



Performance of cobalt silica membranes in gas mixture separation

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ABSTRACT

In this work we investigate the performance of cobalt silica membranes for the separation of gas mixtures at various temperatures and partial pressures. The membranes were prepared by a sol–gel process using tetraethyl orthosilicate (TEOS) in ethanol and H₂O₂ with cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O). The membranes complied with molecular sieving transport mechanism, delivering high single gas selectivities for He/N₂ (4500) and H₂/CO₂ (1000) and high activation energy for the smaller gas molecules (He, H₂) whilst a negative activation energy for larger molecules (CO, CO₂ and N₂). Molecular probing results strongly suggest membranes with a narrow pore size distribution with an average pore size of 3 Å. The effect of gas composition on the membrane operation was studied over both binary and ternary gas mixtures, and compared with the single gas permeance results. It was found in both cases feed concentration had a large impact on both selectivities and flow rates. These followed a trade off inverse relationship, as increasing H₂ feed concentration led to a higher flow rate but a lower H₂ selectivity, though H₂ purity in the permeate stream increased. The use of sweep gas in the permeate stream to increase the driving force of gas permeation was beneficial as the H₂ flow rate and the H₂ recovery rate increased by a factor of 3. It is noteworthy to mention that though the ternary feed flow had only 27% H₂ concentration, the permeate stream delivered CO and CO₂ at very low concentrations, 0.8 and 0.14%, respectively. It was observed that the membrane selectivity in gas mixtures were 10–15% of the single gas selectivity, while permeation decreased with the gas composition (Single > Binary > Ternary). Nevertheless, increased temperature and sweep flow rate allowed the membrane to deliver a permeate stream in excess of 99% H₂ purity and a lower CO concentration of 700 ppm, indicating the quality of these membranes for gas mixture separation.

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1. Introduction

With the advent of a carbon constrained economy and the production of H₂ as an energy carrier for clean energy delivery; there has been a surge in research effort worldwide towards gas separation. There are major benefits for separating gases at higher temperatures (>200 °C) to avoid energy penalties associated with cooling down gases [1]. Inorganic membranes derived from sol–gel, CVD or alloyed palladium is thermally robust for high temperature gas separation [2–7]. The production of H₂ is likely to benefit many sectors of the economy, in particular the transportation sector by using fuel cells fuelled by H₂. The first generation of H₂ production technologies is likely to utilise fossil fuels in processes such as reforming or gasification. What becomes obvious in these industrial processes is the complexity of separating gas mixtures due to the

relatively high number of components and low concentration of H₂ found within the product stream [8]. Typical analysis of membrane permeation and selectivity reported in the literature utilises a single gas permeation test for the given gases. Limited work reported for H₂/CO₂ gas mixtures [9,10], showed that the feed gas concentration affects both H₂ flow rates and selectivities. Recently, Gopalakrishnan and Diniz da Costa [11] used CVD membranes to show the H₂ purity in the permeate stream was controlled by temperature and feed H₂ partial pressure. Hence, single gas values may not fulfil the requirements to predict mixed gas permeation and separation for industrially scaled systems.

The water gas shift (WGS) is an important reaction extensively used in reforming or gasification processes in the optimisation of H₂ production. The WGS reaction is mildly exothermic and equilibrium limited as shown in Eq. (1). It is important to convert as much CO as possible, as even ppm levels of CO poisons the catalyst in PEM fuel cell systems [12–14]. However, this reaction does not go to full completion and there is a requirement to reduce CO concentrations to the level suitable for fuel cell operation, which can be achieved by employing inorganic membranes. By reducing CO down to these

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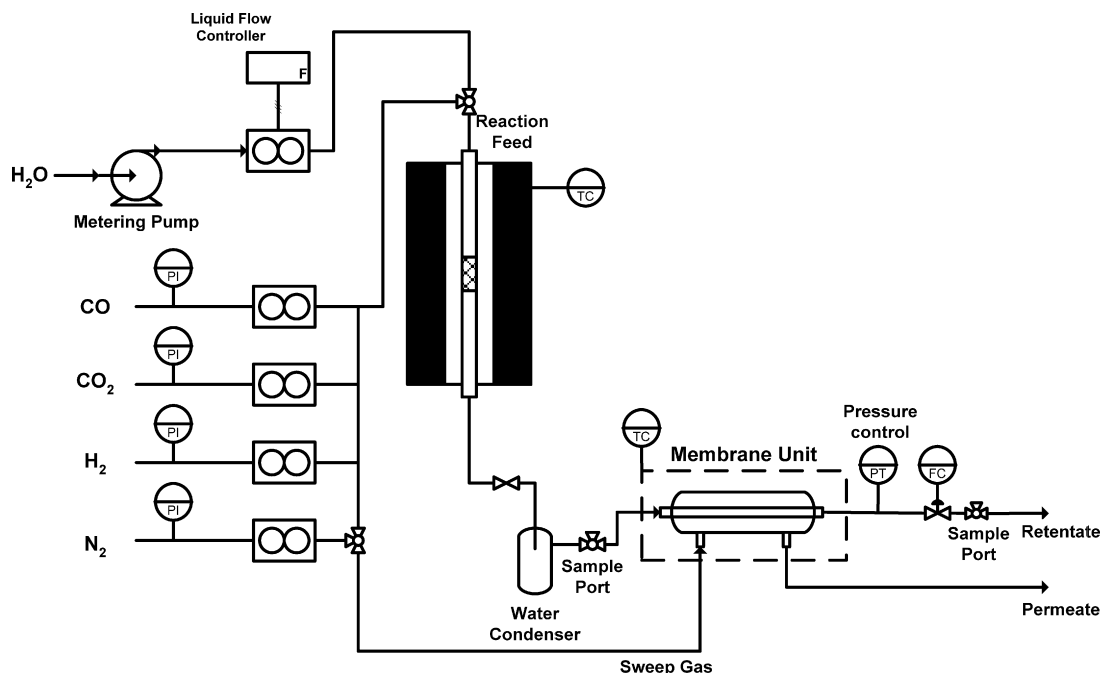
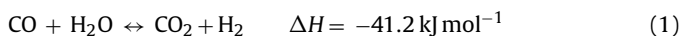


