

H₂ permeable nanoporous SiC membrane for an IGCC application

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Ceramic membranes having less than 1nm size pores have great potential for gas separation at high temperature due to their good thermal stability. Moreover, nanoporous silicon carbide membranes have a potential application under hydrothermal conditions at high temperatures since they are highly stable at high temperature. In this research, a nanoporous SiC membrane has been developed on a porous alumina support using a preceramic polymer. For a gradual pore size distribution, γ -Al₂O₃ interlayer was introduced in between the nanoporous SiC membrane and porous alumina support. The SiC membrane having a controlled pore size was characterized by SEM and pore size measurements. The hydrogen permeability and selectivity towards nitrogen gas of the membrane developed were 0.16×10^{-6} mole/m²·s·pa and 42.5, respectively. The nanoporous hydrogen selective SiC membrane shows a promising application in hydrogen separation from coal gasification such as in the integrated gasification combined cycle (IGCC).

Key words: SiC nanoporous membrane, Hydrogen separation, IGCC.

Introduction

In recent years there has been considerable interest in the development of inorganic membranes for the separation of hydrogen from a mixed gas stream [1-7]. Inorganic membranes can be used under conditions such as at high temperature and in reactive environments where organic membranes are not usable. Amongst the inorganic membranes for the separation of hydrogen, nanoporous inorganic membranes offer many advantages over dense palladium membranes and ion-transport membranes. Nanoporous inorganic membranes that can be used at higher pressures can be fabricated from a variety of materials and are relatively cheaper as compared to palladium membranes. Thus, there have been attempts to produce nanoporous inorganic membranes of alumina, silica, zeolites, silicon carbide, etc. However, silica and alumina membranes show instability at high temperatures specially in the presence of steam. The main advantage of silicon carbide is a combination of strength, thermal and chemical stability at high temperatures, especially under hydrothermal conditions.

For highly efficient gas separation, the control of the effective mean pore diameter is very important. As a very small pore size preferably less than 1 nm is required for hydrogen separation, the membrane must be very thin. There are relatively few reports discussing the control of the effective mean pore diameter. Recently, some researchers have tried to control the pore size by a multi-layer

composite structured membrane and pyrolysis of polymer precursors. The derived microstructure and chemical compositions of the final product are strongly dependent on the composition of the precursor materials used.

The preparation of ceramics from polymeric precursors has generated a great deal of interest because it allows the processing of ceramics at low temperatures as compared to the high sintering temperatures required in the conventional powder routes [8-10].

Suda and coworkers [7], used a polycarbosilane that they cured in oxygen to prepare a Si-O-C membranes on α -Al₂O₃ tubular substrates with an oxygen content of 13-18 wt%, using polystyrene (PS) as the pore former.

In this study, for the purpose of hydrogen separation from CO₂, SiC membranes on porous alumina supports having less than 1nm pore size have been developed by introducing a γ -Al₂O₃ interlayer in between the nanoporous SiC membrane and porous alumina support for a gradual pore size distribution.

Experimental Procedure

Coating the γ -Al₂O₃ interlayer on a porous alumina support

A boehmite solution was obtained from Nanopore Materials Co. Ltd. Korea, which was synthesized by hydrolysis followed by the peptization of aluminium sec butoxide. The boehmite solution obtained was spin coated and penetrated into the near surface layer of the porous alumina support (25 mm diameter, 2 mm thickness). The boehmite-coated porous alumina support was then heated at various temperatures in the range of 400-1000 °C for 1 h in

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air. The pore size was determined by nitrogen physisorption using a Micromeritics ASAP 2010.

Preparation of nanoporous SiC membrane

20% of hydridopolycarbosilane (HPCS, starfiresystem Co.) in cyclohexane was spin coated onto the top of the γ - Al_2O_3 interlayer and converted into an amorphous SiC layer by heat treatment at 600 °C with a heating rate of 10 °C/min, followed by heat treatment at 900 °C for 1 h with a heating rate of 10 °C /min under an inert atmosphere.

A Rigaku D/max-RINT 2500 diffractometer with Cu K α radiation was used for the XRD analysis of the samples. A Hitachi, S-4100 scanning electron microscope was used for morphological observations of SiC nanoporous membranes. The pore size was determined by argon physisorption using a Micromeritics ASAP 2010.

