeability, Perm-selectivity

1. Introduction

Membrane-based separation is used on polymeric, metallic, ceramic, and mixed membrane matrices.[1,2] Metallic membranes, including metal-based membranes and alloys, are used because of their high hydrogen permeability and selectivity. These materials have a basic problem of hydrogen embrittlement due to the thermal instability; the high cost and strong interaction between metal and hydrogen are important disadvantages of these materials. However, multi-component ceramic membranes have merits such as resistance to acids and chemical stability under high operating temperature.

In accordance with the type of materials, hydrogen separation membranes can be classified as polymeric, porous, dense metal, and proton conducting membranes. Proton conducting membranes are classified into dense ceramic and ceramic metal membranes. These membranes are included in perovskite and non-perovskite structures. One especially well-known non-perovskite structured membrane is the fluorite membrane.[3,4] The fluorite structure indicates good chemical stability compared to that of proton conductors, which are called perovskite conductors; this composite oxide has been used in thermal barrier coating.

In order to improve the stability of Ce-based membranes, La_2O_3, due to its own dispersion activity and stability, is an effective additive for catalytic support or as the primary material itself. Several approaches have been applied for the synthesis of CeO_2 with La_2O_3 material.[5,6] These materials have been prepared by homogeneous deposition, co-precipitation, hydrothermal synthesis, and sol-gel process.

Among the preparation methods for powder precursors of several kinds of ceramic membranes, the advantages of the sol-gel method are that it can fabricate the solid precursor powder with good control of the stoichiometry and with various multi-component materials at room temperature. A solid network can be controlled from the liquid phase at the molecular level from the early stages to the final solid product.

In this paper, we will discuss issues regarding the simple preparation of powder precursors (CeO_2 and $La_2Ce_2O_7$ oxide) and the fabrication of $La_2Ce_2O_7$ membranes using a binding agent (PVA) by a routine method. The main purpose of this study is to keep the property of perm-selectivity and maintain the thermo-chemical stability of the membrane even when it passes through the permeating gas.

2. Experimental Procedure

Lanthanum (III) nitrate hexa-hydrate ($La(NO_3)_3 \cdot 6H_2O$) (CAS No. 10277-73-7, Aldrich) and Cerium (III) nitrate hexa-hydrate ($Ce(NO_3)_3 \cdot 6H_2O$) (CAS No.10294-41-4, Aldrich) with HNO_3 were refluxed overnight in distilled water solvent. The obtained solution was treated at 393 K for 24 h to obtain gel powder; sample was retreated at 773 and 1173 K. It was finally sintered at 1473 K under air condition. For comparison, ceria powder was also synthesized using the sol-gel method. These powders with 10 wt% of polyvinyl alcohol (PVA) binder were mixed and pressed by uniaxial pressing at 100 bars to obtain a membrane with a diameter of 14.5 m and a thickness of 2 mm. This membrane was retreated at 1173 K under Ar condition.

The phase composition of the crystal structure was determined by X-ray diffraction (Bruker D8, Focus, Cuκα, 40 kV, 40 mA). Microstructures of the powder and the membrane were observed using a Field Emission-Scanning Electron Microscope (JEOL-JMS 7500F). Pore size distribution was

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analyzed by Barrett-Joyner-Halenda method; the Brunner-Emmett-Teller (BELSORP-max, mini II) method was used for the adsorption-desorption of N_2 gas to determine the surface area (m^2/g). Hydrogen and CO gas permeation measurements were performed at elevated temperatures.[4] Our own device consisted of a pressure controller, mass flow controller (MFC), and stainless steel 1.4-inch cell equipment, all of which was constructed to withstand high temperature.

3. Results and Discussion

Both the CeO_2 and $La_2Ce_2O_7$ powders were synthesized by sol-gel process. After heat-treatment, the materials were found to have remarkable crystalline structures, as shown in the upper parts of the XRD patterns of the designated samples in each diagram in Fig. 1. The shape and position did not change except higher and sharp intensity with increasing temperatures of 393, 773, and 1173 K for the case of $La_2Ce_2O_7$, indicating crystallite growth. The final material was obtained as a cubic fluorite structure with space group Fm3m; our data agreed with the data of the other group.[7] In the case of the CeO_2 powders (JCPDS file No. 01-089-8436), the diffraction peaks were indexed to have a cubic structure (a = b = c = 5.403 nm). No other peaks attributable to individual oxides were detected, even with different heat-treatments. The XRD pattern of the $La_2Ce_2O_7$ was similar to that of the CeO_2, with a small shift of the lattice parameter. Furthermore, the peaks of the powders were unaffected by the increasing heating temperatures, which means that the $La_2Ce_2O_7$ powders have high phase stability.