Fig. 1. Schematic of post-reaction membrane module.

levels a membrane separation system would remove the need for additional expensive downstream processing such as a low temperature shift and partial oxidation reaction step. This is reliant on the quality of the membrane to provide sufficiently low CO levels for PEM fuel cells.



The capability of porous inorganic membranes to separate H_2 (i.e. selectivity) is fundamentally controlled by the tailored narrow pore size distribution, with an average pore size below the kinetic diameter of other gases such as CO_2 , CO , CH_4 and N_2 [9,15]. On the other hand, the thickness of the membrane adds a resistance against the diffusion of gases, thus requiring membranes to be as thin as possible to allow high flow rates. For industrial applications, membranes should ideally deliver very high selectivities and flow rates, though in reality these parameters have to be traded off, as high selectivities are associated with low flow rates and vice-versa. In the case of porous inorganic membranes where the transport mechanism is regimented by molecular sieve properties [16], H_2 exhibits temperature-activated transport whilst CO_2 shows the opposite trend [3,17]. This forms part of an important engineering property, as H_2 flow rate (flow rate or permeation) and H_2/CO_2 selectivity increase with temperature. As previously reported, metal-doped silica membranes conform to an activated transport mechanism [18,19]. However, in the case of membranes operating in industrial processes containing multi-component gas streams, both selectivity and flow rate also become a factor of the operating conditions, such as feed pressure, gas composition and permeate pressure which can be assisted by vacuum pump or a sweep gas.

A number of publications have looked at the application of a sweep gas for different membrane reactor systems [20–22], noting that an increase in sweep led to enhanced conversion through enhanced separation. Although these authors did not report the effect of permeate vacuum or sweep gas on flow rate and product concentration, Brunetti et al. [23] showed that higher feed pressures (4–6 atm) gave an undesirable loss of membrane selectivity resulting in higher concentrations of CO in the permeate for a WGS membrane reactor. The effect of sweep gas or vacuum in separa-

tion of a binary N_2/CO_2 mixture was investigated over both silica [24] and zeolite [25] membranes, resulting in improved flow rate and selectivity. Increasing the total feed pressure [23–25] or the feed partial pressure [11] of a gas mixture stream allowed for the increase in permeate flow rate and selectivity.

In this work, we use high quality hydrogen selective cobalt silica membrane to investigate the effect of operating conditions on the flow rate and selectivity for single, binary and ternary gas compositions. A ternary gas composition was supplied via a WGS packed bed reactor, whilst a binary mixture was made up by mixing gases using mass flow controllers. Cobalt-doped silica tubular membranes were fabricated using sol-gel techniques and tested under dry gas conditions. Membrane characteristics were analysed for varying gas compositions and H_2 feed concentrations, investigating gas mixture effects on H_2 transport and selectivity through the membrane at different temperatures. Pressure and sweep gas were used as methods to improve the membrane driving force for optimised flow rates and selectivity.

2. Experimental

Commercial Noritaki alumina tubes (OD: 11 mm, length: 120 mm) coated with a top γ -alumina layer were used as the membrane substrate. Cobalt silica sol was prepared through the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol and H_2O_2 with cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as described elsewhere [26]. A solution of 42.2 g TEOS in 600 g ethanol was added to a second solution of 51.8 g cobalt nitrate in 30% (w/w) aqueous H_2O_2 and vigorously stirred for 3 h in an ice-cooled bath. The tubular substrates were then dip-coated lengthwise into a beaker of the stable sol using a controlled dipping and removal speed of 2 cm min^{-1} and an immersion time of 1 min. A total of six layers were deposited on the tube substrates. Sintering was carried out for each layer in air at 600°C for 4 h at a ramp rate of $0.7^\circ\text{C min}^{-1}$. Finally the membranes were calcined in H_2 at 500°C for 15 h to reduce the cobalt oxide within the selective silica layer. The membrane had a length of 60 mm and an effective permeation area of 20 cm^2 . SEM was performed using a JEOL JSM-6400F scanning electron microscope. Membrane cross-sections were made

conductive using platinum coating with an EIKO coating apparatus in high purity argon.

The reactor and membrane module set up used in these experiments is depicted in Fig. 1. A reactor for the WGS reaction was set at the front end of the membrane module. Reaction gas was produced in a steel tubular packed bed reactor, utilising a high temperature FeCr catalyst in a tubular furnace. The catalyst was activated prior to experimentation following manufacturer's protocols at 250 °C with 20% H₂ and 20% H₂O in N₂ at 20 ml min⁻¹ total flow. After the reaction furnace, steam was removed from the gas stream using an ice cooled water condenser prior to injection into the membrane unit. The membrane was sealed using Viton rubber O-rings. Gas was fed to the tube side of the membrane with permeate sweep gas applied to the shell side, operated in a counter current manner. Reaction pressure was maintained using a Swagelok backpressure valve and measured with an MKS Baratron type pressure transducer, while both reactor and membrane temperature was controlled individually using separate tubular furnaces connected to a Brainchild PID temperature controller. All gas flows were controlled using high precision Cole Parmer rotameters and permeate flow rate was measured using bubble flow meters. Mixed gas compositions were measured from permeate and retentate outlet streams using a Shimadzu GC-2014 using a Porapak Q column with thermal conductor detector (TCD) and flame ionisation detector (FID).