Gas Separation measurement

Gas permeation experiments were performed at room temperature using a single component hydrogen and nitrogen gas measurement apparatus. Each flow rate was measured with a soap film flow meter. The applied pressure was 6 psi (41,370 Pa) and permeance rate and selectivity were obtained from the following equations:

$$\text{Permeance Rate } Q_i = A_i / (P_{ri} - P_{pi}) \times S \times t, \quad (1)$$

$$\text{Selectivity } \alpha = Q_{\text{H}_2} / Q_{\text{N}_2} \quad (2)$$

Q: Permeance Rate ($\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$), A: Permeate mole (mol), Pr: Feed Pressure (Pa), Pp: Permeate pressure (Pa) S: Membrane area (m^2), T: Time (seconds), i: H_2 , N_2

Result and Discussion

In order to examine the pyrolysis residue of hydridopolycarbosilane which was used as the SiC ceramic precursor, the sample after heat treatment at 1,200 °C for 1 h under an Ar atmosphere was crushed into a powdered form and

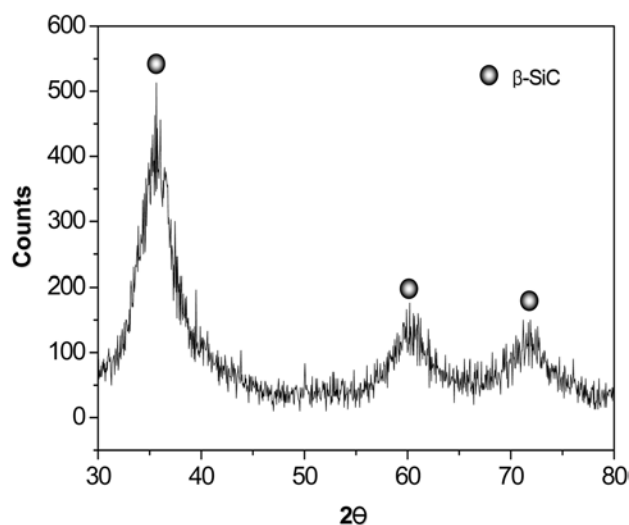
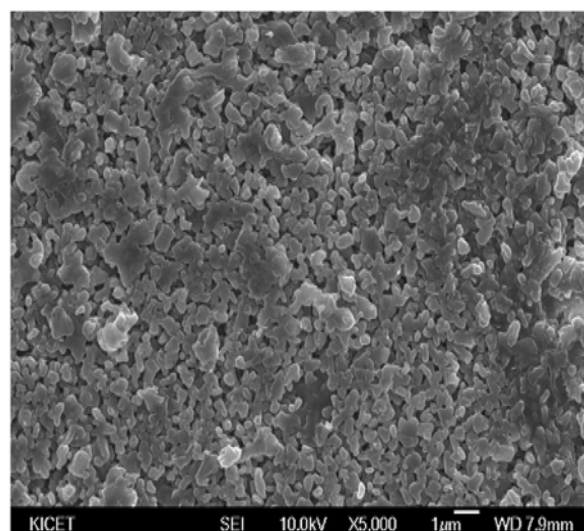


Fig. 1. X-ray diffraction pattern of heat treated HPCS (hydridopolycarbosilane) which is the preceramic polymer after heat treatment at 1200 °C for 1 h in an argon atmosphere.

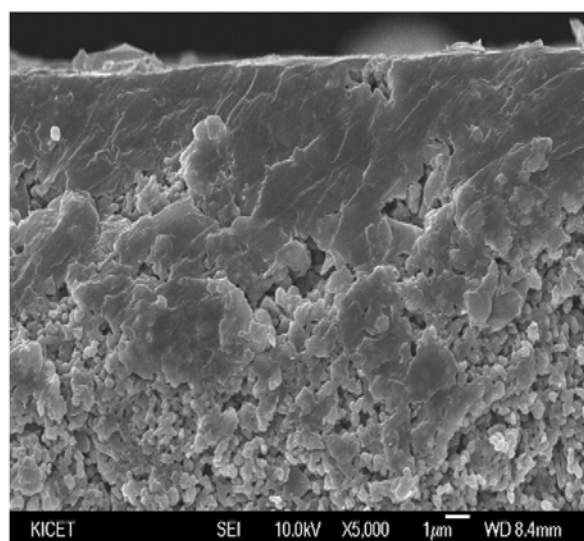
analyzed by XRD. The diffraction peaks of the sample around 35°, 60°, and 73° corresponded to the β -SiC and it is confirmed that hydridopolycarbosilane is suitable as a SiC ceramic precursor (Fig. 1).

