

Hydrogen Permeation of ZnO-SiC Membranes Encapsulated with SiO₂

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ABSTRACT

ZnO and SiC powders were fabricated to make crack-free composite membranes. Parts of some membranes were re-treated with an encapsulation process. These membranes were characterized by XRD, BET, and FE-SEM analyzes. The hydrogen permeation fluxes of the encapsulated and heat-treated membranes after encapsulation were observed using Sievert's type equipment. Values were measured at 1 bar with increasing temperatures. The obtained values of encapsulated and further heat-treated membrane at 298 K were 4.20×10^{-6} and 8.64×10^{-5} mol/m²sPa, respectively.

Key words : Composite membrane, Encapsulation process, Hydrogen permeation

1. Introduction

SiC has a limitation as an inorganic gas separation membrane because of its mechanical hardness and porosity. To solve these problems, SiC-based composite membranes can be used by selecting a variety of materials and employing multiple mixing.^{1,2)} A suitable selection of materials can ensure that the composite membrane will have long a lifetime while maintaining high gas permeation flux and permselectivity. The crystallites, the surface morphology, and the other properties of the composite membrane can be dependent on synthetic process.^{3,4)}

A novel encapsulation process is employed using a modified sol-gel process to control the porosity of the sintered composite membrane. Membrane is first functionalized by 3-Aminopropyltrimethoysilane (APTMS) and then re-treated with silica sol obtained from hydrolysis and polycondensation. APTMS was used as a sol additive surfactant. The sol additive from the liquid phase will promote densification and consolidation of the surface coating to fill only porous membrane. Surface modification will provide a densification of the surface as well as interlayers between the nano-sized composites. In a previous study, it was suggested that membrane separation performance can be improved by an additional operation such as a mixing of additives or a modification of the synthetic conditions, both of which might have the effect of changing pores of membrane.^{6,7)}

To improve the mechanical strength and control the micro-structure of the composite membrane, we fabricated an SiC-based ZnO composite membrane with heat-treat-

ment at 1300°C as a untreated sample. Then, parts of the membrane were re-treated with an encapsulation process; the other parts were further heat-treated after encapsulation. These composite membranes, encapsulated and encapsulated with further heat-treatment at 600°C, were characterized by XRD, FE-SEM, and BET analyses as well as with hydrogen permeation experiments.

2. Experimental Procedure

2.1. Membrane fabrication

Disc shaped membranes were prepared by mixing a 4 : 1 ratio of β-SiC (200 - 400 mesh) (CAS No.409-21-2, Aldrich) and ZnO powder (99 - 100.5%, CAS No. 1314-13-2, Aldrich) including 9 wt% of phenolic resin. By uniaxial pressing at 200 bar, mixed powders were pressed into a mold with a diameter of 14.5 mm and a thickness of 2 mm. The molded membrane was sintered at 1300°C for 3 h under air.

2.2. Encapsulation of membrane with silica sol

Membrane was treated with 1.718 mmol of the 3-Aminopropyltrimethoysilane (APTMS) in 95% ethanol solvent. This membrane was dried at 105°C after washing with the solvent. This membrane was encapsulated with a solution of tetraethyl orthosilicate (TEOS, 10.56 mmol) with 15 ml of 30% ammonium hydroxide in ethanol for 3 h. The encapsulated membrane was washed again with ethanol and dried at 105°C for 12 h. This dried membrane was heat-treated at 600°C for 1 h.

2.3. Characterization of powder and membrane

The crystal structure of the ZnO-SiC membrane was measured by X-ray diffraction analysis (Bruker D8 Focus, CuKα, 40 Kv, 40 mA). The pore size distribution was determined with a Brunauer-Emmett-Teller surface analyzer (BET, BELSORP-max mini II) under the adsorption-desorp-

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tion of N₂ gas. Field Emission-Scanning Electron Microscopy (JEOL JMS 7500F) was used to observe the surface and cross section of the membrane. Hydrogen permeability was measured using our own equipment.⁶⁾ This experiment for encapsulated and heat-treated after encapsulation samples was evaluated from room temperature to 300°C under a pressure of 0.1 MPa.

