Evaluations of hydrogen permeation on Al_2O_3-ITO composite membrane by hot press sintering (HPS)

K.K. Kim, T.W. Hong*
Department of Material Science and Engineering/Research Center of Sustainable Eco-Devices and Materials(ReSEM), Chungju National University, Chungju-si, Chungbuk, Republic Korea
* twhong@cjnu.ac.kr

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1. Introduction

The production of high purity hydrogen is rather complex. The most promising method for high purity hydrogen production makes use of membrane separation to separate hydrogen from other gases, such as in a methanol reformer, or from syngas produced during coal gasification [1-6].

However, the commercialization stage has not yet been reached due to the high production cost and storage problems. The major research fields of hydrogen, which are the electrolysis method, photoelectric/chemical method, thermo-chemical method and photo-biological method, are kown to be able to produce hydrogen [7]. As for the methods to separate only hydrogen form gas, including hydrogen, the methods of separation membranes are common. In particular, a highly efficient method to separate hydrogen is to use a separation membrane. This method has cost-competitive power owing to low energy consumption, low investment cost, and easy operation. The separation membrane method is divided largely into metal separation, polymer, and ceramic membrane [8].

On the other hand, Al_2O_3, one of the ceramic materials, are synthesized by a sol-gel process that is a significant technique making use of controlled hydrolysis of alkoxide, condensation and polymerization reaction. The Al_2O_3 synthesized by way of the sol-gel process is a widely used ceramic material as a catalyst or catalyst support because it has specific properties such as high surface area, durability, chemical and thermal stability [9, 10].

Al_2O_3-based ceramic membrane could separate hydrogen in previous study [11]. This paper was introduced evaluations and fabrications of hydrogen permeation on Al_2O_3-Co/Ni membrane by hot press sintering method. Al_2O_3 ceramic powder was synthesized by sol-gel process. This composite membrane was calculated good hydrogen permeability and developed mechanical properties.

The hydrogen permeation flux for the Al_2O_3-20wt%Co and Al_2O_3-20wt%Ni membranes obtained 2.36 and 0.374 $mol \cdot m^{-2} \cdot s^{-1}$ at 473 K, respectively. It was better than for the Ni/ceramic membrane (2.5 x 10^{-3} $mol \cdot m^{-2} \cdot s^{-1}$ at 873 K), $Pd_{80}Ag_{20}$ alloy supported on porous alumina (0.25 $mol \cdot m^{-2} \cdot s^{-1}$ at 773 K) and $Pd_{95}Ag_5$ alloy supported on ceramic materials consisted of a, γ-Al_2O_3 and ZrO_2 (0.34 $mol \cdot m^{-2} \cdot s^{-1}$ at 673 K).

The material of indium tin oxide (ITO) had known attractive electrical ceramic and using invisible electrode in display application. Therefore ITO coating layer will be good effect to hydrogen dissociation on membrane surface. Ames Kulprathipanja's study was fabricated ITO/Al_2O_3 nanoparticle catalysts. This material used in methanol reforming application [12].

In this work, Al_2O_3-ITO composite membrane would fabricate using hot press sintering process. This membrane would evaluate of hydrogen permeability and selectivity. ITO material could be catalyst to dissociate hydrogen molecules. Al_2O_3-ITO composite membrane could be a good hydrogen separation membrane.

2. Experimental procedure

2.1 Synthesis of nano powders (Al_2O_3 and ITO).

The precursor used in this experiment was aluminum isopropoxide ($Al(OC_3H_7)_3$) (98+%, Aldrich). The aluminum precursor was added to distilled water with a molar ratio of Al:H_2O ¼ 1:50 refluxing at 353 K. Then, HNO_3 as an acid catalyst was added for peptization to obtain heterogeneous sol and stirred overnight to obtain a stable sol solution. The boehmite powder was obtained by drying completed sol at 423 K for 24 h. The obtained boehmite powder

was pre-heat treated at 773 K, then was converted to γ-Al_2O_3 through phase transformation.
ITO nanoparticles were prepared by a low temperature synthetic method. Detailed process is described in the Hong's study [13].

