



Support mass transfer resistance of Pd/ceramic composite membranes in the presence of sweep gas

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ABSTRACT

The present paper aims at reducing the general lack of fundamental understanding about the effects of sweep gas on membranes supported on porous substrates. This is necessary to design better performing membranes for hydrogen purification and CO₂ capture applications. Sweep gas is a widely considered option for enhancing the separation performance of hydrogen-selective Pd membranes in e.g. pre-combustion carbon capture and H₂ production via low-temperature steam reforming. However, additional mass transfer resistance arises when using sweep gas with composite membranes due to its diffusion into the porous support. In order to assess this issue quantitatively, the influence of N₂ sweep gas was systematically studied over a wide permeate pressure range using a 5 μm thick Pd membrane supported on an asymmetric ceramic support tube. Experiments were carried out between 300 and 500 °C at a trans-membrane pressure difference of 100 kPa. These measurements were complemented with mathematical modelling to elucidate the mass transfer resistance associated with the sweep gas. In general, the mass transfer resistance of the support grew substantially with permeate pressure and increasing sweep rate, contributing up to 40% to the total mass transfer resistance at the highest investigated permeate pressure (1 MPa). The negative impact of higher permeate pressures on the permeating fluxes could be effectively compensated by using relatively small sweep flow rates up to 100 mL min⁻¹. Further increase of the sweep gas amount improved the permeation flux only by moderate margins albeit the sweep gas effect was a little stronger at higher permeate pressures. For example, the H₂ permeation rate improved by ca. 29% (38%) when raising the sweep flow rate from 100 mL min⁻¹ to 500 mL min⁻¹ at 400 °C and 100 kPa (900 kPa) permeate pressure. The relative permeation rate improvement with sweep rate became weaker with increasing temperature. The reduction of the support mass transfer resistance appears to be a promising strategy for enhancing hydrogen permeation through Pd composite membranes in situations that require the application of sweep gas.

1. Introduction

Capture and storage of the greenhouse gas CO₂ is deemed to be essential for the utilization of fossil fuels going forward in order to limit the ongoing global warming. The necessary separation step for production of highly concentrated (ideally pure) CO₂ streams for sequestration can be implemented at several stages of stationary power production processes [1]. The most mature technology is separation of CO₂ from N₂ after fuel combustion using liquid and solid sorption agents [1] although polymer membranes are also investigated for this purpose [2].

In general, these post-combustion CO₂/N₂ separation processes result in low-pressure CO₂ streams. In order to avoid this drawback, pure O₂ can be used for fuel combustion which requires air separation via cryogenic methods [1]. High-temperature ceramic membranes operating above 800 °C are widely investigated for this separation task, too [1].

Another intriguing second generation CO₂ capture scheme involves the production of H₂ as an intermediate from fossil fuels via reforming processes. The H₂ can be separated from other reforming products prior to combustion with the help of Pd membranes delivering simultaneously high-pressure CO₂ and H₂ fuel streams [3–12]. Carbon capture

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List of symbols

A_c	Cross-sectional area, m^2
\mathcal{B}	Matrix B (defined in Eq. (A.2)), $s\ m^{-2}$
C_T	Total molar concentration, $mol\ m^{-3}$
D_{ij}	Binary diffusivity, $m^2\ s^{-1}$
D_m	Mean diameter of membrane, m
J	Diffusive molar flux, $mol\ m^{-2}\ s^{-1}$
L	Membrane length, m
m	Number of species in mixture, –
N	Total molar flux, $mol\ m^{-2}\ s^{-1}$
P	Pressure, Pa
u	Mixture velocity, $m\ s^{-1}$
x	Molar fraction, –
z	Reactor abscissa, m
z^*	Dimensionless reactor abscissa ($= z/L$), –

Greek letters

α	Non-ideality index, –
ρ	Density, $kg\ m^{-3}$

Subscripts/superscripts

i, j	Indices of the generic species in mixture, –
m	Number of species in mixture, –
TM	Trans-membrane

Acronyms/abbreviations

<i>Perm</i>	Permeate (side)
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costs and energy efficiency can be greatly improved in this way, since CO_2 needs to be compressed to more than 8 MPa for transportation in order to increase the fluid density and avoid two-phase flow regimes [13]. The H_2 will be combusted in gas turbines using air at elevated pressures, too. For example, membrane feed and permeate pressures of 4.6 and 2.3 MPa, respectively, were adopted in a recent analysis of a natural gas combined cycle (NGCC) power plant with integrated Pd membrane water-gas shift (WGS) reactors for CO_2 capture [13]. Separation of H_2 from other reforming products (mostly steam apart from CO_2 following a high-temperature WGS stage at 400–500 °C) also avoids intermediary cooling of the H_2 fuel to room temperature which is a necessity for most alternative separation techniques [1–3,10–12].