A solution of 5 wt.% of hydridopolycarbosilane in cyclohexane was spin coated directly onto the top of the porous alumina support and converted into an amorphous SiC layer by heat treatment at 600 °C with a heating rate of 10 °C/min, followed by heat treatment at 900 °C for 1 h with a heating rate of 10 °C /min under an inert atmosphere. However, as shown in Fig. 2, hydridopolycarbosilane solution had entirely penetrated into the pores of the alumina support and no SiC membrane was formed.

A SiC membrane was formed using a 20 wt.% of hydridopolycarbosilane solution, however most of the

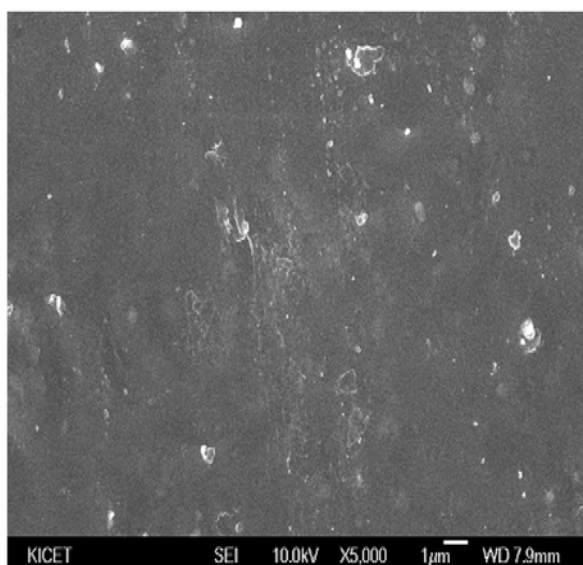


(a)

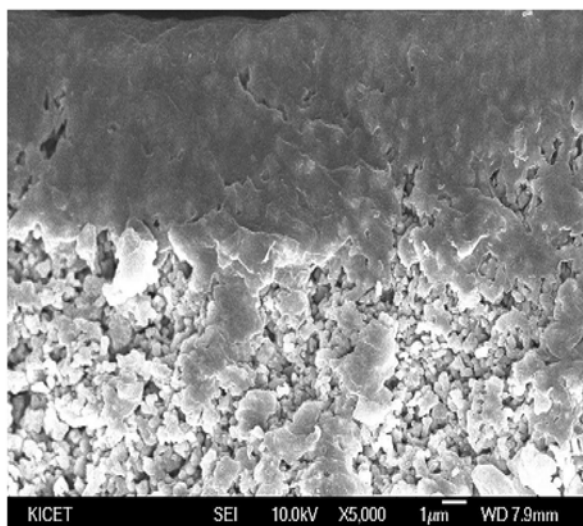


(b)

Fig. 2. SEM data of a SiC membrane prepared at 900 °C by a spin coating method using a 5 wt.% preceramic precursor in cyclohexane (a) surface (b) cross section.



(a)



(b)

Fig. 3. SEM data of a SiC membrane prepared at 900 °C by a spin coating method using a 20 wt.% preceramic precursor in cyclohexane (a) surface (b) cross section.

hydridopolycarbosilane had penetrated into the pores of the alumina support (Fig. 3).

This is attributed to the large pore size of the alumina support. In our experiments, we utilized commercial α -Al₂O₃ supports with an average pore size of 100 nm as the supports for the SiC membrane preparation. To make nanoporous SiC membranes having a pore size of less than 1 nm, an α -Al₂O₃ support with an average pore size of 100 nm was not suitable. To achieve a good quality nanoporous membrane, it is necessary to design in a gradual pore size distribution.

To obtain an asymmetric pore size distribution, we introduced a γ -Al₂O₃ interlayer in between the nanoporous SiC membrane and porous alumina support using a boehmite solution. The average pore diameter varied in the range

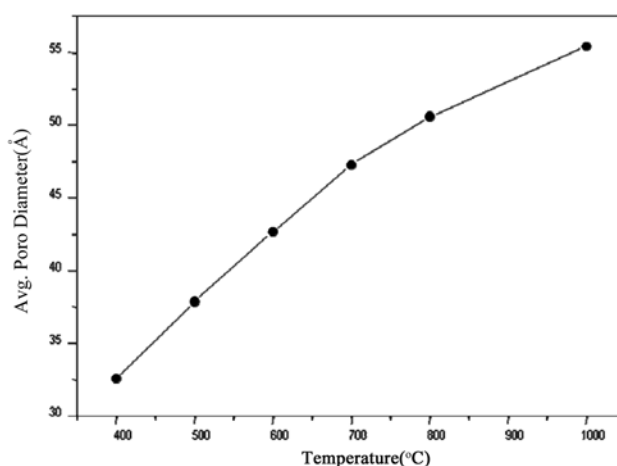


Fig. 4. Variation of average pore diameter of a γ -Al₂O₃ coated porous alumina support with different dehydroxilation temperatures.