2.2 Fabrication of Al_2O_3-ITO membrane.

Synthesized Al_2O_3 and ITO powders were mixed into nano-sized particles using a high energy mill (Fitsch, TH-1080). After zirconia balls and Al_2O_3, ITO powders were loaded into a zirconia container at a ratio of 10:1, it was milled for one hour, th. For the Al_2O_3-30wt.% ITO composite material powder, a sample disk shape was obtained using the double-axis press with a compressive pressure of 40MPa. Isobaric compressive forming was conducted using a cold isostatic pressure (CIP) of approximately 15MPa, compression holding time was 10 seconds. The disk-shaped composite membrane was prepared using the hot press sintering process with Al_2O_3-30wt.% ITO composite material. Sintering of the composite membrane was conducted while applying approximately 808MPa of pressure in a single axis direction within a vacuum chamber atmosphere that was maintained at 1473 K for 2 hours. The thickness of Al_2O_3-30wt.% ITO membrane was 760μm.

2.3 Characterization of Al_2O_3-ITO membrane.

Changes of in the shape and structure for Al_2O_3, ITO, Al_2O_3-ITO powder and Al_2O_3-ITO composite membrane were investigated through scanning electron microscopy (SEM, FEI Co, quanta- 400) and x-ray diffraction analysis (D8 Advance, Bruker AXS Co.). Understanding the correlation for changing a specific surface area and hydrogen permeation rate was attempted through BET (BEL sorp mini II, BEL Co.) analysis. XRD analysis was conducted at up to 10~90° at a scanning speed of 0.03 deg/min. using the Cu Ka ray of 1.54Å. For BET, the specific surface areas of Al_2O_3/ Al_2O_3-ITO membranes were measured using nitrogen adsorption.

2.4 Measuring of hydrogen permeability on Al_2O_3-ITO membrane.

Sievert's type hydrogen permeability equipment was used to measure the hydrogen permeability of Al_2O_3-ITO composite membrane. The Al_2O_3-ITO composite membrane prepared through HPS process was loaded into the cell, and was checked for air leakages. The permeation cell was installed within the heating furnace for temperature control, and the temperature was elevated under a nitrogen atmosphere. To eliminate the oxidation layer that might exist on the sample surface, it was treated for activation under a hydrogen atmosphere for 1 hour. To avoid cracking the hydrogen separation membrane due to thermal shock, the temperature elevation speed was lowered to less than 5K per minutes. Also, the cell equipped with the separation membrane was heated. The hydrogen permeability of Al_2O_3-ITO composite membrane was measured RT, 373, 473, 573 and 673K under 0.1, 0.2 and 0.3MPa hydrogen atmosphere, respectively.