The permeation tests were carried for single, binary and ternary gas mixtures. Single gas permeation was carried out using the dead end method. For binary gas permeation tests, H₂ and CO₂ at the desired concentrations in the feed stream were precisely controlled by MKS flow controllers. In the case of ternary gas mixture, the experimental set up in Fig. 1 was employed. For both binary and ternary gas testing, the feed pressure was set by the gas bottle regulator pressure and precisely controlled via a backpressure regulator on the retentate outlet. This provided a pressurised gas flow through both the reactor and membrane system. Sweep gas flow rate was also used and controlled by a Cole Parmer rotameter connected directly to the permeate inlet at atmospheric pressure. This was applied to the module in counter current flow. Total permeate flow rate was measured using bubble flow meter, with GC gas concentration measurements used to determine H₂ content in the sweep flow, providing the corrected H₂ flow rate through the membrane. Gas composition of the ternary reaction mixture was changed by manipulating reaction conversion in the tube reactor. This was controlled via the reaction temperature in the furnace set by the PID controller. Gas feed to the reactor containing H₂O to CO molar mixture of 2:1 was maintained at a constant flow rate throughout testing. Temperature of permeation was then set by a separate PID controller connected to a jacket heater surrounding the membrane module.

In this work, the selectivities were calculated according to the normalised flow rates of gases as shown in Eq. (2) for single/binary/ternary gas mixtures. The equation includes flow rates F (ml min⁻¹), the driving force Δp (Pa) and two gases (i and j):

$$\alpha_{i/j} = \left(\frac{F_i / \Delta p_i}{F_j / \Delta p_j} \right) \quad (2)$$

3. Results and discussion

Fig. 2 shows an SEM photo of the cross-section of a cobalt-doped silica membrane. The membrane had an γ -alumina intermediate layer of $\sim 3 \mu\text{m}$ to ensure a smooth defect free surface for coating of the selective top layer. The thickness of the cobalt silica top layer was approximately $0.25 \mu\text{m}$ with uniform coverage. Single gas permeance of the membrane was tested for He, H₂, CO, CO₂ and N₂ as shown in Fig. 3a. The ratio of the permeance of two gases at each temperature was calculated to give the single gas selectivity of the

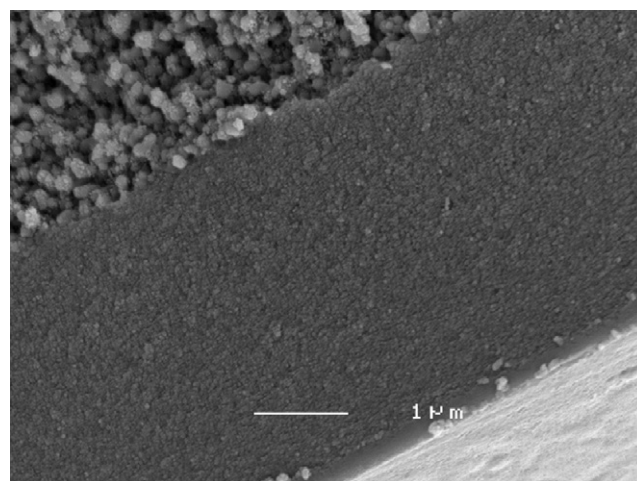


Fig. 2. Cross-section of co-doped silica membrane (5 kV and 19,000 \times). Top left corner (α -Al₂O₃), middle (γ -Al₂O₃) and bottom right corner (cobalt-silica layer).

membrane (Fig. 3b). The permeance of this membrane exhibited significant temperature activation for the smaller gases (He and H₂) whilst negative activation for the larger gases (CO, CO₂ and N₂). Helium showed the greatest permeance, increasing from 7×10^{-10} to $3 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ while H₂ changed from 5×10^{-10} to $6 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, as temperature increased from 100 to

