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Preparation and characterization of SiO_2 composite membrane for purification of hydrogen from methanol steam reforming as an energy carrier system for PEMFC

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Abstract

Silica/porous stainless steel (SUS) composite membranes were prepared for carbon monoxide (CO) removal from products of methanol steam reforming. A support was prepared by coating Ni powder with sub-micron level and SiO_2 sols with particle size of 500 and 150 nm in turns on SUS. Silica top layer was coated on the modified support using colloidal sol with nanoparticle. As a result of mixture gas permeation test of silica composite membrane using H_2(99%)/CO(1%), CO concentration of 10 000 ppm was reduced to under 81 ppm, which is acceptable in polymeric electrolyte membrane fuel cell (PEMFC) anode gas purification. Permeation mechanism through the membrane was mainly molecular sieving.

Keywords: Silica membrane; Hydrogen purification; Sol–gel method; PEMFC

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1. Introduction

Inorganic membranes can be utilized to separate major component or remove minor contaminant gas from a gaseous mixture. In particular, ceramic membranes have attracted considerable attention in applications to bulk separation of the valuable hydrogen from other major gas constituents and removal of acid gases (such as carbon dioxide, hydrogen sulfide and sulfide dioxide) from flue gases [1]. One of the potential applications is the hydrogen purification in the polymeric electrolyte membrane fuel cell (PEMFC). Due to severe poisoning of anode, electrocatalysts of PEMFC in the presence of even low concentration of carbon monoxide (CO) produced by methanol steam reforming should be removed. Several physical and chemical purification methods, such as pressure swing adsorption (PSA), inorganic

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membranes, organic membranes, solvent absorption, water–gas shift reaction, methanation and preferential oxidation (PROX), have been studied in order to reduce CO concentration to below 100 ppm.

Comparing with organic membranes, inorganic membranes have better mechanical strength and thermal stability. Palladium membrane exhibits high-hydrogen permselectivity, but has some disadvantages such as high module cost and instability of performance in the presence of hydrocarbons or steam. Therefore, silica membrane is very attractive for hydrogen purification in the PEMFC system. For industrial applications, membrane synthesis method should be simple, reliable, and easily adaptable to large-scale production. Silica composite membranes are usually prepared by sol–gel method and chemical vapor deposition (CVD) [2–10]. Burggraaf and coworkers [14,15] prepared microporous silica membranes by modification of mesoporous γ-alumina membranes with polymeric sols, and showed activated permeation and molecular sieve-like separation factors in the order of 50–200 for H_2/CH_4. They also prepared alumina–silica membranes for separation of propane and propylene by sol–gel method [16]. Brinker et al. [2] prepared ultramicroporous (pore radius < 10 Å) separation layers onto commercial alumina supports using dip-coating with polymeric silica sols. They demonstrated a template approach to prepare microporous inorganic membranes exhibiting high flux combined with high selectivity, overcoming limitations inherent to both conventional inorganic approaches such as sol–gel method and CVD [17]. CVD is not adaptable to large-scale production due to high processing costs. Therefore, in order to apply inorganic membrane to purification process of hydrogen as anode feed gas of PEMFC, silica composite membranes produced by sol–gel process are better than those by CVD.

In this study, the silica composite membranes as a tool for CO removal were prepared under base-catalyzed condition on a porous stainless steel (SUS) support modified by Ni and SiO_2 sols with large particles and characterized with the scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET).

2. Experimental

We prepared several silica sols for modification of SUS supports and top layers. Colloidal silica sols of 500, 150 and 5 nm were produced under base-catalyzed condition via hydrolysis of tetraethyl orthosilicate (TEOS) purchased from Aldrich. Concentration of NH_3 and water based on TEOS of 0.28 M is varied in the range 0.02–6 and 10–15 M, respectively. After the reaction mixture was refluxed for 3 h under vigorous stirring, stable colloidal silica sol was obtained. We optimized preparation conditions of top layer by changing the variations. Details of silica sol preparation have been reported previously [11].

