The potential for use of cellulose triacetate membranes in Post Combustion Capture

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Abstract

Cellulose triacetate (CTA) membranes occupy much of the gas separation market in natural gas processing. With a high CO₂/N₂ selectivity, this material may also be prospective for post-combustion carbon capture, if the permeance can be optimised. In capture applications, the impacts of liquid water condensate of variable pH, SO_x and NO_x on the gas separation performance are of critical interest to ensure maximum membrane lifetime. In this work, dense CTA membranes were aged in pH solutions of 3, 7 and 13 for a total of 60 days. It was found that the plasticisation of the CTA membrane when aged in pH 3 and pH 7 solutions enhanced the permeability of CO₂ and N₂ by over 30% with little impact on CO₂/N₂ selectivity. Conversely, the membrane aged at pH 13 failed due to hydrolysis reactions. The membrane was selective for SO₂ over CO₂ with a SO₂ permeability of 20 Barrer. Conversely, NO did not readily permeate, so that the permeate composition was below the level of detection. CTA membranes stored in SO₂/N₂ and pure N₂ for a 120 day period at 22°C were relatively stable, with a slight loss in permeability due to membrane aging. Conversely, a significant loss in permeability was observed when these membranes were exposed to 0.74 kPa of NO for the same period. The performance loss appeared to relate to reaction of alcohol groups within the cellulose acetate structure with trace levels of NO₂ in the gas mixture. The results highlight the possibility for use of CTA membranes in post-combustion capture, if the active layer thickness can be reduced to enhance gas flux.

Keywords: Cellulose triacetate, carbon dioxide, sulphur dioxide, nitric oxide, water.

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1. Introduction

Carbon dioxide (CO₂) emissions are the leading cause for anthropogenic global warming, [1-4], with the major source being the combustion of fossil fuels. Carbon Capture and Storage (CCS) is one potential pathway for achieving CO₂ emission reduction targets, securing a sustainable energy industry while taking advantage of vital resources. Membrane gas separation is one technology proposed for the carbon capture step that combines high energy efficiency with high surface area-to-volume ratios and is ‘chemical free’ [5].

Membrane gas separation is already commercialised for carbon capture, in natural gas sweetening for the removal of H₂S and CO₂. Cellulose triacetate (CTA) membranes have the greatest industry acceptance for this application, making up to 80% of this membrane market [6, 7]. CCS from coal-fired power station flue gas is another proposed strategy, known as post-combustion capture, where membrane gas separation has potential. While CTA membranes prepared by the phase inversion technique do not have the ideal permeability for post combustion capture, their high CO₂/N₂ selectivity, commercial readiness and proven industrial resilience means that they could have strong potential. Thin film composite CTA membranes have been prepared by other workers [8-10] and emerging membrane fabrication technologies such as layer by layer[11] and continuous assembly of polymers (CAP) [12] approaches could allow the thickness of the active layer to be reduced further, which would result in adequate permeance to meet gas flux requirements. Alternatively, the use of porous additives within the active layer to form a mixed matrix structure could also improve the permeability of the structure, without compromising the selectivity [13].

However, flue streams normally contain moisture (100ppm – 20 wt% [14, 15]) which is known to alter the separation performance of many membrane materials [16-18]. Chen et al. showed that the presence of water vapour at low partial pressures reduced the permeability of CO₂ and CH₄ through dense CTA membranes due to competitive sorption and “anti-plasticisation” behaviour [19]. Conversely, higher water vapour pressures plasticised or swelled the membrane resulting in an increase in gas permeability and a decline of gas selectivity [19, 20]. Upstream processing can also result in liquid water occasionally reaching the membrane unit, as droplets. In a post-combustion application, highly alkaline water may result from entrained fly ashes or the caustic slurry used in desulfurisation [21, 22]. Conversely, acidic water may overflow from a direct contact cooler if desulfurisation is not employed [21, 23]. As one of the earliest polymer used in membrane applications for both gas separation and water treatment, the hydrolysis of the cellulose acetate polymer in liquid water has been well studied across a range of pH conditions [24-26]. The overall hydrolysis rate constant, k , can be expressed as:

$$k = k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{H_2O} \quad (1)$$

where the quantities in brackets are the ion activities. At ambient temperature, this results in a hydrolysis rate of around $5.4 \times 10^{-10} \text{ s}^{-1}$ at pH 3, 1.4×10^{-10} at pH 7 and 0.0014 s^{-1} at pH 13. However, the impact of this hydrolysis on the gas separation performance of the membrane is less well understood.