3. Results and Discussion

XRD patterns of the (a) SiC and (b) ZnO powders, and (c) untreated, (d) encapsulated, and (e) heat-treated membranes after encapsulation are shown in Fig. 1. All of the

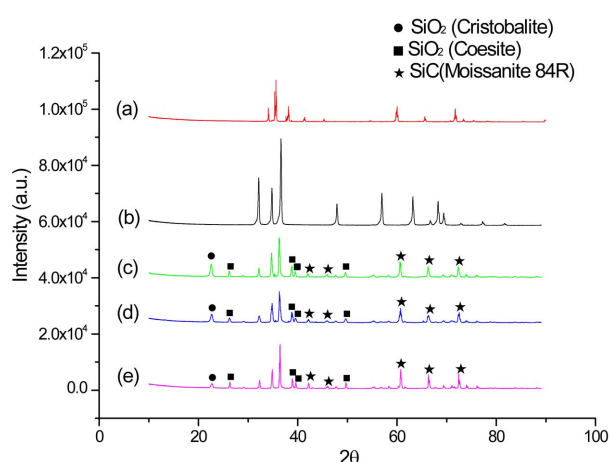


Fig. 1. XRD patterns of (a) SiC powder, (b) ZnO powder, (c) untreated, (d) encapsulated, and (e) heat-treated membranes after encapsulation.

peaks are sharp and the original ZnO (hexagonal) and SiC (moissanite 6H) peaks can be seen. The new SiO₂ peaks were generated by oxidation because the sintering process took place at 1300°C in air. One of the SiO₂ was analyzed to have a cristobalite tetragonal (JCPDS file No. 00-039-1425, a, b = 4.97, c = 6.92 nm) structure; the other peaks indicated a coesite monoclinic structure (JCPDS file No. 00-079-0445, a = 7.14, b = 12.37, c = 7.17 nm). These structures have arisen due to the sintering process and increased by the encapsulation process. The phase of the overall SiC was changed during the sintering process from moissanite 6H (JCPDS file No. 01-075-1541, a, b = 3.095, c = 15.17 nm) to 84R (JCPDS file No. 01-073-2086, a, b = 3.07, c = 210.7 nm). From Fig. 1 (d) and (e), the peaks for SiC and ZnO were significantly reduced after the encapsulation process, with no difference between the membranes.

FE-SEM images of the surface and cross section are shown in Fig. 2. In (b) and (e), the encapsulated membrane indicates a smoother and denser surface than that of the untreated membrane. Densification have arisen and developed due to SiO₂ produced by the encapsulation process. The presence of many -OH groups functionalized on the surface could prevent a strong tendency of nanoparticles to undergo agglomeration. This treatment leads to a modification and densification of the composite membrane. The domain of the heat-treated membrane, shown in (c) and (f), has shown slightly larger pores and a more irregular size than those characteristics of the encapsulated one.

To further elucidate the influence of this treatment, BET analysis was performed using the BJH (Barrett-Joyner-Halenda) method, with results shown in Fig. 3. All membranes have similar meso-porous S-shape patterns. The typical IV