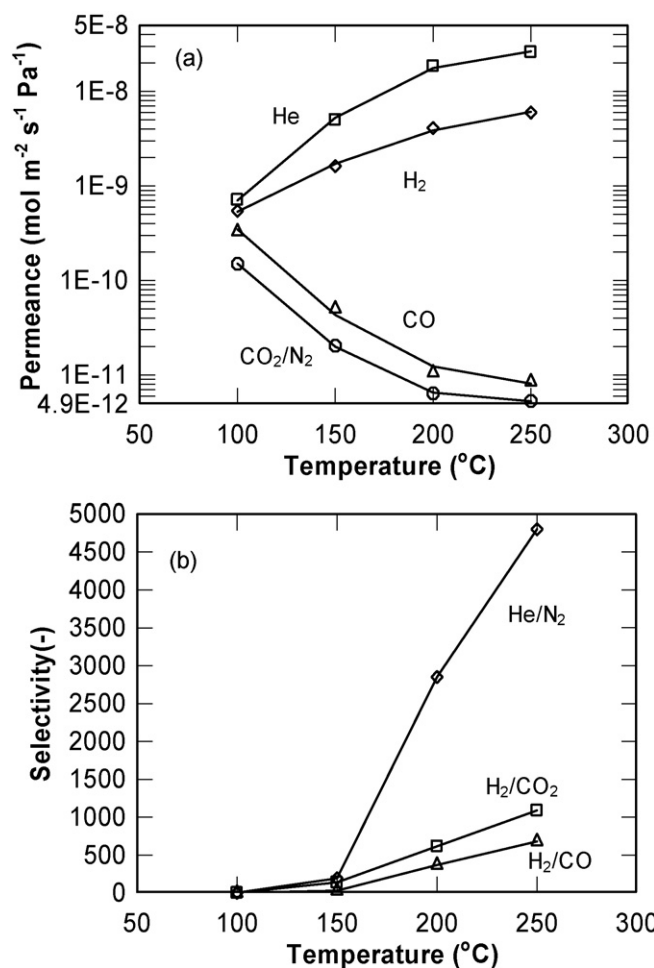


Fig. 3. (a) Temperature dependency of membrane single gas permeance and (b) single gas selectivity.

250 °C. The larger molecular gases exhibited reducing permeance with CO decreasing from 3×10^{-10} to 8×10^{-12} mol m⁻² s⁻¹ Pa⁻¹. These results strongly indicate activated transport or molecular sieving mechanism as observed elsewhere [3,17,27] and following a temperature dependency flow rate equation derived from Barrer's microporous crystalline diffusion [28]:

$$J_x = -D_o K_o \exp\left(\frac{-E_{\text{act}}}{RT}\right) \frac{dp}{dx} \quad (3)$$

where J is the flow rate (mol m⁻² s⁻¹) through the membrane, E_{act} (kJ mol⁻¹) is an apparent activation energy, R the gas constant and T the absolute temperature (K), D_o and K_o are temperature independent proportionalities for the Arrhenius and Van't Hoff equations, respectively. As a result of this temperature dependent transport process, single gas selectivity increased for He/N₂ (200–4800) and H₂/CO₂ (70–1000). The activation energy in kJ mol⁻¹ for single gas permeation calculated according to an Arrhenius relationship was 20.7 (He), 12.8 (H₂), -21.75 (CO) and -20 (CO₂). The large selectivities ($\gg 100$) in tandem with temperature activation for smaller (He and H₂) gas molecules and negative activation for larger molecules (CO, CO₂ and N₂) strongly suggest that the membrane synthesised had high precision pore size tailorability. In view of the high quality of the membrane, the molecular probing results suggest a narrow pore size distribution with an average pore size of 3 Å, between the molecular diameter of H₂ (2.9 Å) and CO₂ (3.3 Å).

Mixed gas separation of the membrane was tested with a binary H₂/CO₂ gas mixture at 150 and 200 °C. The effect of gas composition on the permeate outlet concentration, and on membrane flow rate and selectivity was analysed in Fig. 4(a) and (b), respectively. The permeate concentration of H₂ increased very quickly to 78% at 150 °C and 95% at 200 °C for a feed H₂:CO₂ concentration of 25:75. In other words, the membrane was able to purify H₂ from 25 to 95% in a single stage pass only. From there on, H₂ purity in the permeate streams increased as a function of the H₂ feed concentration reaching 99.5% for H₂:CO₂ concentration of 75:25. These results strongly suggest the production of a high quality membrane which was capable of processing H₂ at low feed concentration. This was further reflected in the membrane H₂/CO₂ selectivity shown in Fig. 4(b). For low H₂ and high CO₂ feed concentrations, the membrane delivered H₂/CO₂ selectivity close to single gas selectivity. However, as the H₂ concentration in the feed stream increased, the selectivity decreased accordingly to a value of 8 at 150 °C and 45 at 200 °C as the feed H₂ concentration approached 100%. Nevertheless, this did not mean that the membrane was not performing. Although the selectivity was only 8, in fact H₂ gas purity in the permeate stream was in excess of 99%. This contradictory trend is closely related to the way the selectivity is calculated as per Eq. (2). In principle, selectivity works very well for showing the difference in single gas permeation, but not for gas mixtures. By the same token, the H₂ feed concentration had a positive impact on the membrane flow rate, with the H₂ flow rate in the permeate stream approaching the values observed for single gas flow (1.41 ml min⁻¹ at 150 °C) as the H₂ feed concentration reached 100%. As the H₂ feed concentration decreased, the feed stream CO₂ concentration was high. As a result, the H₂ flow rate rapidly approached zero as the H₂ partial pressure of the composition became insufficient to provide the required driving force for H₂ permeation. In this case, at 20% H₂ feed the partial pressure across the membrane was 10 kPa and the total flow rate was 0.05 ml min⁻¹.

Separation of a reaction synthesised ternary H₂/CO/CO₂ gas mixture is depicted in Fig. 5. At the membrane temperature of 200 °C with a 5 ml min⁻¹ sweep permeate gas to ensure sufficient partial pressure driving force across the membrane, the H₂ concentration increased from a 20 to 50% in the feed stream to a permeate stream concentration of 97.5–99.25%. This provided up to 77.5% H₂ increase across the membrane and a maximum H₂ recovery rate of 30%. With