Post-combustion flue gas typically contains 200-5000 ppmv SO_x when it exits the combustion chamber[27, 28]. If flue gas desulphurisation is used, this reduces the SO_x content to between 10 and 50 ppmv[27]. This is mainly in the form of SO_2 , with some SO_3 also present. Many polymeric membranes are selective for SO_2 relative to other major gases, because of the strong condensability of SO_2 [29-32]. The permeability of SO_2 within a composite CTA membrane has been reported by Kuehne and Friedlander, who focused on the impact of SO_2 pressure and membrane fabrication technique [28]. However, the impact of SO_2 on a CTA membrane at different temperatures was not considered, which is important given the range of temperatures that can be present in flue gas. Further, the long term effects of SO_2 on CTA membrane performance have not been established.

The concentration of nitrogen oxides in power station flue gas is in the range of 150-300 ppmv, with nitric oxide (NO) the major component and <10 ppmv nitrogen dioxide (NO_2), with some variation dependant on combustion technologies [23]. Again, these levels can be reduced through the use of selective catalytic reduction (SCR), which can remove 85 to 98% of these pollutants [27, 33], but this is not always in place. To the best of the authors' knowledge, there is no reported information on the impact of NO on a CTA membrane, though the effect on another class of polymeric membranes, polyimides, is reported [34]. It is expected that NO will have higher diffusivity than CO_2 because of smaller kinetic diameter, but the solubility of NO will be lower than CO_2 , based on critical temperature behaviour [35]. An understanding of the impact of NO on CTA membranes is of vital importance if they are to be applied to post-combustion capture.

In this investigation, the gas transport performance of CTA membranes in single gas and mixed gas feeds of CO_2 , N_2 and impurities (H_2O , SO_2 and NO) are reported. In addition, the impact of these impurities on the CTA membrane over 60 to 120 day periods is reported. This information will assist in evaluating the potential for CTA membranes to be used in this emerging industrial application.

2. Experimental

2.1. Membrane fabrication

The basic chemical structure of CTA is shown in Figure 1. The CTA polymer utilised in the study was supplied by Cellulose Company – Daicel Corporation, Japan with an acetylation degree of 61.6%. Prior to membrane fabrication, the polymer powder was dried overnight under vacuum at 100°C to remove the moisture. At least two membranes were tested in each experiment to confirm the reproducibility.

Figure 1

Dense membranes were fabricated using dichloromethane (ChemSupply, Australia) as the solvent. The solution (1 wt%) was filtered and cast into glass petri dishes that were kept covered for 24 hours for solvent evaporation. The thickness of each membrane was measured with a micrometer and found to be in the range of 60 to 80 μm .

A thin film CTA membrane was also fabricated by spin coating to measure the permeability of SO₂ and NO [36, 37]. A 4 wt% CTA in dichloromethane solution was spin coated onto a hydrophilic polytetrafluoroethylene (PTFE) membrane filter of 0.2 µm nominal pore size (OmniporeTM, Merck Millipore, Australia). The spinning rate was set at 1500 rpm for 20 s and the substrate was pre-wetted by deionised water to reduce the pore penetration of polymer and solvent [37]. The thickness of the thin film composite CTA was measured by Scanning Electron Microscopy (FEI Quanta 200 ESEM FEG). The membrane was gold-coated by a Dynavac Mini Sputter Coater prior to imaging. The thin film thickness was found to be in the range of 3 to 6 µm.

All membranes were dried under vacuum at 35°C for 24 hours and then 100°C for a further 24 hours. The fabricated membranes were kept in a desiccator to minimise the exposure to moisture. The membranes were stored for 14 days prior to permeability measurements. Densification due to loss of free volume (physical aging) is greatest for any glassy membrane during these first two weeks and hence the delay ensures that this densification does not overpower any other more subtle changes in membrane permeability. Further, in engineering practice, at least 14 days would be needed to transport and install the membrane module after fabrication, hence the performance in this initial period is less relevant.

