Preparation of the silica composite membranes for CO removal from PEMFC anode feed gas

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Abstract

Silica/SUS composite membranes were prepared for CO removal from products of methanol steam reforming. A support was prepared by coating Ni powder of sub-micron and SiO_2 sols of particle size of 500nm and 150nm in turns on a porous stainless steel (SUS) substrate. 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 10000 ppm was reduced to under 81 ppm, which is acceptable in PEMFC anode gas specification. Permeation mechanism through the membrane was mainly molecular sieving.

Introduction

In recent years, the development of alternative drive systems such as fuel cell has attracted a great deal of interest, due to several problems of drive system based on internal combustion engine. For vehicle applications, the polymer electrolyte membrane fuel cell (PEMFC), which operates at 80℃, has proved the most attractive option. The drive systems for cars using PEMFC can lead to increased energy usage efficiency and, especially, substantially reduced emissions compared with the best foreseeable drive system based on the internal combustion engine. Methanol is the best energy carrier for such systems, when taking availability, costs and safety aspects into account.[1-3] However, PEMFC is extremely sensitive to even low concentrations of carbon monoxide (CO) produced by methanol steam reforming due to severe poisoning of anode electrocatalysts of PEMFC in the presence of low concentration of CO. PEMFC anode feed gas specification is shown in Table 1.[3] Several physical and chemical purification methods, such as pressure swing adsorption (PSA), inorganic membranes, organic membranes, solvent absorption, water-gas shift reaction, methanation and preferential oxidation (PROX), have been studied in order to reduce CO concentration to under 100 ppm.

Experimental

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 (500nm) and SiO_2 (150nm). Pore size and pore size distribution were controlled by changing calcination temperature, dipping time and repeating number of dipping-drying process. 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 a feed gas. Ar and N2 was used as a sweeping gas. The flow rate of feed and sweeping gas was 40 and 20 cc/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 below.

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

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.).

Results and discussion

In this study, in order to prevent CO gas produced by methanol steam reforming from poisoning anode electrocatalyst of PEMFC, the silica composite membranes as a CO removal method were prepared by sol-gel process. Stainless steel substrates, which were used to improve mechanical strength of membranes, were successfully modified using Ni, SiO_2 (500nm), SiO_2 (150nm) so that pores of the modified supports were in Knudsen region. Silica top layer was prepared on the support by dip-coating method using polymeric or colloidal silica sol. Comparing with the membrane prepared by polymeric sol, higher hydrogen permeance with good selectivity were obtained by microporous thin film derived from colloidal silica sol with nanoparticles. For mixture gas permeation test of the silica composite membrane using H_2(99%)/CO(1%) feed, as shown in Table 2, CO concentration of 10000ppm was reduced to under 81 ppm. It is attributed to the structure of individual clusters in the sols that the silica composite membrane prepared under base-catalyzed condition showed higher permeance. 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, 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 can not interpenetrate due to steric hindrance, so microporous thin film is formed during consolidation. However, the low-branched silica particles in polymeric sols can interpenetrate and lead to dense thin film.

Conclusions

The SUS supports were successfully modified using Ni, SiO_2 (500nm) and SiO_2 (150nm) 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 4 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 can not 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 H_2(99%)/CO(1%) feed, CO concentration of 10000 ppm was reduced to under 81 ppm.

References

1. B. Emonts, J.B. Hansen, S.L. Jørgensen, B. Höhlein, and R. Peters, J. Power Sources, 288-293 (1998) 71.

2. F. Panik, J. Power Sources, 36-38 (1998) 71.

3. J.C. Amphlett, R.F. Mann, and B.A. Peppley, Int. J. Hydrogen Energy, 673-678 (1996), 21.

Table 1. PEMFC Anode Feed Gas Specification

Component	Specification
Hydrogen	50-100%
CO	Max.10-100 ppm
N_2, CO_2	0-50%
Water	Variable
Methane	0% desirable
Formic acid	0%
Methanol	0% desirable
Formaldehyde	0% desirable
Methyl formate	0% desirable

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

Feed (H_2 balance)	Permeate concentration (H_2 balance)		
	25℃	150℃	250℃
N_2 (10000ppm)	90 ppm	90 ppm	< 90 ppm
CO_2(10000ppm)	100 ppm	100 ppm	< 100ppm
CO(10000ppm)	85 ppm	81 ppm	< 81 ppm