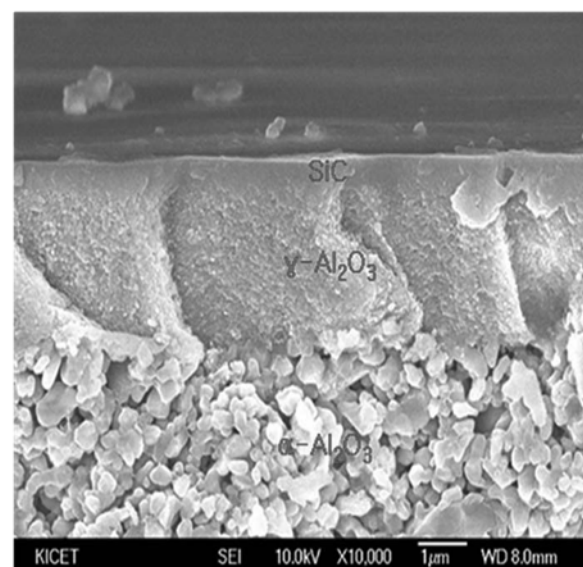
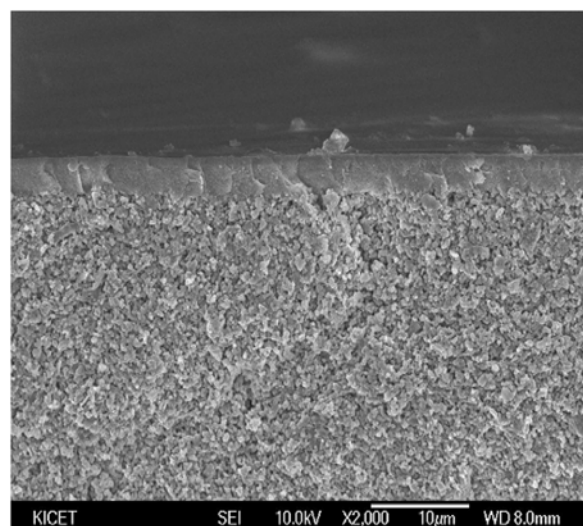


Fig. 5. SEM data of a SiC membrane prepared on the top of a γ -Al₂O₃ coated porous alumina support.

of 3.3-5.5 nm for the as dried boehmite solution heated in the range of 400-1000 °C as shown in Fig. 4. The pore size was found to increase with the dehydroxilation temperature. The increase in pore size was likely due to the loss of the O-H groups (dehydroxilation) during heating. The pore size was found to increase linearly with temperature up to 700 °C above which it was non-linear. The non-linearity above 700 °C might be due to the transformation of γ -alumina into δ -alumina. In the present case the transformation of γ -alumina to δ -alumina may occur between 700-800 °C.

As shown in Fig. 5, the SEM microstructure of a SiC membrane with a γ -Al₂O₃ interlayer does not show any penetration of the preceramic polymer into the support after heat treatment at 900 °C under an argon atmosphere. Pore size distribution measurements show that the sample contains around 1 nm sized nanopores (Fig. 6). Also nanopores existing in a SiC membrane are known to be able to be selectively more permeable to H₂ gas than CO, CO₂, N₂ gases.

As shown in Table 1, the hydrogen gas permeance of a SiC membrane with a γ -Al₂O₃ interlayer was 0.16×10^{-6} mole/m²·s·Pa and the hydrogen selectivity toward N₂ gas was 42.5. However, the hydrogen selectivity of a SiC membrane without a γ -Al₂O₃ interlayer was 4.37 and this value is similar to the Kundsens diffusion selectivity

for H₂/N₂, which is 3.74 [11]. In the Knudsen flow regime, selectivity is based on the reverse square root ratio of the molecular weights of A and B : $\alpha_{AB} = [M_B/M_A]^{1/2}$ [12].