2.2. Characterisation

The sorption kinetics of the membrane was determined by immersing the membrane samples into solutions at 35°C. Solutions of pH 3.0, 7.0 and 13.0 were prepared from sulphuric acid (Chem-supply, Australia), purified water (Millipore Elix) and sodium hydroxide (Sigma Aldrich, Australia). After a specified immersion time, the membrane was removed from the solution, excess liquid droplets on the membrane surfaces removed by wiping with a tissue and weighed on an analytical balance (XS205 Mettler Toledo Australia) with maximum error of 0.06% [38]. The mass change per unit time allowed the diffusion coefficient (D) to be determined from (2) [39].

$$\frac{m_0 - m}{m_0 - m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2}{l^2} \pi^2 D t\right) \quad (2)$$

where m is the mass at time t , m_0 the initial mass, m_∞ the mass at equilibrium and l the thickness of the membrane. At least five membranes, from more than one fabrication batch, were used to determine the diffusion coefficient using Equation 2.

The total water uptake was also obtained by determining the mass of the CTA membrane when equilibrium sorption had been achieved. The membrane was removed from the solutions at equilibrium and again wiped free of surface liquid before weighing the equilibrium mass (m_∞). As the CTA membrane could be hydrolysed by the pH solutions [26] causing the mass of polymer to change, the total uptake was calculated via Equation (3) where the dried membrane mass ($m_{\infty, \text{dried}}$) was obtained by drying the wet membrane under vacuum.

$$\text{Water uptake (\%)} = \frac{m_\infty - m_{\infty, \text{dried}}}{m_{\infty, \text{dried}}} \times 100 \quad (3)$$

The impact of pH on gas separation performance was also determined by immersion of the dense membranes in solutions of varying pH for periods of up to 60 days. After immersion, the membranes were well-dried by vacuum at ambient temperature (22°C) overnight before permeation testing.

The impact of toxic gases was similarly determined by placing dense membranes into a sealed chamber at ambient temperature ($22 \pm 2^\circ\text{C}$). The chamber was evacuated and then filled with a gas mixture (pure N_2 , 1000 ppm SO_2 or 979 ppm NO (988 ppm NO_x) in balance N_2 , Coregas Australia) to a pressure of 7.5 bar. The pressure in the chamber was monitored to ensure that leakage did not occur. After a period of up to 100 days, a vacuum was applied for 5 minutes to remove the toxic gases before the chamber was opened and the membranes removed for permeation testing.

Changes in membrane structure were determined using Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer Frontier) fitted with an attenuated total reflectance (ATR) attachment.

2.3. Gas permeation measurement

The gas permeability (P) of individual gases (CO_2 (99.5% purity), N_2 , He (99.99% purity), CH_4 (99.9% purity, Coregas Australia) through the dense CTA membranes was measured by a constant volume - variable pressure (CVVP) gas permeation apparatus operating at 35°C and 7.5 and 10 bar transmembrane pressure difference as reported in our previous studies [40]. These pressures are higher than that expected in a flue gas environment but were chosen to ensure accuracy in the use of a CVVP approach. The membrane was installed into the membrane cell and placed under vacuum overnight before the gas permeation measurement.

A constant pressure variable volume (CPVV) method was used to test gas permeability of both dense and thin film composite membranes in gas mixtures across a temperature range of 22 to 80°C , again as reported in previous studies [17, 41]. The mixed gas (10% CO_2 in balance N_2 , 1000 ppm SO_2 in N_2 , or 979 ppm NO , 9 ppm NO_2 in N_2 , Coregas Australia) was introduced into the feed side of the permeation cell at a feed pressure of 100 to 900 kPa gauge (stage cut less than 0.3%). These pressures are typical of those that might be experienced in a post-combustion environment. A helium sweep gas at 1 bar absolute pressure flowed across the permeate side of the permeation cell at a flowrate of 35 ml/min and was fed directly to the concentration analyser.

The concentrations of SO_2 and NO in the sweep gas were measured through Fourier transform infrared spectroscopy (FT-IR), as set out in ISO 19702:2006 [42, 43], in the wave number range of $1410 - 1290 \text{ cm}^{-1}$ and $2000 - 1775 \text{ cm}^{-1}$, respectively (Perkin Elmer Frontier FT-IR). The concentration of CO_2 and N_2 was determined by gas chromatography with an infrared detector (490 micro GC Agilent technologies, Australia). The FT-IR was calibrated against SO_2 and NO gas mixtures at a range of pressures to generate the calibration curves while the calibration curves for the GC were generated by calibration against four standard compositions of $\text{CO}_2 - \text{N}_2$ gas mixtures.

