Interfacial permeation phenomena of hydrogen purification and carbon dioxide separation in a non-isothermal palladium membrane tube

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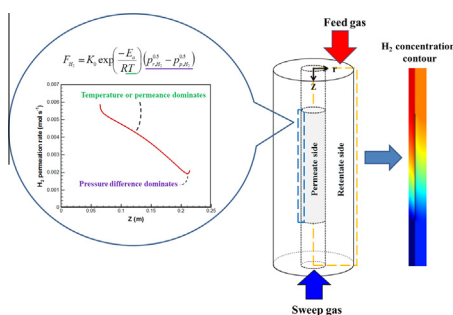[c] Department of Mechanical Engineering, National Chung Hsing University, Taichung 402, Taiwan
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HIGHLIGHTS

- Hydrogen permeation through a Pd membrane in a non-isothermal environment is studied.
- A minimum distribution in H_2 partial pressure difference and permeation rate develops.
- A dimensionless mass transfer parameter is conducted to illustrate mass transfer behavior.
- H_2 permeation at the front portion of the membrane is dominated by temperature.
- With low H_2 inlet concentration, all H_2 in the feed gas is recovered and all CO_2 is separated.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Hydrogen can be purified and carbon dioxide can be separated from their gas mixtures in a palladium (Pd) membrane tube. To figure out the hydrogen permeation characteristics in a non-isothermal Pd membrane tube, a numerical method is developed. The influence of the Reynolds numbers at the retentate and permeate sides, the temperatures of feed gas and sweep gas, and the H_2 concentration in the feed gas on the interfacial H_2 permeation and H_2 recovery are analyzed. The results indicate that the minimum H_2 partial pressure difference and permeation rate along the membrane surface develops, as a consequence of competition between the membrane permeance and the H_2 partial pressure difference. A dimensionless mass transfer parameter (ξ), which is a non-dimensional driving force ratio between H_2 diffusion in the gas phase and H_2 permeation across the membrane, is conducted to aid in illustrating the mass transfer characteristics along the membrane surface. The ξ curve is insensitive to the Reynolds numbers, but depends significantly on interfacial temperature and H_2 inlet concentration. When the H_2 inlet concentration is low, all H_2 in the feed gas can be recovered and the minimum distribution no long appears. This also implies that all CO_2 is separated.

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1. Introduction

Membrane-based gas separation is an important unit operation in industry [1]. When hydrogen is separated from hydrogen-rich gases using membranes, palladium (Pd) has demonstrated its

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Nomenclature

A_c	cross sectional area (m^2)
C_p	specific heat (J mol^{-1} K^{-1})
D	diffusion coefficient (cm^2 s^{-1})
D_H	hydraulic diameter (m)
D_i	inner diameter (m)
D_o	outer diameter (m)
E_a	activation energy (J mol^{-1})
F	flux (mol m^{-2} s^{-1})
K	permeance (mol m^{-2} s^{-1} Pa^{-n})
K_0	pre-exponential term (mol m^{-2} s^{-1} Pa^{-n})
k	thermal conductivity (W m^{-1} K^{-1})
$\bar{k}$	Boltzmann constant (=1.380648 × 10^{-23} J K^{-1})
l	membrane thickness (m)
M_i	molar mass of species i (g mol^{-1})
$\dot{m}$	mass flow rate (mg s^{-1})
p	pressure (atm)
P_e	permeability pre-exponential factor (mol m^{-1} s^{-1} Pa^{-n})
P_w	wetted perimeter (m)
R	universal gas constant (=8.314 m^3 Pa K^{-1} mol^{-1})
Re	Reynolds number (–)
T	temperature (K)
V	velocity (m s^{-1})
w_i	mass fraction of species i (–)
x_i	mole fraction of species i (–)

z	axial coordinate (m)

Greek letters

μ	viscosity (Pa s)
ξ	mass transfer parameter (–)
ρ	density (kg m^{-3})
ϕ	binding factor (–)
Ω_d	diffusion collision integral (–)
ε_i	Lennard-Jones parameters (J)
σ_i	Lennard-Jones parameters (Å)

