Preparation and Permeation of La$_2$Ce$_2$O$_7$ Membrane

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ABSTRACT

La$_3$Ce$_2$O$_9$ 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$_3$Ce$_2$O$_9$ membrane was found to be $7.27 \times 10^{-5}$ mol/m$^2$sPa, with perm-selectivity of 72.4 at 303 K.

Key words : La$_3$Ce$_2$O$_9$, 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 mixed 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$_3$O$_9$ 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$_3$O$_9$ 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$_3$Ce$_2$O$_7$ oxide) and the fabrication of La$_3$Ce$_2$O$_9$ 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$_3$)$_3$·6H$_2$O) (CAS No. 10277-73-7, Aldrich) and Cerium (III) nitrate hexa-hydrate (Ce(NO$_3$)$_3$·6H$_2$O) (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, Cuka, 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...
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. 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$_2$Ce$_2$O$_7$ 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$_2$Ce$_2$O$_7$, indicating crystallite growth. The final material was obtained as a cubic fluorite structure with space group Fm$ar{3}$m; our data agreed with the data of the other group. 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$_2$Ce$_2$O$_7$ 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$_2$Ce$_2$O$_7$ powders have high phase stability.

FE-SEM images of the CeO$_2$ and La$_2$Ce$_2$O$_7$ powders prepared after sintering at 1173 K are shown in Fig. 2. The CeO$_2$ and La$_2$Ce$_2$O$_7$ 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$_2$Ce$_2$O$_7$ powder have similar morphology and very fine grains of nano-scale.

To analyze the morphology of the La$_2$Ce$_2$O$_7$ 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
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 in Table 1; the membrane is mainly composed of meso-pores. It has a narrow average pore diameter of about 10 nm with 9.65 m²/g of surface area.

Gas permeation tests for the CeO₂ and La₂Ce₂O₇ membranes were attempted for H₂ 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.

The perm-selectivity of H₂ and that of CO were compared and this value of the La₂Ce₂O₇ membrane at 303 K was found to be the best. This value was better than that of the CeO₂ 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/m²sPa at 303 K. The reaction enthalpy (ΔH°), 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 La₂Ce₂O₇ (a), (b) were also taken before the H₂ gas permeation test; (c), (d) are images after the H₂ gas permeation test as shown in Fig. 5. Also (e), (f) were taken after the test for the CeO₂ membrane. No change was observed and both membranes were thermo-chemically stable during these tests.

4. Conclusions

CeO₂ and La₂Ce₂O₇ 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 H₂/CO gases was the highest at 303 K. Both membranes maintained thermo-chemical stability during and after the gas permeation tests.

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REFERENCES

