Scale-Up of Molecular Sieve Silica Membranes for Reformate Purification

M. Duke, V. Rudolph, G. Q. (Max) Lu, and J. C. Diniz da Costa
The Nanomaterials Centre, School of Engineering, The University of Queensland, Brisbane 4072, Australia

DOI 10.1002/aic.10200

Keywords: molecular sieve silica, nanotechnology, reformate, scale-up, fuel cells, membrane reactors

Introduction

Molecular sieve silica (MSS) membranes are a developing technology involving nanotechnology techniques. These membranes demonstrate excellent properties for permeation of hydrogen molecules with a very high selectivity, as presented in Table 1 (de Vos and Verweij, 1998; Diniz de Costa et al., 2002; Kusakabe et al., 1999; Tsai et al., 2000), making them ideal for applications requiring separation of hydrogen from other gases. The permeation of hydrogen is now approaching the limit of 1×10^{-6} mol m^{-2} s^{-1} Pa^{-1}, equivalent to 0.7 kg of hydrogen per square meter of membrane area per hour, and at 1 atmosphere differential pressure across the membrane. MSS membranes can operate at temperatures up to 500°C and up to 20 atmospheres. However, there are limited reports in the literature regarding scale-up of silica-based membranes. To cite but one example, Koukou et al. (1999) scaled-up alpha-alumina tubes (length: 20 cm; outer diameter: 1.4 cm) with silica-derived films for gas separation. They tested their membranes using a feed-gas mixture of 62% H_2 and 38% CH_4 for pressure differences ranging from 5 to 20 bar, resulting in best H_2/CH_4 selectivities of 5. Potential applications of the MSS membranes include gas separation, such as extracting H_2 from a gas stream in a petrochemical refinery process; filtration of contaminants (such as CO) from H_2 supply for proton-exchange membrane (PEM) fuel cells; and chemical production using membrane reactors to carry out dehydrogenation.

MSS membranes are envisioned to be integrated into PEM fuel cell systems, which is a technology being developed for motor vehicles (50–100 kW), residential (2–10 kW) and commercial (250–500 kW) power generation, as well as small/portable generators and battery replacement (ECW, 2000). PEM fuel cells usually require a pure H_2 source for operation. However, for most of these applications, tank storage of H_2 at extremely high pressure (up to 35 MPa) presents serious concerns with respect to safety. Hydrogen is thus typically obtained by reforming a hydrocarbon fuel (methanol or gasoline) onboard. In this reaction, the product termed as "reformate" consists of H_2, CO, CO_2, and water. CO is detrimental for the fuel cell operation because of catalyst poisoning and severe fuel cell degradation. Thus, CO levels must be reduced to 10 parts per million (ppm) for standard anodes or 100 ppm for CO-tolerant anodes in fuel cell technology (Hasegawa et al., 2002; Sotawa et al., 2002). Metal membranes based on palladium and its alloys can provide high H_2 purification and various research groups have reported their use in fuel cell systems (Koros and Mahajan, 2000; Ledjeff-Hey et al., 1998; Lin and Rei, 2000). However, palladium membranes are a major economic impediment in fuel cell technology, particularly because they cost in the order of US$1,250 to US$2,000 per square meter of membrane area (Illgen et al., 2001). Thus, there is a major advantage of using silica-derived membranes because such materials are cheap and readily available. Given that the cost effectiveness of technologies such as fuel cells and membrane reactors is paramount to making these technologies competitive against traditional technologies (Ogden et al., 2001), MSS membranes can potentially deliver cost savings over use of metal membranes.

Much of the current MSS membrane research has been limited to laboratory testing. Operating systems in fuel cells, membrane reactors, and gas separation undergo cycles of start-up to shutdown with varying compositions and heating rates. The development of inorganic membranes displaying outstanding chemical and thermal resistance is required to open new fields of industrial applications (Jonquieres et al., 2002). Although laboratory testing has shown the potential of MSS membranes, there is a need to scale-up to test how the technology can perform under as close as possible to real application conditions. Thus, in this work we scaled-up MSS membrane tubes for fuel cell reformate purification. Of particular

---

Correspondence concerning this article should be addressed to J. C. Diniz da Costa at joedac@cheque.uq.edu.au.