FE-SEM images of the CeO_2 and $La_2Ce_2O_7$ powders prepared after sintering at 1173 K are shown in Fig. 2. The CeO_2 and $La_2Ce_2O_7$ powders showed worm shaped surfaces without clustering; however, the powders had smooth round edges. In agreement with the results of XRD, the CeO_2 and the slightly larger sized $La_2Ce_2O_7$ powder have similar morphology and very fine grains of nano-scale.

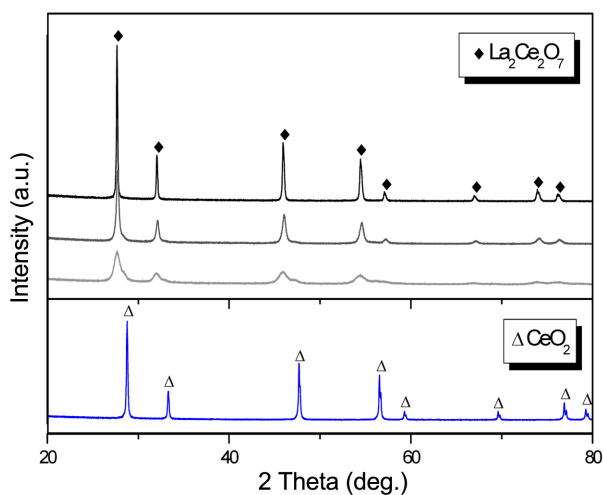To analyze the morphology of the $La_2Ce_2O_7$ membrane in more detail, the results of BET adsorption and desorption were measured only for this membrane, with results shown in Fig. 3. These results were compiled using a type IV hysteresis loop isotherm, as defined by the IUPAC (International Union of Pure and Applied Chemistry). Measurement
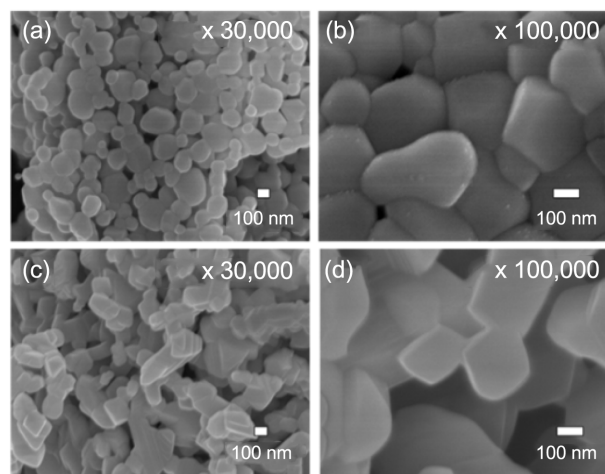

Fig. 2. FE-SEM images of (a), (b) CeO_2 and (c), (d) $La_2Ce_2O_7$ powders.
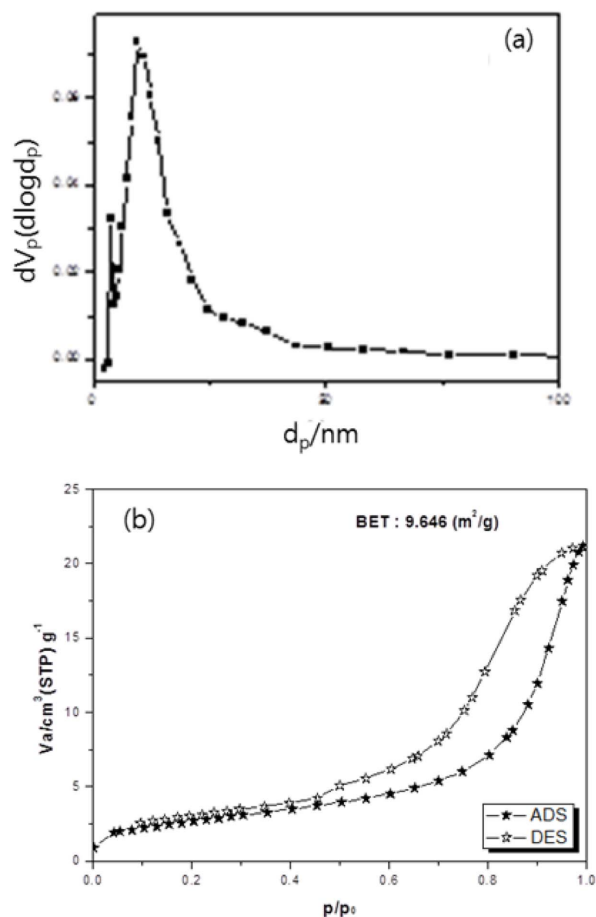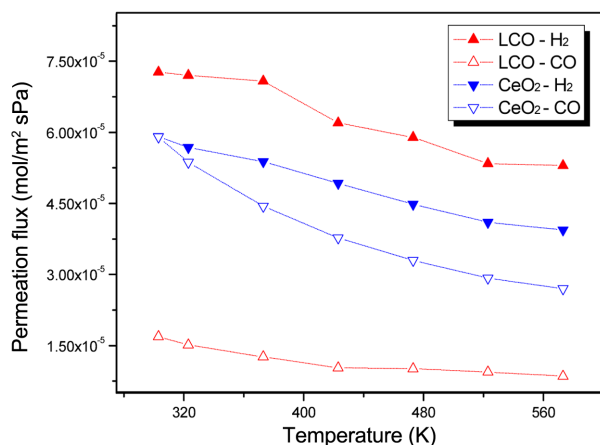