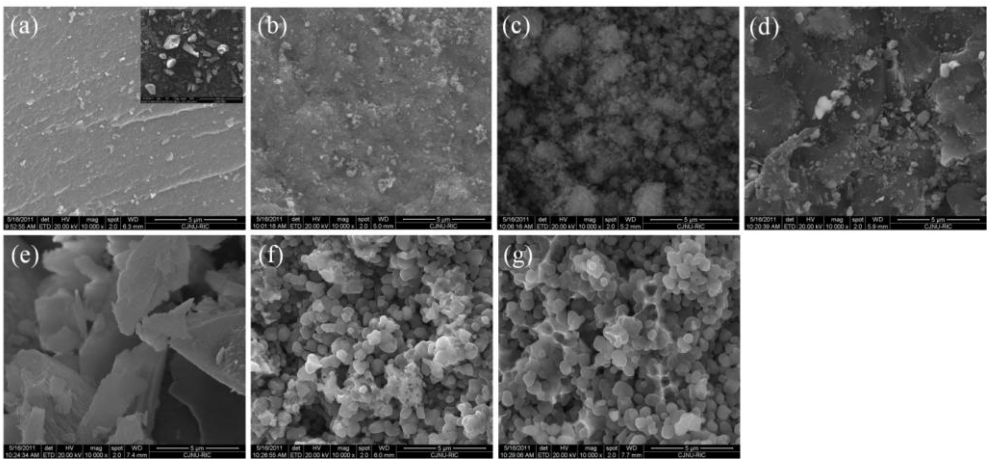

Fig.1 The images of (a) Al_2O_3, (b) ITO, (c) Al_2O_3-ITO, (d) surface and (e) cross-section on Al_2O_3 membrane, (f) surface and (g) cross-section on Al_2O_3-ITO composite membrane.

3. Results and discussion.

Fig. 1 shows a SEM images on synthesized Al_2O_3, ITO, milled Al_2O_3-ITO composite powder and membrane of Al_2O_3 and Al_2O_3-ITO. The synthesized Al_2O_3 powder had a large lump particles and ITO powder was made up nanoparticles. The morphologies of Al_2O_3 were to be seen like fragments and this particle was magnified ten thousand times. This surface came in sight of wave patterns. In this situation, Al_2O_3 powder was not enough sintering, 723K was not clearly temperature to find γ-Al_2O_3 phases. This result was similar in XRD results on (a) peak. The ITO particles were consist of 10~30nm. In fig. 1, the (c) image show milled for 1hour Al_2O_3-ITO powder. The particle sizes of Al_2O_3 were decrease because of grinding effect and ITO particle size was aggregation which increased by high energy milling. The (d) and (e) images were Al_2O_3 after HPS process. While the surface of Al_2O_3 membrane exposed dense morphology, cross-section seemed as particles overlap with each other. The (f) and (e) images show a sintered Al_2O_3-ITO composite membrane. This membrane had very small size of pore and sintered particles, this particle size was to measure 0.3~1.5μm. This membrane morphologies show likely on surface and cross-section.

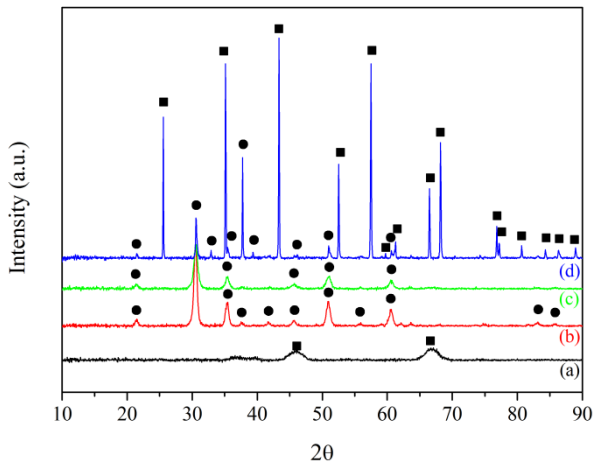

Fig. 2 Results of XRD patterns on powder of (a) Al_2O_3, (b) ITO, (c) Al_2O_3-ITO and membrane of (d) Al_2O_3-ITO.

The results of XRD analysis could show in Fig. 1. The (a) pattern did not detect crystalline phase and it looked for broad peaks such as amorphous phase by to low heat treat temperature. The (b) pattern was revealed ITO polycrystalline phase and it has low x-ray intensity by nano structure. The (c) pattern was show traditional milling x-ray peaks such as too low intensity and somewhat broad peaks. The Al_2O_3-ITO composite membrane was clearly sintering through high x-ray intense and peaks shape was very sharp. It could look for Fig. 2 (d).