Moreover, H_2 has to be diluted to 50–60% to prevent fuel burn-outs in the currently used gas turbines [13]. The diluent, e.g. N_2 or steam, can be advantageously added as sweep gas on the permeate side of the membrane unit to boost H_2 permeation rates and effectively reduce the required membrane area. On the other hand, state-of-the-art Pd membranes consist of noble metal layers of a few micron thickness supported on porous ceramic or metal substrates in order to minimize consumption of the precious metal [14–16]. Typically, the feed will be directed to the side with the Pd layer while the permeate exits through the porous substrate of this type of composite membrane. Therefore, the sweep gas counter-flow into the porous substrate will introduce an additional mass transfer resistance, as shown by recent modelling studies [17,18].

Li et al. simulated the effect of various sweep gases (He , N_2 , H_2O) on separation of 65% H_2 mixtures with $Pd_{75}Ag_{25}$ membranes supported on porous stainless steel (PSS) substrates at atmospheric permeate pressure [17]. The substrate contribution to the mass transfer resistance was marginal ($\leq 1\%$) in the absence of sweep gas but could climb to ca. 10% when sweep gas was included. The choice of sweep gas made little difference ($\leq 5\%$) but sweeping was clearly more effective when omitting the substrate in the modelling [17].

Boon et al. studied the separation of 55% H_2 /45% N_2 mixtures with Pd/ceramic composite membranes applying N_2 sweep gas at permeate pressures up to 2 MPa [18]. Their model overestimated the H_2 permeation rates by ca. 16% on average. Nevertheless, the general agreement between experimental and simulated H_2 fluxes improved noticeably when sweep gas diffusion into the substrate was included in the simulation. Accordingly, they concluded that a significant diffusion barrier to H_2 transfer formed upon penetration of the support by sweep gas [18]. However, they did not analyse the correlation between sweep gas-related mass transfer resistance and permeate pressure.

We assumed that the sweep gas-induced mass transfer resistance of the support will increase with increasing permeate pressure and may become a critical parameter for optimizing such Pd membrane units for CO_2 capture in power generation. Therefore, we have studied the

influence of sweep gas on H_2 permeation rate through a thin-layered Pd/ceramic composite membrane varying systematically sweep flow rate and permeate pressure in the temperature window 300–500 °C. The experimental results have been analysed using an advanced mathematical model to quantify the H_2 flux inhibition caused by the sweep gas as function of sweep rate, temperature and pressure.

2. Experimental methods

2.1. Membrane preparation

The Pd/ceramic membrane used here was prepared in the same way as the one used previously for a 3600 h stability test under simulated CO_2 capture conditions [10]. All preparation steps are described there in detail including surface modification and Pd seeding of the ceramic substrate, Pd deposition via electroless plating, and high-temperature activation of the composite membrane. In brief, the membrane consisted of a 5 μm thick Pd layer (gravimetric estimate) supported on the outside of an asymmetric porous ceramic support tube with 14 mm outer and 10 mm inner diameter that was provided by the Energy research Centre of the Netherlands (ECN). The structural properties of the three ceramic layers of the support tube are summarized in Table 1 as specified by the provider [18]. The effective membrane length was approximately 48 mm after sealing with graphite gaskets giving a surface area of ca. 21 cm^2 .

2.2. Permeation measurements

The layout of the homemade setup for permeation measurements has been elsewhere reported [10]. The membrane was mounted in a cylindrical reactor shell (ID = 25 mm) placed inside a furnace with a programmable temperature controller. Hydrogen ($\geq 99\%$ purity) or nitrogen (99.999%) were fed into the shell in contact with the outer membrane surface. Sweep gas (N_2) was fed in counter-current configuration through a stainless steel tube inserted into the lumen of the membrane tube. The feed and sweep flow rates were metered with mass flow controllers (MFC, Brooks 5850E). The permeation temperature

Table 1
Geometrical properties of the support according to provider specifications [18].

Support layer	Thickness μm	Mean pore diameter nm	Porosity –	Tortuosity –
Surface Layer 1 ($\alpha-Al_2O_3$)	40	160	0.35	1.25
Surface Layer 2 ($\alpha-Al_2O_3$)	40	160	0.35	1.25
Backbone ($\alpha-Al_2O_3$)	2000	3400	0.43	1.25

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