Conclusions

Nanoporous SiC membranes having less than 1 nm pore size were fabricated on porous alumina substrates. For a gradual pore size distribution, a γ -Al₂O₃ interlayer was introduced in between the nanoporous SiC membrane and a porous alumina support. To prepare SiC nanoporous membranes, 20 wt.% hydridopolycarbosilane was spin coated and penetrated into the near surface layer of the porous alumina substrate. Then, the surface layer was converted into amorphous SiC layer by heat treatment at 900 °C under an inert atmosphere. SiC coated porous alumina possesses an asymmetric pore size distribution. There are micropores originating from the porous alumina substrate and nanopores derived from the amorphous state of SiC membranes. The hydrogen gas permeance of the SiC membrane prepared was 0.16×10^{-6} mole/m²·s·Pa and the hydrogen selectivity toward N₂ gas was 42.5. The nanoporous hydrogen selective SiC membranes developed show promise for application in hydrogen separation from coal gasification such as integrated gasification combined cycle (IGCC)

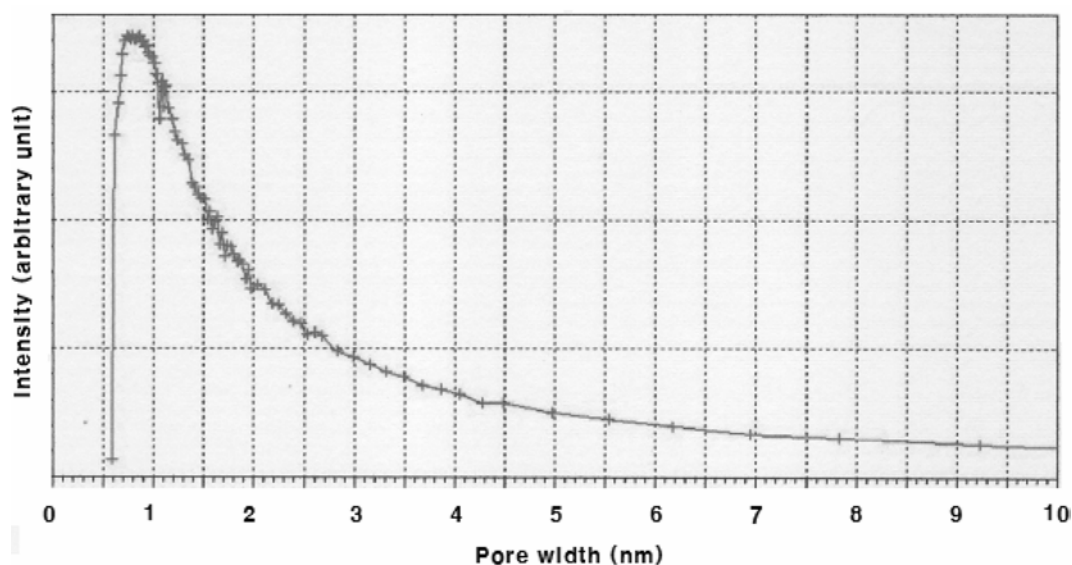


Fig. 6. Pore size distribution of a SiC membrane prepared on the top of a γ -Al₂O₃ coated porous alumina support.

Table 1. Hydroegn permeance and separation factor of the prepared membranes

Samples	Applied pressure	H ₂ Flow	N ₂ Flow	H ₂ Permeance	N ₂ Permeance	Separation Factor
γ -Al ₂ O ₃ coated a-Al ₂ O ₃ substrate	6 psi (41,370 Pa)	22.5 SCCM	5.7 SCCM	2.06×10^{-6} mole/m ² ·S·Pa	0.52×10^{-6} mole/m ² ·S·Pa	4.12
SiC coated a-Al ₂ O ₃ substrate	6 psi (41,370 Pa)	20.5 SCCM	4.7 SCCM	1.88×10^{-6} mole/m ² ·S·Pa	0.43×10^{-6} mole/m ² ·S·Pa	4.37
SiC/ γ -Al ₂ O ₃ coated a-Al ₂ O ₃ substrate	6 psi (41,370 Pa)	1.7 SCCM	0.0 SCCM	0.16×10^{-6} mole/m ² ·S·Pa	$> 0.37 \times 10^{-8}$ mole/m ² ·S·Pa	> 42.5

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