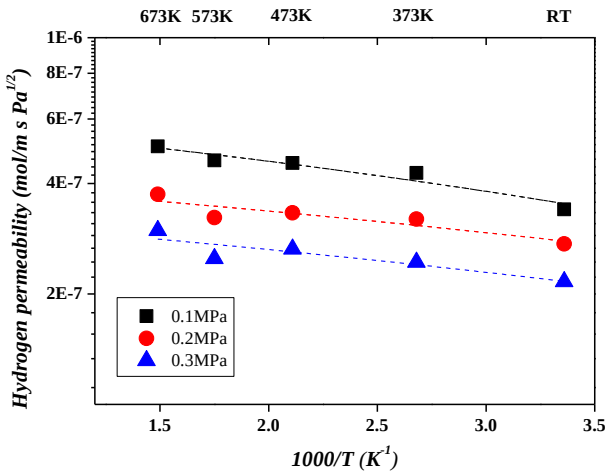

Fig. 3 Results of hydrogen permeability on Al_2O_3-ITO composite membrane.

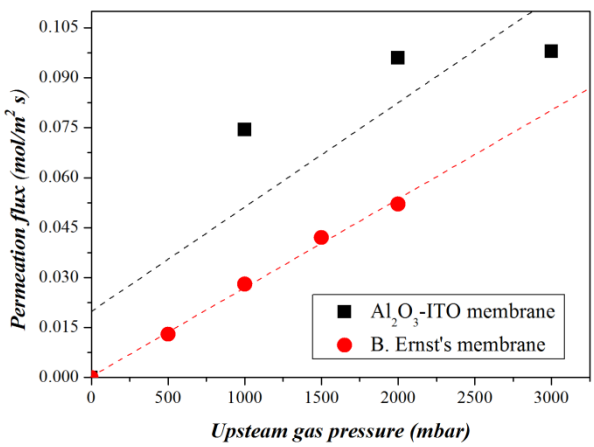

Fig. 4 Hydrogen flux through the Al_2O_3-ITO composite membrane as a function of trans-pressure on upsteam part at room temperature. [15]

Fig. 3 shows a result of hydrogen permeability on Al_2O_3-ITO composite membrane by HPS process.

This membrane was calculated as 3.40, 4.28, 4.55, 4.63 and 5.05x10^{-7} (under H_2 0.1MPa), 2.74, 3.20, 3.33, 3.23 and 3.74x10^{-7} (under H_2 0.2MPa), and 2.16, 2.44, 2.65, 2.50 and 2.98x10^{-7} (under H_2 0.3MPa) mol/m·s·$Pa^{1/2}$, respectively. The Al_2O_3-ITO composite membrane was calculated better value than Pd-Ag amorphous membrane [14]. In Y. Shimpo study, Pd-Ag membrane was fabricated by arc melting process and it was amorphous and dense metallic membrane. This membrane was calculated 1.6 and 3.0$10^{-8}$ mol/m·s·$Pa^{1/2}$, at temperatures of 573 and 673K under a hydrogen atmosphere of 0.2MPa [15]. Commercial dense metallic membrane has been Pd-Ag amorphous membrane. The transport mechanism of hydrogen through dense metallic membranes is solution diffusion. Therefore, hydrogen permeation of Pd-Ag membrane depends on solubility and diffusivity, hydrogen permeability is proportional increasing temperature and hydrogen pressure [14]. However, Al_2O_3-ITO composite membrane did not measure like to dense metallic membrane and it directly has nothing to do with hydrogen pressure. Increasing hydrogen pressure was interrupted hydrogen molecules sorption on membrane surface because of interference effect between hydrogen molecules. Therefore, the Al_2O_3-ITO composite membrane has Knudsen diffusion mechanism as hydrogen transition. The pore size and pore volume of Al_2O_3-ITO membrane could be showing in table 1 [16].

Fig. 4 shows a hydrogen permeation flux of Al_2O_3-ITO membrane. This membrane was measured flux value better than B. Ernst's membrane. B. Ernst's membrane based on porous Al_2O_3 which had Knudsen diffusion mechanism as hydrogen transfer [17].

Table 1 Results of BET analysis on Al_2O_3 and Al_2O_3-ITO membranes.