Table 1. Gas Permeation of Membranes (10^{-8} mol m^{-2} s^{-1} Pa^{-1}) and Permselectivity

P_{H2}	P_{CO2}	P_{CH4}	P_{H2}/P_{CO2}	P_{H2}/P_{CH4}	Temperature (°C)	Reference
2	0.03	0.006	67	333	150	Diniz da Costa et al. (2002)
10	0.9	0.25	11	40	100	Kusakabe et al. (1999)
170	27	0.27	6.3	630	150	de Vos and Verweij (1998)*
68	23	1.3	3.0	52	150	Tsai et al. (2000)*

*Membranes fabricated in clean rooms.

attention, issues related to permeation of single-gas and reformate gas mixtures as well as H_2 separation are addressed in terms of scale-up performance. The membrane operating life is investigated under the cycling temperature operating conditions to verify the technology suitability for fuel cell application.

Scale-Up

Gas permeation and separation experiments for both single-gas (He, H_2, CO_2, and CO) and synthetic reformate containing H_2 (42.3%), CO_2 (12.4%), CO (9.2%), and N_2 (36.1%), were carried out in a permeation apparatus shown in Figure 1. The permeation of single gases was determined according to normalized flux measurements described elsewhere (de Vos and Verweij, 1998; Diniz da Costa et al., 2002). Ports (P) in the permeate and retentate streams were used to collect gas samples and to determine the concentrations of the gases by gas chromatography (GC) analysis. The sweep gas used was argon and its flow was controlled (FC) at 100 mL min^{-1}. Pressure transducers (PT) were used to monitor the pressures in both feed and permeate lines. Experiments were carried out in the temperature range of 50°C (room temperature) to 250°C. GC analyses of the gases in the retentate and permeate streams were conducted in a Shimadzu (Kyoto, Japan) GC with TCD and FID detectors in series. The selectivity (α) of the membranes for gas mixtures was determined as a function of the concentration of the gas components in the permeate ($c_{p,i}$) over the retentate ($c_{r,i}$) according to the following equation

$$\alpha_{1/2} = \frac{c_{p,1}}{c_{r,1}}\frac{c_{r,2}}{c_{p,2}} \tag{1}$$

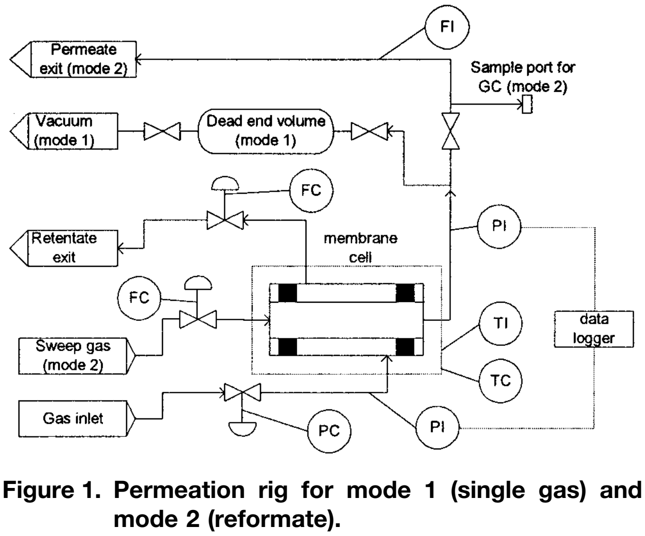

Figure 1. Permeation rig for mode 1 (single gas) and mode 2 (reformate).

Table 2 lists the number of layers and calcination procedure to coat the scaled-up tubes. The primary layers were prepared using Locron alumina sols (supplied by Bayer AG, Leverkusen, Germany), whereas the intermediate layers were prepared using a templated [methyltriethoxysilane (MTES)] sol–gel method. The two top layers, including the selective layer, were synthesized by a catalyzed hydrolysis process using tetraethylorthosilicate (TEOS), absolute ethanol (EtOH), 1 M nitric acid (HNO_3), and distilled water. The preparation procedures are described elsewhere (Diniz da Costa et al., 2002).