The ratio of gas permeability of two gas species (i and j) is defined as the ideal gas selectivity (α_{ij}) (Equation 4).

$$\alpha_{ij} = P_i/P_j \quad (4)$$

3. Results and discussion

3.1. Impact of water

The water uptake at pH 3 and pH 7 was comparable to that previously published [19]. After an initial uptake over 2 hours, these values were stable over the experimental period (Figure 2a). It should be noted that this uptake period of two hours would be reduced to few seconds for a thinner active layer of say 50 nm, as would be used in an industrial application. The diffusion coefficient determined for water in these membranes was calculated from Equation 2 as $3.8 \pm 0.4 \times 10^{-8} \text{ cm}^2/\text{s}$ at both pH values, already consistent with literature results, $4.6 \times 10^{-8} \text{ cm}^2/\text{s}$ [39].

Figure 2

Conversely, the water uptake of the membrane at pH 13 increases dramatically over time. This is consistent with the significant hydrolysis of CTA under alkali conditions [26, 44]. A significant reduction in the membrane dry mass was also observed for this membrane (Figure 2b), which reflects the dissolution of cellulosic polymers into the aqueous phase [45].

In general, the permeability of CTA membrane was enhanced after exposure to pH 3 and pH 7 solutions due to water-induced plasticisation, while the CO_2/N_2 selectivity changed little (Figure 3). The changes were roughly 6 % greater at pH 3 than at pH 7, which could be due to the stronger plasticisation impact of the hydronium ions in the acidic solution. Cellulose acetate polymer chains are known to become more flexible in strongly polar solvents [46]. Results in mixed gas conditions were comparable.

Membranes aged at pH 13, however, showed a significant and rapid decline in permeability, which is attributed to the hydrolysis of the CTA membrane in alkaline solution. The hydrolysis reactions converted the acetyl functional groups in the polymer matrix into hydroxyl functional groups (see Figure S1) [26, 47]. This significantly reduced the fractional free volume due to the strong intermolecular hydrogen bonding of these hydroxyl groups [26, 47].

Remarkably, the mass loss due to hydrolysis of the CTA membrane at pH 13 occurred continuously over 6 days (Figure 2), while the permeabilities of CO_2 and N_2 declined by 97% after just after few hours of immersion (Figure 3). This phenomenon suggests that the hydrolysis of the CTA membrane occurred initially on the membrane surfaces, converting these surfaces into impermeable regions. The solvated hydroxide ions then diffused through these hydrophilic surface regions and continued to hydrolyse the bulk of the CTA matrix.

As the permeability CO_2 and N_2 for the pH 13 case rapidly approached the detection limits of the gas permeation measurement methodologies, the CO_2/N_2 selectivity could not be determined with any precision and so is not reported in Figure 3c.

Figure 3

3.2. Permeability of SO_2 and NO

The mixed gas permeability of CO_2 , N_2 and SO_2 through thin film composite CTA membranes was studied at different feed pressures (Figure 4). The use of asymmetric membranes here was necessary to ensure the permeability of SO_2 could be detected, given the low partial pressure supplied.

For the temperature range 22 – 50°C, the permeabilities of N_2 , CO_2 and SO_2 were independent of the feed gas pressure within error. Indeed, the permeabilities of N_2 and CO_2 at 35°C are also identical within error to that measured at much higher pressures during pure gas testing (Figure 3). It should be noted that while Figure 4b provides the N_2 permeability in the CO_2 - N_2 mixture, the data for the N_2 - SO_2 mixture is highly comparable (Figure S1). At 80°C, the permeability of CO_2 and SO_2 both initially decrease with pressure as the Langmuir microvoid regions typical of glassy polymers become saturated [48-50]. However within the error margins, plasticization is not clearly observed. Conversely, there is a slight increase in N_2 permeability in both CO_2 - N_2 (Figure 4b) and N_2 - SO_2 (Figure S1) mixtures across the entire partial pressure range, which might be indicative of plasticisation affecting the N_2 diffusivity. For CO_2 , the literature reports that plasticisation occurs at 1200 kPa at 24°C for dense films [51] and 500 – 800 kPa for thin films at 50 – 53°C [52, 53]. Given, the plasticisation pressure should increase with temperature for a glassy membrane [40] a significantly higher CO_2 partial pressure than tested in this study should be required to observe CO_2 plasticisation. Conversely, Kuehne et al. [28] observe a continuous increase in permeability across an SO_2 partial pressure range of 13 – 93 kPa for dense membranes, consistent with the plasticisation pressure having been exceeded at these pressures.