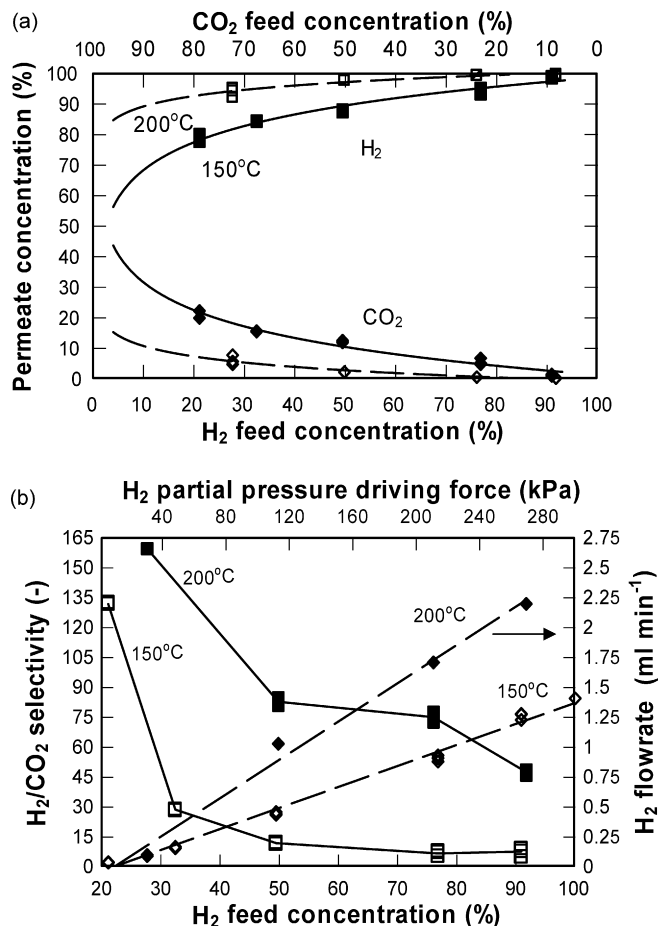


Fig. 4. Concentration dependant separation of binary H₂/CO₂ mixture (a) permeate stream concentration and (b) membrane flow rate and H₂/CO₂ selectivity (selectivity, solid line; membrane flow rate, dashed line) 4 atm inlet pressure, no sweep gas.

decreasing CO content in the feed stream, the membrane was able to reduce CO permeate concentration down to 700 ppm (0.07%). CO₂ was not so sensitive to feed concentration, varying only slightly around the 0.5% concentration mark. At H₂ feed concentrations below 20%, the H₂ partial pressure was unable to provide enough permeate flow for feasible testing. In this case, the H₂ driving force became negligible. Fig. 5(b) compares the selectivity and flow rate of membrane operation both with (solid line) and without (dashed line) sweep gas. Sweep gas increased the driving force for H₂ permeation and was more prominent in the case of H₂/CO₂ selectivity which increased from 50 to 200. By reducing the partial pressure on the permeate side of the membrane, which comprises of 99% H₂, a sweep gas selectively improved H₂ driving force, while providing only minimal change (1%) to the CO₂ driving force.

The change in membrane permeation rate, with and without sweep, over varying feed concentrations is shown in Fig. 6. With the use of a 5 ml min⁻¹ sweep gas, the membrane flow rate increased by a factor of 3, from 0.6 to 1.8 ml min⁻¹. This had a large effect on the effective H₂ recovery of the membrane increasing from 10 up to 30%. However, increasing H₂ feed concentration also increased the flow rate, though the recovery rate decreased. With higher volumes of H₂ in the feed stream, the membrane must separate more H₂ or the feed flow rate must be decreased to maintain the recovery rate. Therefore, there is a trade off between these two parameters.

Increasing feed pressure or permeate sweep gas are the two main methods utilised to optimise membrane flow rate during operation. For the sweep test (Fig. 7a) at low feed pressure (404 kPa), low concentration of H₂ (27%) was used to investigate the effect of

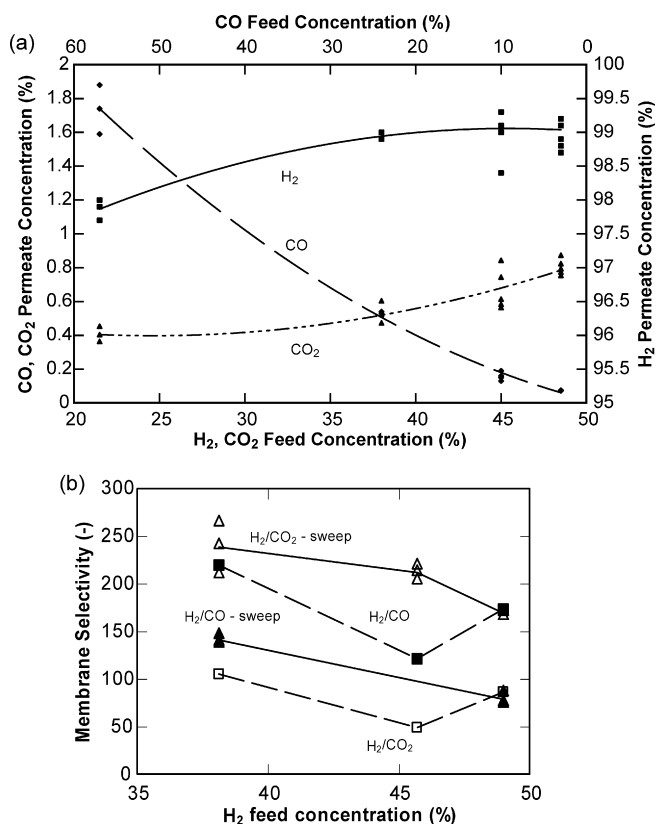


Fig. 5. (a) Concentration dependant separation of ternary H₂/CO/CO₂ gas mixture at 200 °C and 4 atm inlet pressure and (b) H₂/CO₂ selectivity under the same testing conditions (Δ , H₂/CO; \square , H₂/CO₂; closed symbol, 5 ml min⁻¹ sweep gas; open symbol, no sweep).