α-Alumina tubes (length: 10 cm; outer diameter: 1.5 cm) were used for MSS membrane scale-up. The effective surface area was 20 cm^2, which is 15–20 times larger than that used in previously published work for small platelet–supported MSS membranes (Diniz da Costa et al., 2002; Kusakabe et al., 1999). The tubes were initially sanded to obtain a smooth surface for film coating. The tubes were then cleaned and conditioned in an oven at 600°C before film coating. The dip-coating process was performed on the outside shell of the tubes in a clean room–type fume hood to avoid dust. Subsequently the tubes were calcined as described in Table 2. The dip-coating–calcination process was repeated for each film layer coated on the substrate. The tube coated with the selective layer was assembled in a membrane module depicted in Figure 2. The module was of cylindrical shape to accommodate a tube membrane with a graphite disc placed at each end side of the tube.

Results

Single-gas permeation results, depicted in Figure 3A, show a typical activated permeation (that is, permeation increased with temperature) for all gases tested except for CO_2. It was also observed that H_2 permeation slightly decreased after 200°C. Activated permeation is a property of molecular sieve materials applicable to all types of gases from room temperature to about 200–250°C (Diniz da Costa et al., 2000), except for CO_2 (de Vos and Verweij, 1998). Figure 3B shows that the

Table 2. MSS Tube Membrane Film Synthesis

Layer	Number of Layers	Chemical Synthesis	Calcination
Top selective	2	Two-step sol–gel	500°C at 0.5°C m^{-1}
Top	2	Single-step sol–gel	500°C at 0.5°C m^{-1}
Intermediate	2	Templated sol–gel	500°C at 1°C m^{-1}
Prime	2	Locron	600°C at 1°C m^{-1}

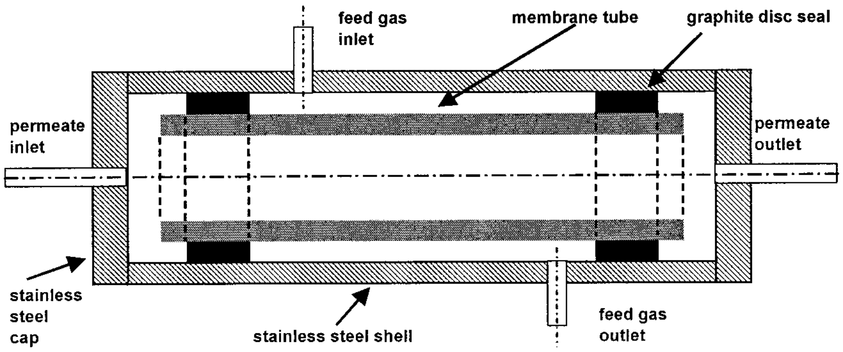

Figure 2. MSS tube membrane module system.

permeation did not vary that much with respect to pressure difference across the membrane for each temperature point, giving a clear indication that the graphite seals functioned very well. In addition, the pressure difference did not affect permeance rates in silica-derived membranes because these materials have low adsorption rates (de Lange et al., 1995) that comply with Henry's law.

The results for permeation of synthetic reformate are listed in Table 3. The permeation also increased with temperature for all gases except CO_2, thus indicating that activated transport is also regimenting the transport of gas mixtures through the membrane. Doubling the pressure difference across the membrane resulted in an increase of concentration of all gases, a direct result of altering the driving force. CO is a major problem for fuel cell application because it poisons the electrochemical catalysts in the PEM fuel cell, and should be reduced to levels below 100 ppm. At 50°C and 1 atm pressure difference (ΔP), the scaled-up membrane shows that CO concentration was less than 200 ppmv. Therefore, these results strongly suggest that these membranes can be optimized to meet the technology requirements for fuel cell application.

