

# Hydrostability and Scaling Up Molecular Sieve Silica (MSS) Membranes for H<sub>2</sub>/CO Separation in Fuel Cell Systems

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## Abstract

MSS membranes are a good candidate for CO cleanup in fuel cell fuel processing systems due to their ability to selectively permeate H<sub>2</sub> over CO via molecular sieving. Successfully scaled up tubular membranes were stable under dry conditions to 400°C with H<sub>2</sub> permeance as high as  $2 \times 10^{-6} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$  at 200°C and H<sub>2</sub>/CO selectivity up to 6.4, indicating molecular sieving was the dominant mechanism. A novel carbonised template molecular sieve silica (CTMSS) technology gave the scaled up membranes resilience in hydrothermal conditions up to 400°C in 34% steam and synthetic reformat, which is required for use in fuel cell CO cleanup systems.

## 1 Introduction

Development of cost effective and efficient technologies are required to make fuel cell technologies a viable clean energy alternative [1-4] requiring H<sub>2</sub> as the fuel. A reformer can produce H<sub>2</sub> from hydrocarbon fuels, leaving the by-product CO. A CO clean up stage is then required to bring CO to levels to < 100ppm [5, 6] to avoid poisoning the fuel cell catalyst. MSS membranes have shown over the past decade to have good gas separation over a range of temperatures (0-500°C), some of which are shown in Table 1.

Table 1: Permeance,  $P$ , ( $\times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) and ideal permselectivity of silica membranes reported in literature formed by sol-gel process

P(H <sub>2</sub> )	P(H <sub>2</sub> )/P(N <sub>2</sub> )	P(H <sub>2</sub> )/P(CO)	Area (cm <sup>2</sup> )	Temperature (°C)	Reference
160	20	-	11	200	[7]
100	65	-	11	200	[8]
170	-	33	11	200	[8]
0.38	84	-	2	150	[9]*
10	100	-	1.2	100	[10]
34	320	200	17	80	[11]
20	40	110	13	200	[12]

\* MSS membrane procedure adopted in this work

The above results are for laboratory scales which are in reality too small for most practical applications. For example a reformer produces flow rates in the order of 450slm for a 10kWe fuel cell unit. CO cleanup stages also involve steam yet standard silica membranes are not resistant to steam. However, surfactant templated silica membranes have been proven to be hydrothermally stable as part of membrane reactors for the water gas shift reaction [13]. This paper reports on work done to target these technology hurdles: preparation of

membranes at larger scales, and testing normal and hydrothermally stable carbonised template molecular sieve silica (CTMSS) membranes in synthetic wet reformat.

## 2 Experimental

Porous ceramic tubes supplied by Nikato Ceramics (Japan) were used as membrane supports. The dimensions of the ceramic tubes were external diameter (OD) of 15.6mm, internal diameter (ID) 11.6mm, length of 70mm, a porosity of 43% and average pore size of 0.6 $\mu$ m. The tube surface was smoothed in three stages with 600, 1000 then 2400 grade sandpaper followed by cleaning in an ultrasonic bath then heat treated to 1250°C. Tubes were coated with a pseudo-boehmite sol made from Disperal P2 (Sasol Germany GmbH), UHP water and dilute HNO<sub>3</sub> made into a dipping solution using poly-vinyl alcohol (PVOH) (87-98% hydrolysed, avg MW: 31 000 – 50 000, Aldrich) at a withdrawal speed of 10cm per minute.  $\alpha$ -alumina films were then formed by calcination to 1250°C at a ramping rate of 1°C per minute. The coating stage was repeated then a  $\gamma$ -alumina layer was formed by coating again and heating to 600°C, leaving a smooth surface for preparation of the membrane films.

Membrane formation followed methods covered in previous work [14]. An alumina sol was prepared using Locron (Clariant GmbH, Germany) and coated on the tube at 2cm per minute, followed by heat treatment to 600°C. Intermediate sols for tube coating were prepared using the acid catalysed sol-gel process with tetraethyl orthosilicate (TEOS, Aldrich), methyl triethoxy silane (MTES, Aldrich) ethanol, UHP water and dilute HNO<sub>3</sub>. Selective silica sols were prepared from a highly diluted sol prepared similarly to the intermediate sol, but without methyl templates to form MSS membranes. CTMSS tubes were formed identically, but all sols contained the surfactant triethylhexyl ammonium bromide (Aldrich) at 0.125M. All silica layers were calcined to 500°C in air, except for CTMSS which was calcined in vacuum to preserve organic surfactant groups within the silica structure.

Tubes were sealed in test cells with graphite seals for permeation via a continuous mode setup where active permeation area was 20cm<sup>2</sup>. Gases (He, H<sub>2</sub>, CO<sub>2</sub>, CO and N<sub>2</sub>) were used on the feed side of the membrane at about 2 slm at a pressure of 3 bara. Permeate was recorded by an Aera mass flow meter, venting to atmospheric pressure. Permeance was calculated by dividing flux by the pressure drop and active membrane permeation area. Permselectivity was determined by the ratio of the two calculated permeances. Hydrothermal testing on the CTMSS tubes involved inputting wet reformat at (mol) 34% H<sub>2</sub>O, 26% H<sub>2</sub>, 25% N<sub>2</sub>, 8% CO<sub>2</sub>, 7% CO while permeate and retentate concentration was measured with Maihak gas analysers.