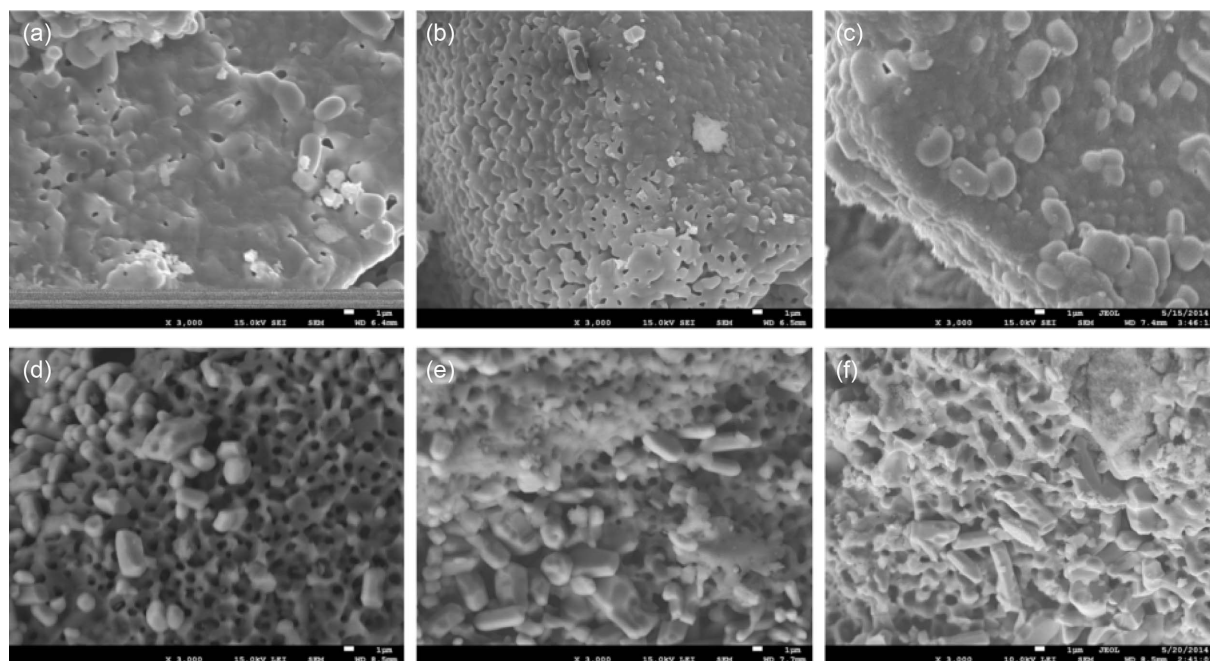


Fig. 2. The surface photographs of (a) untreated, (b) encapsulated and (c) heat-treated membranes after encapsulation and the cross sectional images of (d) untreated, (e) encapsulated and (f) heat-treated membranes after encapsulation.

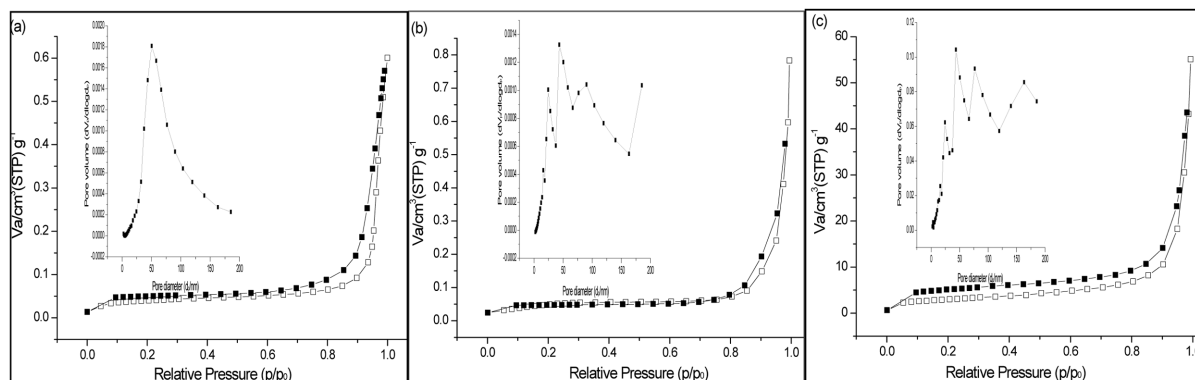


Fig. 3. Pore size distribution and N_2 adsorption-desorption isotherms of (a) untreated, (b) encapsulated, and (c) heat-treated membranes after encapsulation.

type of the N_2 hysteresis loops are defined by the IUPAC (International Union of Pure and Applied Chemistry). This is commonly associated with slit pores or voids between close-packed spherical particles.⁶⁾ Pore diameters of the corresponding membranes were about 23.28, 13.70, and 29.88 nm. As can be seen in the inset graph, the pore volume was reduced from the untreated to the encapsulated sample, and then increased for the heat-treated membrane. Therefore, the size of the pores seems to be reduced and the membrane becomes denser after encapsulation.