An increase in temperature led to higher selectivities, as shown in Figure 4. The selectivity of H_2/CO increased by twofold (6.3 to 12.6), whereas H_2/CO_2 trebled in value (1.5 to 5.5). The increases in selectivity were largely attributed to the adsorption characteristics of the gases tested, leading to activated transport. For instance, in Figure 3A it was observed that H_2 single-gas permeation increased with temperature, whereas CO_2 decreased and CO increased only slightly. The same trend was also observed in Table 3. Thus, as the temperature increased the selectivity of H_2 to CO and CO_2 followed suit.

The MSS membrane tubes were tested for He permeation for up to 36 days, as shown in Figure 5 under heating and cooling cycles. During this testing period, the He permeation was measured after heating the tube membrane to 250°C from room temperature. The initial increase in permeation from day 1 to day 2 was attributed to membrane initial conditioning, in particular that water and atmospheric gases were expelled from the membrane structure, thus deblocking pores and resulting in higher permeation rates. He permeation remained quite constant for an additional 5 days and then slightly decayed at a rate of 7.7×10^{-11} mol m^{-2} s^{-1} Pa^{-1} per day. Thus, fouling or decaying rates were two orders of magnitude lower than the current permeation rates, suggesting that MSS tubes may last up to half a year in fuel systems before regeneration or replacement should be required. These results also indicate that the

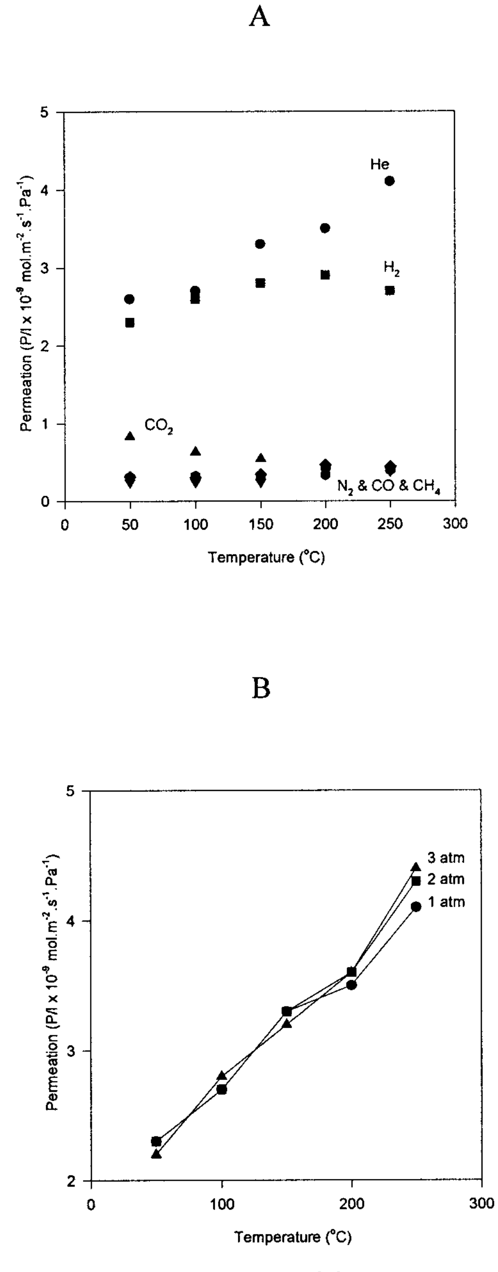

Figure 3. Permeation results for (A) 1 atm pressure difference as function of temperature and (B) He permeation at various pressure regimes.

Table 3. Concentration (±10%) in ppmv in the Permeate

Test	H_2	N_2	CO_2	CO
250°C (ΔP = 1 atm)	10107	9667	585	195
250°C (ΔP = 2 atm)	15798	13433	835	272
150°C (ΔP = 1 atm)	8166	7127	611	220
150°C (ΔP = 2 atm)	12986	8482	1119	327
50°C (ΔP = 1 atm)	6321	2809	930	169
50°C (ΔP = 2 atm)	9813	6722	1726	339

heating and cooling cycles did not affect the tube membrane performance, suggesting that silica derived films were stable under temperature-cycling conditions. In addition, the membranes were also tested for high temperatures at 450°C. However, high-temperature heat induced stress resulted in the membrane tubes cracking at the interface with graphite seals, which is a problem related to the module design, rather than the membrane performance.