Disks of 316L SUS used as a porous substrate were purchased from Mott Metallurgical. The SUS support has a thickness of 1 mm, a surface area of 5 cm^2 and an average pore size of 0.5 μm. In order to obtain smoother surface and reduce the average pore size, macroporous SUS substrates were modified by introducing intermediate layer such as nickel, SiO_2 (500 nm) and SiO_2 (150 nm). Pore size and pore size distribution were controlled by changing calcination temperature, dipping time and repeating number of dipping–drying process. We controlled density of membrane surface by repeating dipping–drying or the whole process of dipping–drying–calcination and controlled nanostructure of pores by changing top layer materials.

Permeation measurements for single gas were made with gases of nitrogen, carbon dioxide and hydrogen between room temperature and 250 °C. The permeation apparatus consists of a membrane cell, furnace, temperature controller, pressure gauge, pressure transducer and mass flow meter. The transmembrane pressure difference was varied from 0.014 to 0.069 MPa. The selectivity is defined as the ratio of the permeance of hydrogen to that of nitrogen under the same transmembrane pressure difference and temperature. For permeation test of mixture gas, H_2(99%)/N_2(1%), H_2(99%)/CO_2(1%) and H_2(99%)/CO(1%) were used as feed gas. Ar and N_2 were used as sweeping gas. The flow rate of feed and sweeping gas was 40 and 20 cm^3/min, respectively. The parameter to describe the separation efficiency for a binary mixture is the separation factor, which is a measurement of the enrichment of a gas component after it has passed the membrane. Separation factor for a binary gas mixture is defined as follows:

$$\alpha = \frac{y}{1-y}\frac{1-x}{x},$$

where x and y are the mole fractions of feed and permeate, respectively. The mole fractions of permeate side were measured using gas chromatography (DS6200, Donam system, Inc.).

SEM (JOEL JSM-840A) was used to characterize the silica composite membrane. We observed cross-section and surface of the membrane and particle size of colloidal silica sols. For analysis of silica nanoparticles, TEM (EM 912 OMEGA, Carl Zeiss) was used due to measurement limitation of SEM. Pore size distribution and average pore size of the unsupported silica film were measured by BET (ASAP 2400) method with argon adsorption.

3. Results and discussion

An SUS support was used to improve mechanical strength of the supports. From the viewpoint of a practical application, SUS has the merit of getting more readily sealed into a commercial unit. In view of the membrane reactor design, stainless steel membranes also offer the most promising perspectives [12,13]. First, we modified SUS support using sub-micron nickel powder in order to reduce pore size and surface roughness of SUS support. The Ni-SUS support was modified again with SiO_2 (500 nm) by dip-coating. Then, the support was modified further with SiO_2 (150 nm).

Colloidal silica sol with nanoparticles as a top layer coating material was prepared under base-catalyzed condition in order to get molecular sieving layer. As shown in Fig. 1, uniform silica sol was obtained and particle size of the silica, which is sphere-shaped, is about 5 nm. Using the colloidal silica sol, top layer was coated on the support by repeating dipping–drying–calcination process for four times. SEM images of the silica-coated composite membrane calcined at 500 °C are shown in Fig. 2. Surface and cross-section of the silica top layer became somewhat rough comparing with those of the silica top layer prepared under acid-catalyzed condition [11]. It is due to different pore formation by colloidal or polymeric silica sol. The structure of individual clusters resulting from sol–gel process depends on the pH. The dissolution is very important under base-catalyzed condition. In other words, produced small silica particles are dissolved and provided as a monomer in solution. Thus, under base-catalyzed condition, highly branched silica particles grow by monomer-cluster growth model due to large concentration of monomers produced by the dissolution reaction. On the contrary, under acid-catalyzed condition, dissolution is ignored and hydrolysis is faster than condensation. So monomers hydrolyzed perfectly grow into network structure. In comparison with the case of base-catalyzed condition, low-branched silica particles are produced under acid-catalyzed condition. When silica top layer is prepared using the polymeric and the colloidal silica sol, the size and the structure of the pores created in the coated silica top layer will highly depend on the structure of individual clusters resulting from polymerization. Highly branched silica particles in colloidal sols cannot interpenetrate due to steric hindrance, and so microporous thin film is formed during consolidation. However, the low-branched silica