Figure 4

The activation energy for permeation was determined at a total pressure differential of zero pressure to avoid any impact of plasticisation (Table 1). Increasing temperature enhances the diffusion of penetrants through membrane ($E_D > 0$) but diminishes the solubility of gas species in polymer ($\Delta H_S < 0$). The positive values of E_P in this study showed that the permeation of gas penetrants is diffusion controlled.

Table 1

For species with relatively low critical temperatures (CH_4 , N_2) the activation energy for permeation declines with the decrease of kinetic diameter of the penetrant species. This result is similar to other studies in both CTA [54] and other glassy polymers [48, 55]. However, the activation energies for permeation of SO_2 and CO_2 are smaller, reflecting the high critical temperature of these penetrants that results in a large absolute value of heat of sorption and thus reduces the final activation energy for permeation [56].

CO_2/N_2 and SO_2/N_2 selectivities decreased with increasing temperature, consisted with diffusion controlled permeation (Figure 5). Importantly, the selectivity was constant with respect to partial pressure, even for SO_2/N_2 , indicating that SO_2 plasticization was not significant enough to alter this parameter.

Figure 5

We also attempted to record the NO permeability. However, the concentration of NO in the sweep gas was under the detection limit, even for a membrane of 3 μm active layer thickness and a reduced sweep gas flowrate. This indicates that the permeability of NO at 35°C is below 4 Barrer.

3.3. Aging of CTA membrane in SO_2 and NO

The CTA membranes were aged separately in pure N_2 , 1000 ppm SO_2 and 979 ppm NO (988 ppm NO_x) to study the long term impact of these impurities on membrane performance. After a specified aging period (up to 120 days), the single gas permeation of He and N_2 was determined. The permeability of helium through the fresh CTA membranes at 7.5 bar and 35°C was recorded as 21.8 ± 0.8 Barrer, which is comparable with the literature [44]. The permeability and selectivity of the aged membranes was expressed as the ratio to the permeability and selectivity of the original fresh membrane to eliminate the variability between membrane samples (Figure 6).

Figure 6

Generally, the polymer chains of a glassy polymer are in a non-equilibrium state when a membrane is formed and so membrane densification or aging will occur over time [36]. As the excess free volume of the membrane is reduced, gas permeability declines, as observed in this study (Figure 6) [36, 48, 57]. The decline in permeability is less in helium than in nitrogen, which is due to its smaller kinetic diameter [36, 48]. This results in an increasing (He/N_2) selectivity as reported in Figure 6c.

This aging process was not affected by a partial pressure of 0.75 kPa SO_2 (Figure 6). Although SO_2 plasticisation was possibly observed at 80°C in the previous permeation experiment (Figure 4b), this effect was not sufficient at 22°C to alter the membrane aging process within experimental error. As the membranes used here are significantly thicker than the ones used for Figure 4b, this result is not unexpected.

Conversely, aging in the presence of 0.74 kPa NO_x was significantly faster despite the relatively low critical temperature of NO. This could be caused by the presence of small quantities of NO_2 in the gas, both due to impurities in the original NO - N_2 gas mixture (1% NO_2 in total NO_x) and possibly due to oxidation of residual NO with ambient oxygen [58] at the end of the aging process. It is well-known that NO_2 can oxidise the primary alcohol of cellulosic materials into a carboxyl moiety [59, 60]. To determine if this has occurred, an additional FT-IR - Attenuated total reflectance (ATR) experiment was conducted on the aged membrane. The results indeed showed evidence of an increased ratio of carboxyl groups relative to alcohol groups (Table 2) for this membrane. The hydrogen bonding capacity of the carboxyl functional group is stronger than that of a primary alcohol and this could enhance

the polymer interchain interactions, increasing chain packing and reducing the transport of gas penetrants.

Table 2

4. Conclusions

This work has shown that cellulose triacetate membranes are relatively stable when exposed to liquid water at pH 3 or pH 7, with a 30% increase in permeability and no loss of selectivity after immersion for 6 days, after which the performance stabilised. Conversely, caustic solutions (pH 13) hydrolysed and dissolved the membrane significantly over time. The CTA membranes also showed stable performance upon exposure to 0.75kPa SO₂ for up to 100 days, with the membranes aging at the same rate as when exposed to inert nitrogen. Conversely, exposure of 0.74 kPa of NO_x resulted in a significantly greater loss of permeability. This loss in permeability was attributed to reaction of the alcohol moieties in the cellulose acetate structure with trace quantities of NO₂ in the gas mixture.