Fig. 3. (a) Pore size distribution and (b) N_2 adsorption-desorption isotherm of $La_2Ce_2O_7$ membrane.

Fig. 1. XRD patterns of CeO_2 and $La_2Ce_2O_7$ powders.

Table 1. Pore Size Distribution Data

	Pore volume (cm^3/g)
1. Total pore volume	0.032665
2. Micropore volume	0.0034123 (10.45%)
3. Mesopore volume	0.0292527 (89.55%)

Fig. 4. H_2 vs. CO gas permeation values of $La_2Ce_2O_7$ and CeO_2 membranes.

indicates a meso-porous structure that demonstrates the existence of ink-bottle like pores, each having a narrow entrance and a large cavity. The corresponding BJH pore size distributions for this membrane are listed on Table 1; the membrane is mainly composed of meso-pores. It has a narrow average pore diameter of about 10 nm with 9.65 m^2/g of surface area.

Gas permeation tests for the CeO_2 and $La_2Ce_2O_7$ membranes were attempted for H_2 and CO gases with changing temperatures; results are shown in Fig. 4. The hydrogen and CO permeation fluxes of both the membranes are shown to have a decreasing tendency with increasing temperatures. The formation of meso-pores in the membranes was referred to following the surface and Knudsen diffusion, which is the decreasing tendency of the permeation fluxes as temperature increases.[4]

The perm-selectivity of H_2 and that of CO were compared and this value of the $La_2Ce_2O_7$ membrane at 303 K was found to be the best. This value was better than that of the CeO_2 membrane because it formed a meso-porous membrane with bigger pore size, as mentioned regarding the FE-SEM results. The highest obtained value for this membrane was 7.27×10^{-5} mol/m^2sPa at 303 K. The reaction enthalpy ($\Delta H°$), obtained from the fluxes of the gas permeation, was calculated from the slope of Arrhenius's plot and found to be -4.30 kJ/mol. More systematic study of this mechanism is needed, with an emphasis on controlling the porosity as well as the characteristics that relate to the ion conducting mechanism.

FE-SEM images of $La_2Ce_2O_7$ (a), (b) were also taken before the H_2 gas permeation test; (c), (d) are images after
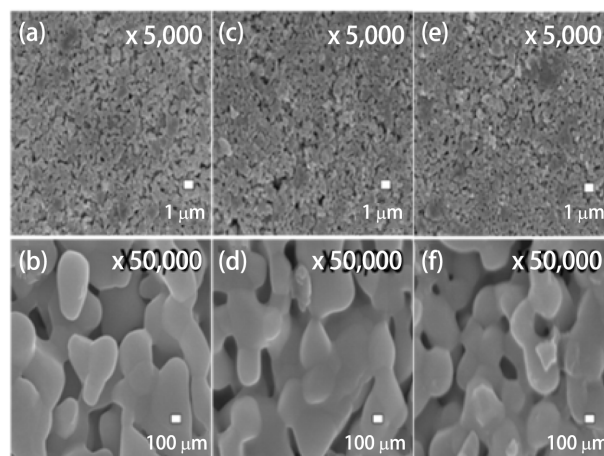
Fig. 5. FE-SEM images of membranes obtained before (a), (b) and after (c), (d) hydrogen testing; (e), (f) are images taken after the CO permeation tests.

the H_2 gas permeation test as shown in Fig. 5. Also (e), (f) were taken after the test for the CeO_2 membrane. No change was observed and both membranes were thermo-chemically stable during these tests.

4. Conclusions

CeO_2 and $La_2Ce_2O_7$ powders with nano-crystalline structure have been successfully prepared. These membranes, which use a binder, were fabricated by routine powder method and evaluated by gas permeation tests. As the temperature increased, these membranes responded with Knudsen and surface diffusion. Selectivity of permeation via H_2/CO gases was the highest at 303 K. Both membranes maintained thermo-chemical stability during and after the gas permeation tests.

Acknowledgments

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