The results discussed above are very encouraging and further work will be carried out to optimize the MSS membrane scaled-up tubes. The major problems encountered in the scale-up process were related to seal technology rather than membrane production. There are two major advantages for MSS membranes to operate at high temperatures. First, reformate systems for fuel cell PEM technology deliver gas streams around 400°C and membrane systems for CO cleanup should be able to withstand such high temperatures. Second, adsorption characteristics of gases change with temperature. High temperatures enhance gas-separation properties, in particular for H_2 as discussed above, leading to an engineering benchmark required to achieve CO concentration to amounts below 100 ppm for fuel cell technology. Thus, the tube membrane module design will be revisited to address problems related to heat stress cracks caused on the tube. Furthermore, H_2 permeation was relatively low, two orders of magnitudes below laboratory-scale results reported in the literature. Further work will thus need to address permeation flux enhancement. This can be achieved by reducing the number of film layers, as described in Table 2, provided that selectivity is not compromised. Film-layer reduction leads to flux enhancement, given that the flux of gases increases proportionally as membrane thickness decreases.

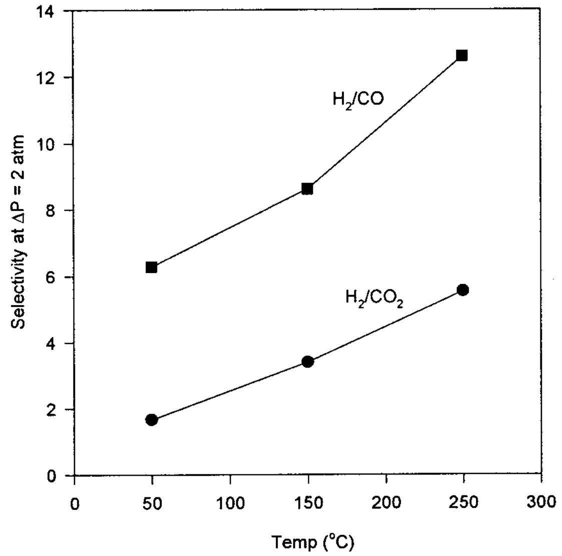

Figure 4. Selectivity of H_2 to CO and CO_2 in gas mixture as a function of temperature at 2 atm pressure drop.

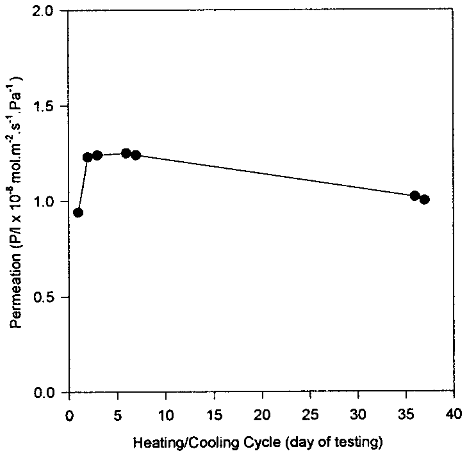

Figure 5. He permeation in heating and cooling cycles for membrane tubes at 200°C, 2 atm pressure drop.

Conclusion

High-quality silica-derived films were scaled-up to MSS tube membranes, which exhibited activated transport, a characteristic of molecular sieving materials. Separation of synthetic reformate resulted in CO concentrations below 200 ppmv, strongly suggesting that MSS tube membranes can be further developed for PEM fuel cell technology. The scaled-up MSS tube membranes showed good robustness to thermal cycling and long-life operation because permeation decayed at two orders of magnitude below permeation rates. High-temperature testing (that is, 450°C) resulted in high thermal stress, causing the tubes to crack, which is an important issue to be addressed in future membrane module design.

Acknowledgments

The authors acknowledge support from NanoQuest Pty Ltd. (Australia) and the Queensland Government Department of Innovation and Information Economy's ISUS grants. Our special thanks go to Drs. Peter Gray and Mike Petch from the Fuel Cell Division of Johnson Matthey Plc (UK) for their assistance.