SO₂ permeated through a CTA membrane more readily than CO₂ and N₂ with a permeability at 35°C of 20 Barrer. There was some evidence of plasticisation in the N₂ permeability data for both SO₂ and CO₂ mixtures at 80°C in short term permeability testing, but no membrane plasticisation was observed after a 120 days aging period at 22°C and 0.75kPa SO₂. The permeability of NO was below detection limits indicating a permeability of below 4 Barrer.

It should be noted that the aging studies were conducted here on relatively thick membranes (60-80 microns). In industrial practice, a membrane with a much thinner dense layer (< 1 micron) would be used. It is likely that the effects observed here would occur more rapidly in this thinner structure, as it is well known that both plasticisation[61] and loss of free volume[36] occurs more rapidly in thinner glassy systems. However, the magnitude of the effect should be unchanged.

The results suggest that CTA membranes could be applied in post combustion capture operations if a sufficiently thin film composite membrane could be prepared. Both water and SO₂ could be tolerated in the flue gas stream under most common operating conditions. However, the control and removal of NO₂ down to very low levels is essential to maintain the membrane performance in the long term. The resulting CO₂ permeate from the gas separation process will be enriched with SO₂ but depleted in NO. The increased SO₂ concentration may cause concern with downstream corrosion of piping and this may also need careful consideration.

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1 **Tables**

2 **Table 1**

3 Activation energy for permeation in CTA membrane at zero pressure.

4 **Table 2**

5 The absorbance ratio between carbonyl functional groups and C – O functional groups in
6 fresh and aged membranes.

7

1 **Table 1**

	CH ₄ [*]	N ₂	CO ₂	SO ₂	NO
Kinetic diameter (Å) [62]	3.80	3.64	3.30 ^{**}	3.60	3.20
Critical temperature (K) [63]	190.6	126.2	304.2	430.8	180.0
Activation energy for permeation, E _p (kJ/mol)	18.6 ± 0.2	18.8 ± 2	8.5 ± 0.7	7.3 ± 0.7	

2 ^{*} The permeability of methane was also measured by single gas permeation through a dense membrane to
3 provide a comparison between different penetrants

4 ^{**} Many authors believe this diameter to be an underestimate of the diameter relevant to diffusion, with alternate
5 values of 3.43 to 3.63 Å often preferred [64-66].
6

1 **Table 2**

	Original CTA	CTA aged 120 days in N ₂	CTA aged 120 days in NO/N ₂ mixture
<u>Max absorbance (C=O)</u>	0.715 ± 0.08	0.712 ± 0.002	0.750 ± 0.02
<u>Max absorbance (C – O)</u>			

2

3

1 **Figures**

2 **Figure 1.** Chemical structure of cellulose triacetate polymer

3 **Figure 2.** (a) Water uptake of a CTA membrane after immersion in water of variable pH at
4 35°C for a specified time; (b) Mass loss of a CTA membrane after immersion in pH 13

5 **Figure 3.** Gas separation performance of CTA membranes at 10 bar, 35°C after immersion in
6 pH (3, 7 and 13) solutions (a) permeability of CO₂; (b) permeability of N₂; (c) selectivity of
7 CO₂/N₂

8 **Figure 4.** Gas permeability in CTA thin film composite membranes. (a) permeability of CO₂
9 in 10 v/v% CO₂ in N₂ ; (b) permeability of N₂ in 10 v/v% CO₂ in N₂; (c) permeability of
10 SO₂ 1000 ppm SO₂ in N₂.

11 **Figure 5.** Temperature dependence of the SO₂/N₂ and CO₂/N₂ selectivity in a CTA
12 membrane at zero transmembrane pressure difference.

13 **Figure 6.** Change in permeability of (a) He; (b) N₂ and (c) He/N₂ selectivity as time
14 progresses for CTA membranes at 35°C, 7.5 bar after aging separately in pure N₂, 979 ppm
15 NO in balance N₂ and 1000 ppm SO₂ in balance N₂ at 7.5 bar, at 22 ± 2°C.

R: COCH_3 or H

a

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