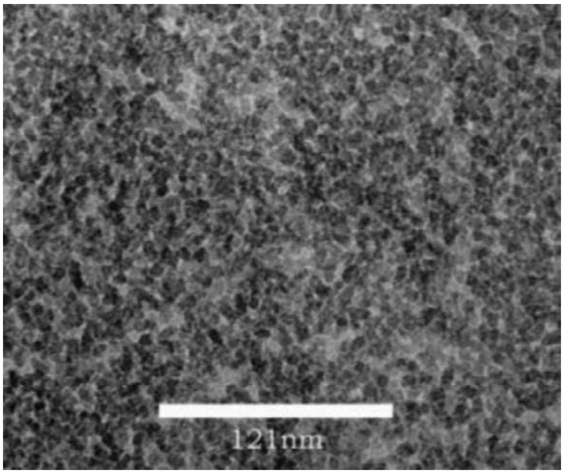
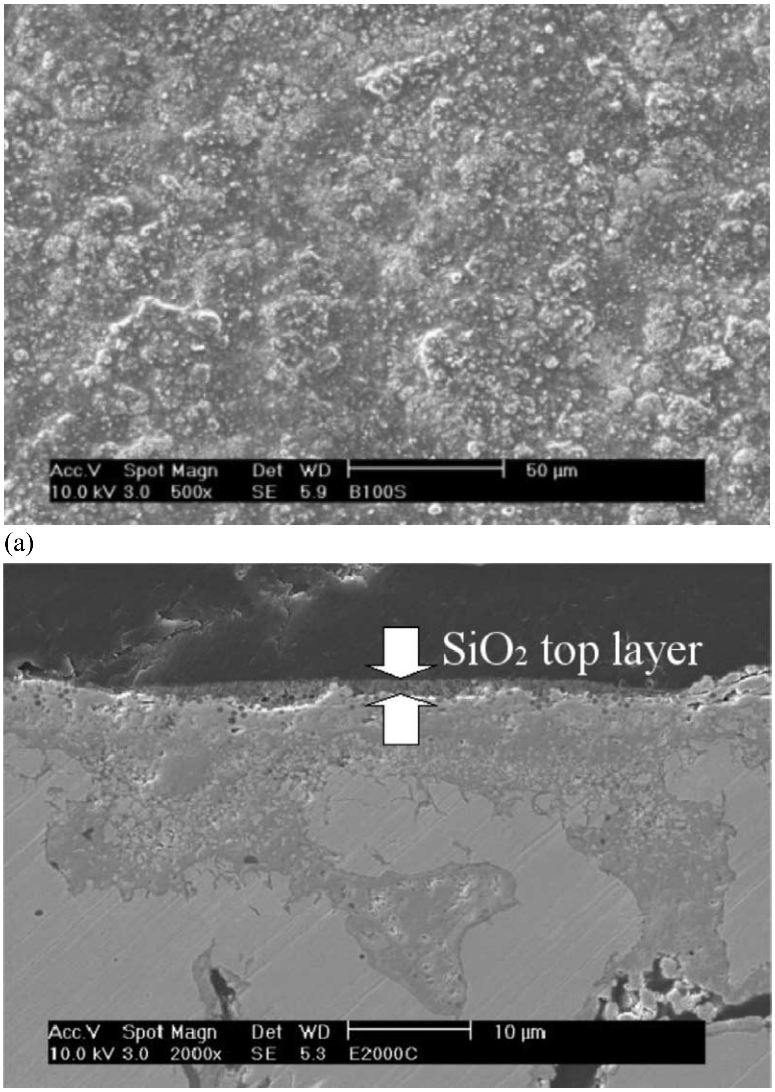


Fig. 1. TEM image of colloidal silica sol prepared under base-catalyzed condition.



(a)

(b)

Fig. 2. SEM images of (a) surface and (b) cross-section of SiO_2 composite membrane with top layer prepared under base-catalyzed condition by repeating dipping–drying–calcination process.

particles in polymeric sols can interpenetrate and lead to dense thin film [2].