Literature Cited

de Lange, R. S. A., K. Keizer, and A. J. Burggraaf, "Analysis and Theory of Gas Transport in Microporous Sol–Gel Derived Ceramic Membranes," *J. Membr. Sci.*, **104**, 81 (1995).

de Vos, R. M., and H. Verweij, "Improved Performance of Silica Membranes for Gas Separation," *J. Membr. Sci.*, **143**, 37 (1998).

Diniz da Costa, J. C., G. Q. Lu, and V. Rudolph, "Transport Mechanism in Weakly Branched Silica Films," *Adsorption Science and Technology*, D. D. Do, ed., World Scientific Publishing, Singapore, pp. 381–385 (2000).

Diniz da Costa, J. C., G. Q. Lu, V. Rudolph, and Y. S. Lin, "Novel Molecular Sieve Silica (MSS) Membranes: Characterisation and Permeation of Single-Step and Two-Step Sol–Gel Membranes," *J. Membr. Sci.*, **198**, 9 (2002).

Energy Center of Wisconsin (ECW), *Fuel Cells for Distributed Genera-*

tion: A Technology and Marketing Summary, ECW, Madison, WI (2000).

Hasegawa, Y., A. Ueda, K. Kusakabe, and S. Morooka, "Oxidation of CO in Hydrogen-Rich Gas Using a Novel Membrane Combined with a Microporous SiO_2 Layer and a Metal-Loaded γ-Al_2O_3 Layer," *Appl. Catal. A: General*, **225**(1–2), 109 (2002).

Illgen, U., R. Schäfer, M. Noack, P. Kölsch, A. Kühnle, and J. Caro, "Membrane Supported Catalytic Dehydrogenation of SiO–Butane Using an MFI Zeolite Membrane Reactor," *Catal. Commun.*, **2**, 395 (2001).

Jonquieres, A., R. Clement, P. Lochon, J. Neel, M. Dresch, and B. Chretien, "Industrial State-of-the-Art of Pervaporation and Vapour Permeation in the Western Countries," *J. Membr. Sci.*, **206**(1–2), 87 (2002).

Koros, W. J., and R. Mahajan, "Pushing the Limits on Possibilities for Large Scale Gas Separations: Which Strategies?," *J. Membr. Sci.*, **175**, 181 (2000).

Koukou, M. K., N. Papayannakos, N. C. Markatos, M. Bracht, H. M. van Veen, and A. Roskam, "Performance of Ceramic Membranes at Elevated Pressure and Temperature: Effect of Non-Ideal Flow Conditions in a Pilot Scale Membrane Separator," *J. Membr. Sci.*, **155**, 241 (1999).

Kusakabe, K., S. Sakamoto, T. Saie, and S. Morooka, "Pore Structure of Silica Membranes Formed by a Sol–Gel Technique Using Tetraethoxysilane and Alkyltriethoxysilanes," *Sep. Purif. Technol.*, **16**, 139 (1999).

Ledjeff-Hey, K., V. Formanski, T. Kalk, and J. Roes, "Compact Hydrogen Production Systems for Solid Polymer Fuel Cells," *J. Power Sources*, **71**(1–2), 199 (1998).

Lin, Y. M. and M. H. Rei, "Process Development for Generating High Purity Hydrogen by Using Supported Palladium Membrane Reactors as Steam Reformer," *Int. J. Hydrogen Energy*, **25**(3), 2211 (2000).

Ogden, J. M., R. H. Williams, and E. D. Larson, *Toward a Hydrogen Based Transportation System*, Center for Energy and Environmental Studies, Princeton University, Princeton, NJ (2001).

Sotawa, K. I., Y. Hasegawa, K. Kusakabe, and S. Morooka, "Enhancement of CO Oxidation by Use of H_2 Selective Membranes Impregnated with Noble-Metal Catalysts," *Int. J. Hydrogen Energy*, **27**(3), 339 (2002).

Tsai, C., S. Tam, Y. Lu, and C. J. Brinker, "Dual-Layer Asymmetric Microporous Silica Membranes," *J. Membr. Sci.*, **169**, 255 (2000).

Manuscript received Nov. 18, 2003, and revision received Jan. 25, 2004.