sweep at a low partial pressure driving force commonly found in industrial gas mixtures. The initial increase of sweep flow rate to 2 ml min⁻¹ (sweep/permeate ratio = 2.5) had a large effect on the H₂ concentration in the permeate stream which increased from 94 to 98%. However, further increases delivered marginal improvements with a top H₂ purity of 99.1% achieved using 12 ml min⁻¹ sweep flow rate (sweep/permeate ratio = 10). The CO permeate concentration was reduced down to a minimum of 0.8%, while the CO₂ was substantially reduced, reaching a permeate concentration of 0.14%. The sweep had a positive effect on membrane selectivity,

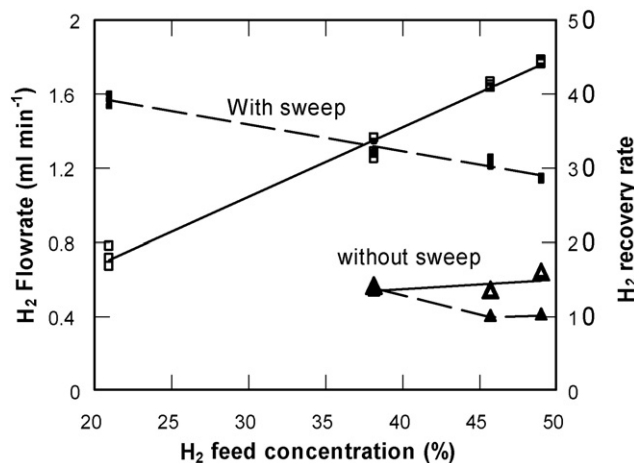


Fig. 6. H₂ concentration dependant flow rate of membrane for ternary gas separation with permeate sweep (closed symbols) and without permeate sweep (open symbols). Solid lines, membrane flow rate; dashed line, H₂ recovery factor.

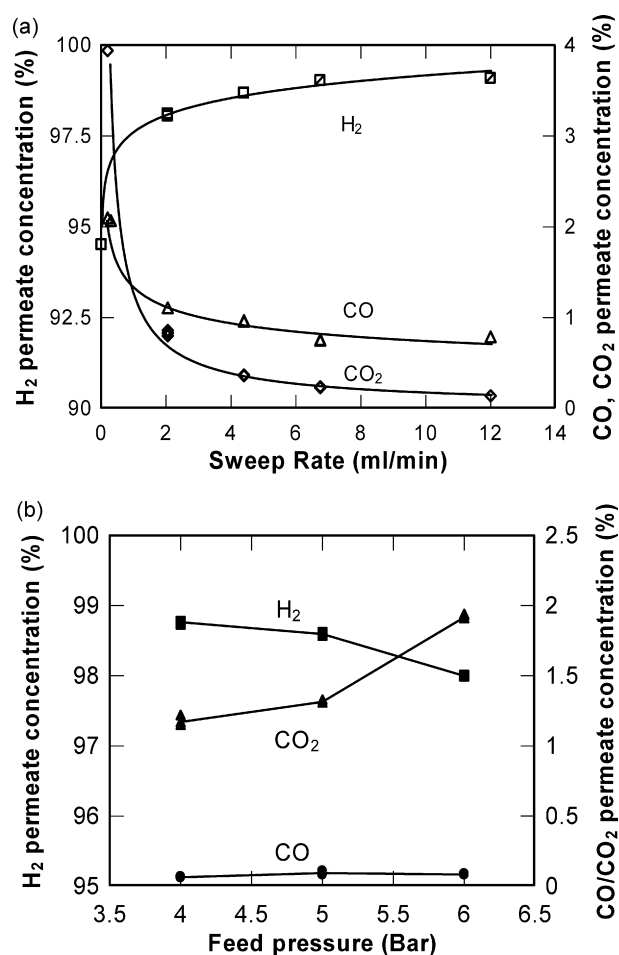


Fig. 7. Effect of sweep gas (a) and feed pressure (b) on membrane permeate concentration (temperature -250 °C): (a) 4 atm inlet pressure, 27/27/45% mix of H₂/CO₂/CO and (b) no sweep, 47/47/6% mix of H₂/CO₂/CO.

increasing H₂ concentration while decreasing the CO and CO₂ concentrations.

The effect of increasing feed pressure (Fig. 7b) was also investigated over higher H₂ concentrations (47%) to ensure sufficient partial pressure driving force for membrane permeation without the need of a sweep gas. At the lower CO feed concentration (6%) the membrane was able to provide improved separation over the high concentration scenario, reducing the CO permeate concentration down to 700 ppm. However, the H₂ permeate concentration did not change significantly over those results as shown in Fig. 7a, reaching a maximum of 99%. In addition, increasing pressure proved to have no major benefit on selectivity, with H₂ concentration slightly decreasing with higher pressure, while CO increased to 1000 ppm and CO₂ increased from 1 to 2%.

Both sweep gas and feed pressure worked by improving the driving force for the component gases within the mixture. However, they were applied to different sides of the membrane tube and these parameters give different performance depending on the membrane operation conditions. Fig. 8 shows the effect of both conditions on the membranes selectivity. It can be seen that sweep gas had an improving effect on selectivity contrary to the effects of feed. In this case the sweep gas provided a H₂/CO₂ selectivity of 700 at its optimum driving force, compared to a selectivity of 125 found at the highest feed pressure, whilst H₂/CO selectivity improved from 50 to 225 with the use of a sweep gas.