Figure 4 shows the values of the flux for the encapsulated and the heat-treated membranes after encapsulation through H_2 gas. In the untreated membrane, flux value was not measure because hydrogen was passing through. However, the values were found to drop with increasing temperatures both case of encapsulated and heat-treated membranes. This indicates that these membranes follow the Knudsen diffusion mechanism and the values in heat-treated one are larger than those of the simply encapsulated one. This is caused by the pore size and volume changes, which were observed by FE-SEM and BET analyses. Permeability is generally found to decrease along with decreases of the pore size and the total porosity of the membrane. The porosity was measured using the specific gravity method and were approximately 15.7, 15.3, and 23.5%. This trend was the same as those found in the BET results.

The heat changes in this process, obtained from the Arrhenius' plot, were similar and were calculated for both the encapsulated membranes and the membranes that were heat-treated after encapsulation. The values obtained were 1.21 and 1.76 J/mol, respectively. However, the porosity, density, and microstructure of these samples should be studied more to consider the gas perm-selectivity because the separation mechanism is known to depend on physical-chemical factors and several other, combined factors.

4. Conclusions

A sintered ZnO-SiC membrane was re-treated using an encapsulation process. A good quality membrane was

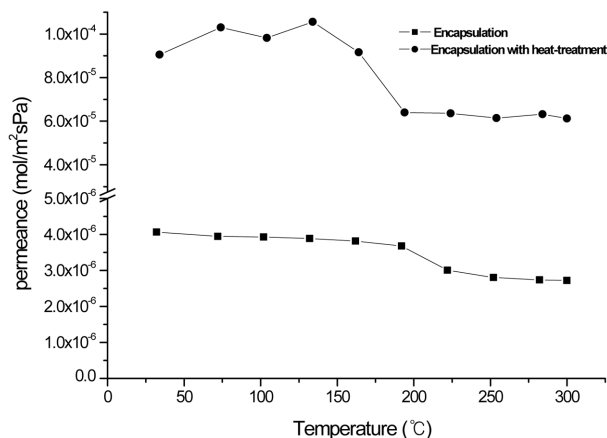


Fig. 4. Hydrogen permeance of encapsulated and heat-treated membrane after encapsulation.

obtained with no cracks even after annealing. Hydrogen permeation values of the encapsulated and further heat-treated membranes were obtained with variation of the temperature. The values of hydrogen flux between the untreated and the encapsulated membranes were different; it was not possible to measure the hydrogen flux value for the untreated membrane. In this process, values for heat change of the encapsulated and heat-treated membranes, obtained from the Arrhenius' plot, were similar. To control the membrane morphology in the inorganic network matrix and hence to enhance the permeability of the resulting composite membranes, permselectivity of gas membranes will require more study.

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REFERENCES

1. M. R. Rahimpour, H. R. Mottaghi, and M. M. Barmaki,

- “Hydrogen Production from Urea Wastewater Using a Combination of Urea Thermal Hydrolyser-desorber Loop and a Hydrogen-permselective Membrane Reactor,” *Fuel-Process. Technol.*, **91** [6] 600-12 (2010).
2. H. Suda, H. Yamauchi, Y. Uchimaru, I. Fujiwara, and K. Haraya, “Preparation and Gas Permeation Properties of Silicon Carbide-based Inorganic Membranes for Hydrogen Separation,” *Desalination*, **193** 252-55 (2006).
 3. M. A. Tshabalala, B. F. Dejene, and H. C. Swart, “Synthesis and Characterization of ZnO Nanoparticles Using Polyethyleneglycol (PEG),” *Phys. B*, **407** [10] 1668-71 (2012).
 4. S. Walter, G.D Soraru, H Bréquel, and S Enzo, “Microstructural and Mechanical Characterization of Sol Gel-derived Si-O-C Glasses,” *J. Eur. Ceram. Soc.*, **22** [13] 2389-400 (2002).
 5. G. Jakša, B. Štefane, and J. Kovač, “Influence of Different Solvents on the Morphology of APTMS-modified Silicon Surfaces,” *Appl. Surf. Sci.*, **315** 516-22 (2014).
 6. J. Park and M. Jung, “Fabrication and Characterization of CeO₂-NiO/SiC Membranes for Hydrogen Permeation,” *Defect Diffus. Forum*, **353** 143-47 (2014).
 7. R. M. Matsuda, A. V. Gubarevich, H. Wada, and O. Odawara, “Encapsulation of Solutions for Controlling Heat Transfer,” *Powder Technol.*, **268** 387-91 (2014).