	Al_2O_3 membrane	Al_2O_3-ITO membrane
BET surface area(m^2/g)	0.82841	1.12530
total pore volume(cm^3/g)	0.00129	0.00174
Average pore diameter(nm)	6.21590	6.20240
pore structure	mesoporous membrane	mesoporous membrane
Gas diffusion mechanism	Knudsen diffusion	Knudsen diffusion

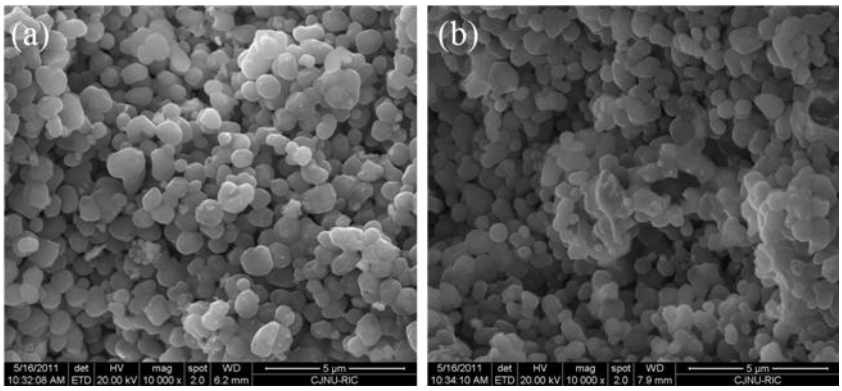

Fig. 5 The SEM images of (a) surface and (b) cross-section on Al_2O_3-ITO composite membrane after hydrogen permeation measuring.

Table 1 show a result of BET analysis on Al_2O_3 and Al_2O_3-ITO membranes. These membranes were fabricated same HPS process and BET results were measured very similar pore volume and pore diameter. These membranes were shown hydrogen separation based on Knudsen diffusion. The hydrogen permeability of Al_2O_3 and Al_2O_3-ITO membrane were calculated to similar behavior because of same hydrogen permeation mechanism, total pore volume and average pore diameter.

The diffusivity for Knudsen diffusion is obtained from the self-diffusion coefficient derived from the kinetics theory of gases.

$$D_{KA}=4850 \cdot d_{pore} \cdot (T/M_A)^{1/2} \qquad (1)$$

Where d_{pore} has units of cm, M_A has units of g/mol and temperature T has units of K. Knudsen diffusivity D_{KA} is thus dependent on the pore diameter, species A molecular weight and temperature.

The Knudsen diffusion coefficient of Al_2O_3-ITO membrane was calculated to 7.37 x 10^{13}, 8.25 x 10^{13}, 9.29 x 10^{13}, 1.02 x 10^{14} and 1.11 x 10^{14} $cm \cdot K^{1/2} \cdot g^{1/2} \cdot mol^{-1/2}$ at RT, 373, 473, 573 and 673K using equation (1) [18].

Fig. 5 show SEM images of Al_2O_3-ITO membrane after hydrogen permeation test. These images were showed similar surface and cross section morphology, sintered particles. After hydrogen permeation test, hydrogen molecules were separated through grain boundary and pore [19]. A repetitive pattern of behavior hydrogen transition was happened on between particles. Therefore, Al_2O_3-ITO membrane could not look like overlap and combination form between particles.

4. Conclusion

This work was conducted to investigate the hydrogen permeation characteristics of Al_2O_3-ITO membrane. The Al_2O_3-ITO membrane was evaluated good hydrogen permeability and flux rate than Pd-Ag amorphous [14] and Al_2O_3 porous membrane [17], which depended on Knudsen diffusion coefficient. This membrane has high mechanical properties by HPS process. The diffusion coefficient of Al_2O_3-ITO membrane was calculated to 7.37 x 10^{13}, 1.11 x 10^{14} $cm \cdot K^{1/2} \cdot g^{1/2} \cdot mol^{-1/2}$, respectively, at RT and 673K. This membrane is going to study about relationships between ITO additive and hydrogen permeation. This result will be reported in the near future.

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