The employment of a sweep gas is largely directed to the relatively low partial pressure resulting in a low driving force. As it

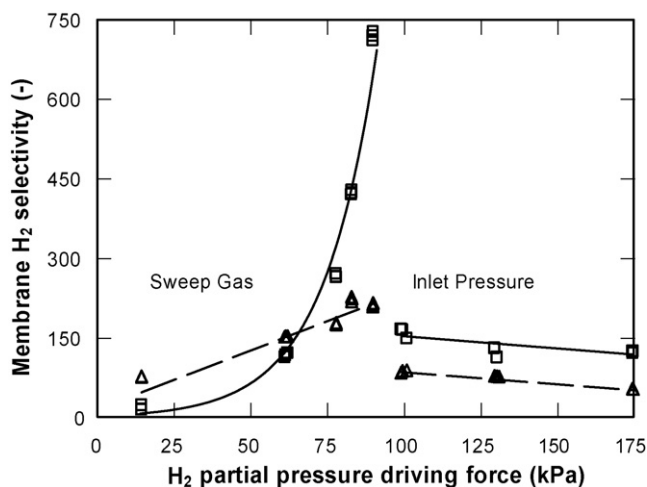


Fig. 8. Comparison of sweep gas and pressure effects on membrane selectivity (H_2/CO : ■, solid line; H_2/CO_2 : ♦, dashed line).

works on the permeate side of the membrane, sweep gas can only provide a maximum of 101 kPa of potential driving force, while there are no limits for the feed pressure with values reported up to 1500–2000 kPa [29–31]. Fig. 9 shows the effect of both conditions on the permeate flow rate of the membrane. For the case of a low H_2 feed concentration (27%) the use of a sweep gas doubled the membranes permeation rate. However when the concentration was not such a limitation to operation (~50%) feed pressure could be used to provide increased permeation. The application of a 600 kPa feed pressure doubled the partial pressure driving force, and as a consequence the permeation also doubled. As feed pressure was applied to all gases in the mixture, a low concentration H_2 feed reduced the effectiveness of H_2 feed pressure to improve its driving force. The useful application of sweep gas is therefore limited to low pressure or low concentration applications where increased pressure is insufficient for feasibly removing H_2 from a gas mixture in a membrane operation.

Fig. 10 shows the effects of single, binary and ternary gas mixtures on the permeance and selectivity of H_2 for a given driving force (100 kPa). It is observed that the membrane permeance decreased with the gas composition (i.e. Single > Binary > Ternary) as single gas flow rates were 25% and 100% higher than binary and ternary flow rates, respectively at the lower temperature (150 °C). For ternary gas mixtures, a 3–4% addition of CO to the H_2/CO_2 feed stream had

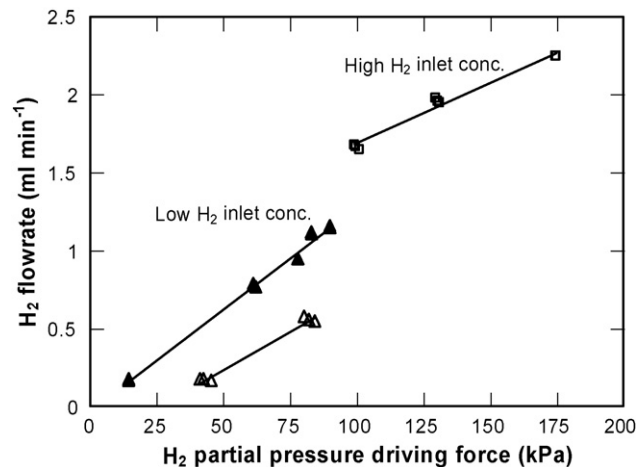


Fig. 9. Comparison of sweep gas and pressure effects on membrane flow rate (sweep gas, closed symbols; pressure, open symbols).

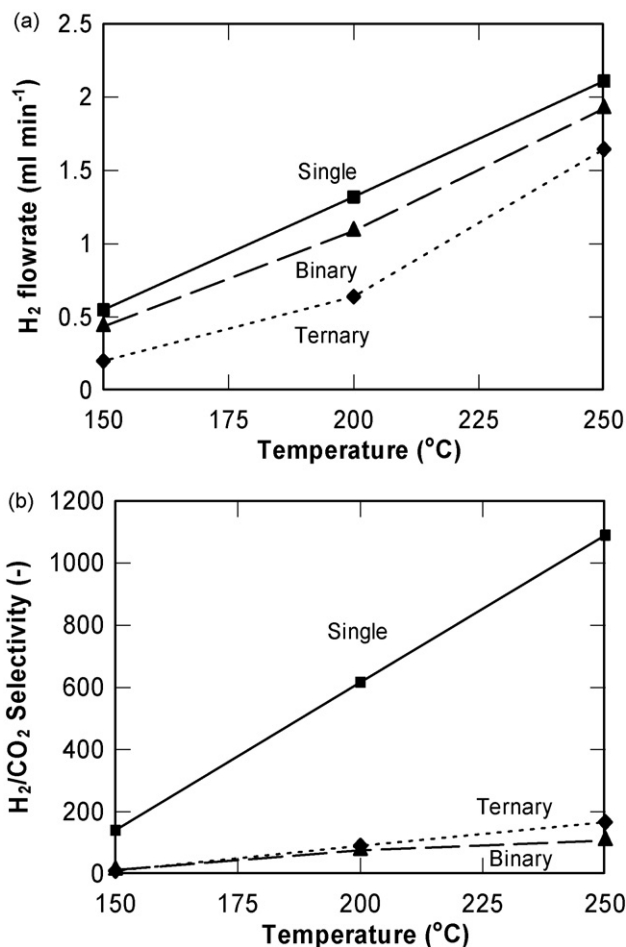


Fig. 10. Effect of binary and ternary gas mixtures on (a) normalised membrane H_2 flow rate ($\Delta P_{\text{H}_2} = 100$ kPa) and (b) membrane H_2/CO_2 selectivity.