Subscript

atm	atmosphere
H$_2$	hydrogen
i	species i
in	inlet
j	species j
m	membrane
p	permeate side
r	retentate side
ref	reference conditions
out	outlet

excellent features of high hydrogen permeability and selectivity, which are two important factors in determining membrane performance [2–5]. Pd membranes also possess the advantages of easy operation and maintain, long lifetime, low energy consumption, and lower facility cost [6–8]. For these reasons, hydrogen separated by Pd membranes is a promising route to produce pure hydrogen for fuel cell applications, especially for small-scale H$_2$ production and on-board utilization [9–11]. In recent years, a great deal of attention has been further paid to the preparation of Pd-alloy membranes to improve the properties of pure Pd membranes such as permeability, selectivity, chemical compatibility, and durability, and to eliminate their drawbacks such as hydrogen embrittlement and narrower operating temperature range [12].

In addition to H$_2$ separation and purification, Pd-based membranes can also be thought of as a potential tool to fulfill CO$_2$ capture. Binary H$_2$/CO$_2$ gas mixtures can be produced from methanol partial oxidation, steam methane reforming, and partial oxidation of methane followed by water gas shift reaction, or water gas shift reaction alone, as shown in Table 1. For H$_2$ permeating through a Pd-based membrane, the mass transfer pertains to a "solution-diffusion" mechanism in nature [13]. While H$_2$ is separated from a binary H$_2$/CO$_2$ gas mixture, CO$_2$ in the gas mixture is enriched. This is conducive to the subsequent CO$_2$ capture, thereby abating greenhouse gas emissions into the atmosphere [14,15].

The H$_2$ permeation flux through a Pd-based membrane has been widely described by the following equation:

$$F_{H_2} = K\left(p_{r,H_2}^n - p_{p,H_2}^n\right) \tag{1}$$

where K and n are the permeance (mol m^{-2} s^{-1} Pa^{-n}) and pressure exponent, respectively. The value of n is between 0.5 and 1 [16], and the Sieverts' law with n = 0.5 is the most commonly employed formula [17]. Eq. (1) reveals that the mass transfer is subject to the H$_2$ partial pressure difference across the membrane and the permeance. The former is the driving force of H$_2$ permeation, whereas the latter is related to material nature and fabrication process.

While H$_2$ permeates through a membrane, a H$_2$ concentration boundary layer along the membrane surface develops. The H$_2$ partial pressure is reduced at the retentate side and enriched at the permeate side, thereby causing a phenomenon termed concentration polarization [17]. The concentration polarization can be lessened via designing reactor geometry [18], installing baffles at the retentate side [19,20], and introducing a sweep gas at the permeate side [21,22].

The permeance of a membrane is a function of permeability, thickness, and temperature. An Arrhenius-type equation has been developed to correlate these parameters and is expressed as [23,24]

$$K = \frac{P_e}{l}\exp\left(\frac{-E_a}{RT}\right) = K_0\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where P_e is the permeability pre-exponential factor (mol m^{-1} s^{-1} Pa$^{-0.5}$), l is the membrane thickness (m), E_a is the activation energy (J mol^{-1}), R is the universal gas constant (=8.314 m^3 Pa K^{-1} mol^{-1}), T is the membrane temperature (K), and K_0 is the pre-exponential

Table 1
Binary H$_2$/CO$_2$ gas mixtures produced from a number of chemical reactions.

Chemical reaction	CO$_2$:H$_2$
Steam methane reforming followed by water gas shift reaction	
CH$_4$ + H$_2$O ↔ CO + 3H$_2$	
CO + H$_2$O ↔ CO$_2$ + H$_2$	
Total reaction CH$_4$ + H$_2$O ↔ CO$_2$ + 4H$_2$	1:4
Methane partial oxidation followed by water gas shift reaction	
CH$_4$ + 0.5O$_2$ ↔ CO + 2H$_2$	
CO + H$_2$O ↔ CO$_2$ + H$_2$	
Total reaction CH$_4$ + 0.5O$_2$ ↔ CO$_2$ + 3H$_2$	1:3
Methanol partial oxidation	
CH$_3$OH + 0.5O$_2$ → CO$_2$ + 2H$_2$	1:2
Water gas shift reaction	
CO + H$_2$O ↔ CO$_2$ + H$_2$	1:1