Fig. 3 shows pure nitrogen permeance of the SiO_2(150 nm)/SiO_2(500 nm)/Ni-SUS support and pure hydrogen permeance of silica composite membrane with top layer prepared under base-catalyzed condition. For support, there is a decrease of permeance with increasing permeation temperature and the permeance was nearly constant with increasing pressure difference. It means that the contribution of Knudsen diffusion increased by modification with SiO_2 (150 nm) and the SiO_2(150 nm)/SiO_2(500 nm)/Ni-SUS support is suitable for producing stable silica top layer. When silica top layer of the membrane was prepared under base-catalyzed condition, hydrogen permeance was about 1.0×10^{-8} mol m^{-2} s^{-1} Pa^{-1} at $\Delta P = 0.069$ MPa and permeance of

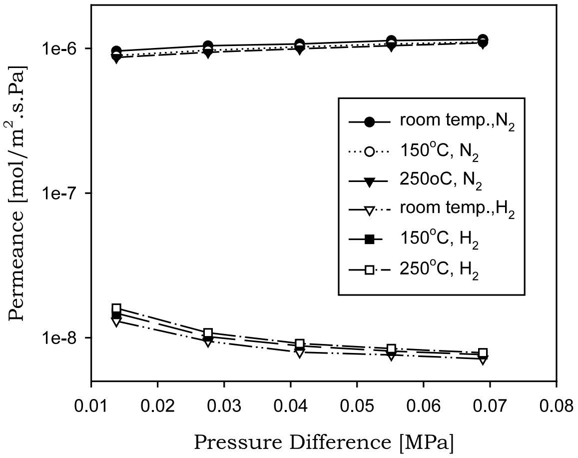


Fig. 3. Nitrogen permeance of support and hydrogen permeance of SiO_2 composite membrane with top layer prepared under base-catalyzed condition.

Table 2
Selectivities at different temperatures for mixture gas permeation test of SiO_2 composite membrane with top layer prepared under base-catalyzed condition

Permeation temperature (°C)	Selectivity		
	H_2/N_2	H_2/CO_2	H_2/CO
Room temperature	112.22	101.00	118.83
150	112.22	101.00	124.69
250	> 112.22	> 101.00	> 124.69

nitrogen and carbon dioxide was under detection limit (1.3×10^{-10} mol m^{-2} s^{-1} Pa^{-1} at $\Delta P =$ 0.069 MPa) of mass flow meter. However, the mass flow meter is insensitive and mixture gas test with gas chromatography was conducted. Tables 1 and 2 show permeate concentration and selectivity for mixture gas (H_2/N_2, H_2/CO_2 and H_2/CO) permeation test of the silica composite membrane with top layer prepared under base-catalyzed condition. The gas permeation through the membrane is followed the order $H_2 > CO_2 > N_2 > CO$, which is consistent with molecular-sieving mechanism. Especially, permeate concentration for H_2/CO binary mixture is below 81 ppm, which is remarkable result satisfying PEMFC anode gas specification.

4. Conclusions

The SUS supports were successfully modified using Ni, SiO_2 (500 nm) and SiO_2 (150 nm), and so those pores of the modified supports were in Knudsen region. Silica top layer was coated on the support by repeating the whole process of dipping–drying–calcination for four times using colloidal silica sol prepared under base-catalyzed condition. Average pore size of the silica top layer increased slightly comparing with that of the silica top layer prepared by polymeric sol. Highly branched silica particles in colloidal sols cannot interpenetrate due to steric hindrance, so microporous thin film is formed during consolidation, while dense thin film is induced by polymeric silica sols. For mixture gas permeation test using

Table 1
Permeate concentrations at different temperatures for mixture gas permeation test of SiO_2 composite membrane with top layer prepared under base-catalyzed condition

Feed concentration (H_2 balance) (10 000 ppm)	Permeate concentration (H_2 balance) (ppm)		
	Room temperature	150 °C	250 °C
N_2	90	90	< 90
CO_2	100	100	< 100
CO	85	81	< 81

H_2(99%)/CO(1%) feed, CO concentration of 10 000 ppm was reduced to under 81 ppm.

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