a significant effect on membrane permeance, reducing to 50% of the binary mixture permeation rate. Increased temperature mitigated the effect of gas composition; with single gas providing only 10 and 16% more flow rate than binary and ternary gas mixtures at 250 °C. The membrane H_2/CO_2 selectivity (Fig. 10b) also decreased for gas mixtures, exhibiting 10% of the selectivity for single gas permeance. However, little difference was seen between H_2 separation in binary and ternary gas mixtures. Gas mixture selectivity improved slightly with temperature, increasing to 15% of the single gas selectivity, which could be attributed to the reduction in gas adsorption on the membrane surface and thus reduced pore blockage.

The effect of gas mixtures on permeation and selectivity is attributed to several factors. The chemical potential of the feed gas mixture may allow for the larger kinetic diameter molecules (CO_2 and CO) to momentarily block those smaller pores that are accessible only to H_2 molecules [11]. The blockage of the micropores reduced the effective percolation of H_2 through the membrane as discussed elsewhere [32], thus influencing the flow rates and selectivity at different gas compositions (Fig. 10). This process was competitive and more prominent for higher CO and CO_2 feed concentrations, substantiated by a significant reduction in the H_2 flow rate (Fig. 6). Temperature played a vital role in this competitive process, as H_2 diffusivity and CO and CO_2 adsorption followed an inverse trend. Thus, increasing temperature leads to higher H_2 pore diffusivity, while decreasing the competitive effect of CO and CO_2 adsorption into the micropores [5]. By the same token, the opposite effect was observed for lower temperatures also substantiated by the results in Fig. 10.

In this work, high selectivities were achieved, but the trade off was low gas permeation. This can be related to the cobalt silica film thickness of 250 nm as observed via the SEM micrograph. As the permeation is inversely proportional to the membrane thickness, then reducing the thickness will likely to increase permeation. Nevertheless, the separation of gas mixtures showed that using single gas permeation only does not provide the required engineering parameters to design unit operations for industrial applications. Gas separation becomes more complex as the number of species increase from 2 (binary) to 3 (ternary). It was also demonstrated that using sweep gas enhanced gas separation, which is a technique generally used in laboratory scale experiments. Again, industrial systems are likely not to operate with sweep gases as it may defeat the purpose of separating gases. This means that separations are likely to be lower for industrial systems due to reduced partial pressure or driving force. On the other hand, separating gases at high temperatures is very advantageous in industrial processes. Conventional separation technologies such as adsorption or desorption require processing gases at low temperatures, many times below 50 °C, which attracts a major energy penalty associated with cooling duties. In addition, the combined effect of high temperature and activation energy are very attractive as shown in this work. Both H₂ permeation and H₂ purity in the permeate stream increased with temperature.

4. Conclusions

High quality cobalt silica membranes were synthesised in this work giving a H₂ permeance ($1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) at 250 °C and high single gas selectivities (He/N₂ 4500). Single gas tests indicated temperature activation for smaller (He, H₂) gas molecules and negative activation for larger molecules (CO, CO₂ and N₂). Molecular probing results strongly suggest a membrane having a narrow pore size distribution with an average pore size of 3 Å, between the molecular diameter of H₂ (2.9 Å) and CO₂ (3.4 Å).

The effect of gas composition on the membrane operation was studied over both binary and ternary gas mixtures, and compared with the single gas permeance results. It was found in both cases feed concentration had a large impact on both the selectivity and the flow rate of the membrane. These followed an inverse relationship, as increasing H₂ feed concentration improved the flow rate but decreased the H₂ selectivity, indicating that there is a trade off between the two characteristics for gas mixture separation. Nevertheless, H₂ purity increased though selectivity reduced, which is closely related to the way that selectivity is calculated for gas mixtures. The use of sweep gas on the permeate stream to increase the H₂ partial pressure driving force was beneficial as the H₂ flow rate and the H₂ recovery rate increased by a factor of 3. On the other hand, increasing H₂ feed concentration also increased the flow rate, though the recovery rate decreased. With higher volumes of H₂ in the feed stream, the membrane must separate more H₂ or the feed flow rate must be decreased to maintain the recovery rate.

It was observed that the membrane permeation decreased with the gas composition (i.e. Single > Binary > Ternary) with single gas providing up to three times the flow rate and nine times the selectivity of binary and ternary gas mixture separation. It could be seen that mixed gas separation was more complex than single gas, with more variables to control both flow rates and selectivity. While there was little difference between selectivity of binary and ternary mixtures, the H₂ flow rate in ternary gas was 50% lower than in a binary mixture, thus showing of the competitive effect of separating complex gas mixtures.

It is noteworthy to mention that during separation of the ternary mixture, both at 200 and 250 °C, the membrane delivered 99% purified H₂ in the permeate stream, in addition to reducing the CO concentration from 10% down to 700 ppm. The H₂ purity was

increased in the permeate stream by using both higher feed concentration, increased temperatures and the application of a sweep gas, with a maximum of 99.5% purity.

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