## 3 Results and Discussion

### 3.1 Pure Gas Permeation

Stable permeation results to 400°C for MSS and CTMSS membranes are shown Figure 1. At 200°C, the H<sub>2</sub> permeance for the MSS tube was 9.8 x 10<sup>-7</sup> mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>, and H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CO permselectivities were both 5.9. The CTMSS tube performed even better, with H<sub>2</sub> permeance (200°C) at 19 x 10<sup>-7</sup> mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>, and H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CO permselectivities both 6.4. Permeance

and permselectivity of both tubes were similar, suggesting the presence of carbonised surfactant in the CTMSS tube did not affect the silica sieve matrix. Permeance in the tubes was high compared to the smaller scales presented in Table 1, while permselectivity was 1 - 2 orders of magnitude less. This may be attributed to a greater contribution of defects from the larger scaled up area. Greater care must be taken when scaling up MSS technology. The ceramic must have a smooth defect free surface before careful coating of selective layers in dust-free conditions.

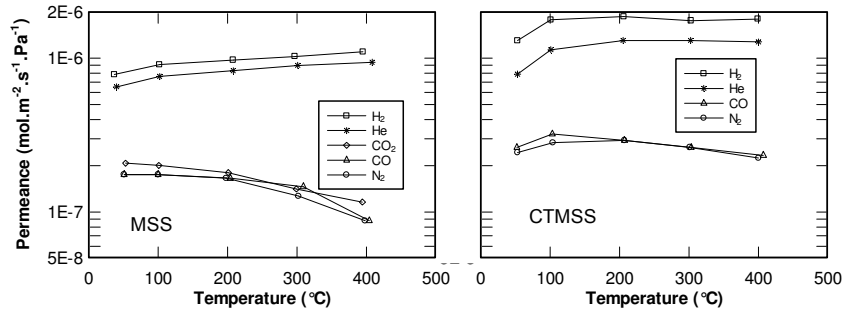


Figure 1: Pure gas permeance against temperature for scaled up MSS and CTMSS tubes, 2 bar  $\Delta P$ .

Permselectivity was higher than the ideal Knudsen separation value of 3.7, indicating the domination of the more selective separation mechanism molecular sieving. Permeation was activated with temperature for  $H_2$  and He only. According to Barrer's model for activated transport [15], molecules require an activation energy to 'jump' between sites through the pores of the selective film. If the heat of adsorption is greater than the mobility energy through the membrane, permeance will decrease with temperature, which was true in our case for  $CO_2$ , CO and  $N_2$ . The plateau at 100°C observed only for the CTMSS tube may be due to sealing leaks at low temperature.

### 3.2 Hydrothermal Stability

Hydrothermal stability of the MSS and CTMSS tubes in wet synthetic reformat is shown in Figure 2.

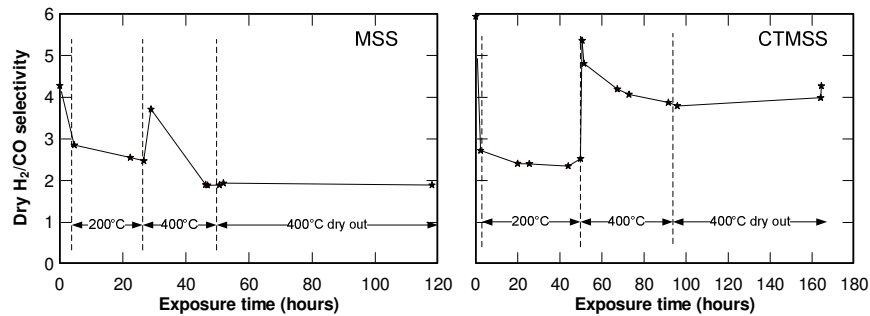


Figure 2: Hydrothermal stability of NS (MSS) and NLC (CTMSS) membranes in wet synthetic reformat

Both membranes shown reduced permselectivity at 200°C from an initial dry condition at  $t=0$ . However, upon heating to 400°C, some permselectivity returned on the CTMSS tube, while MSS tube selectivity continued to drop. Since CTMSS was more hydrothermally stable, irreversible structure change was greatly reduced. In both cases, the highly hydrophilic silica surface impeded the flux of H<sub>2</sub> at 200°C. When temperature was increased, micropore occupancy of water decreased, as shown by the increase and eventual stabilisation in CTMSS selectivity. By the same token, the MSS membranes showed evidence of irreversible pore widening as selectivity never returned, even after water was stopped at 50 hours. This effect has also been observed in literature [13]. Hence, the CTMSS technology showed its potential for practical application in wet reformat CO clean up.

#### 4 Conclusions

Our scale up work produced tubes that displayed domination of selective transport mechanisms better than Knudsen ideal selectivity, but inherent substrate defects led to contributions from less selective transport. Use of a substrate specifically tailored to this application would be expected to minimise these defects. CTMSS membrane technology showed equivalent permselectivity to the MSS tube, but superior hydrothermal stability. These results suggest the potential of CTMSS technology to develop membranes for CO clean up in fuel cells.

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