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Effects of surface activity, defects and mass transfer on hydrogen permeance and *n*-value in composite palladium-porous stainless steel membranes

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Abstract

The H_2 permeance of composite palladium-porous stainless steel (Pd-PSS) membranes was determined: (1) by assuming Sieverts' law ($n = 0.5$) and (2) by performing a non-linear fit in order to obtain the hydrogen permeance and the *n*-value. For all membranes (thickness > 15 μm) the *n*-value was higher than 0.6 at low temperatures (<350 °C) and close to 0.5 at higher temperatures (>400 °C). The activation of the membrane with the surface either seeded with palladium or oxidized in air at 350 °C for 48 h led to lower *n*-values indicating that the surface reaction rate even in thick membranes with selectivities (H_2/He) above 400 might still contribute, though to a minor extent, to the overall hydrogen permeation mechanism. For leaky membranes (selectivity $\ll$ 400) the Knudsen diffusion and viscous flow of molecular H_2 through the defects led to *n*-values as high as 0.75 at 500 °C. *n*-Values higher than 0.5 were also found for Pd-PSS membranes when the PSS support had a large resistance.

Keywords: *n*-Value; Hydrogen permeance; Hydrogen flux; Palladium membranes; Surface poisoning; Leaks; Selectivity

1. Introduction

The use of composite palladium and palladium alloy membranes coupled with steam reforming of hydrocarbons in a single reaction/separation unit operation is one of the most attractive technologies for hydrogen production [1–3]. Several membrane reactor studies have shown the feasibility of methane steam reforming at temperatures ranging from 500 to 650 °C [2–5]. Membrane reactors for methanol steam reforming at 300–400 °C were also found to be a practical route for hydrogen production [6–8]. Syngas ($CO + H_2$) production from methane dry reforming at 550–650 °C using palladium based membranes was also reported [9]. It has been largely accepted that hydrogen flux through palladium films (foils and supported membranes) is governed by Eq. (1):

$$J = \frac{Q_0}{L}\exp\left(-\frac{E_p}{RT}\right)\left(P^n_{H_2hp} - P^n_{H_2lp}\right) \quad (1)$$

The terms in Eq. (1) are defined in the Nomenclature. The hydrogen flux follows the Sieverts' law when the hydrogen pressure exponent n is equal to 0.5, which is usually valid for thick Pd films. Deviations from the Sieverts' law ($n > 0.5$) were reported for very thin membranes [10–13]. Based on a hydrogen permeation model, Ward and Dao [14] showed that at temperatures above 400 °C, n was equal to 0.5 for membranes thicker than 1 μm. However, *n*-values equal to 0.6–0.7 have been reported for thick palladium membranes [15,16].

For thick membranes (>1 μm), deviations from the Sieverts' law can be caused by high pressures of hydrogen. Indeed, the derivation of the Sieverts' law assumes Eq. (2) to be valid:

$$C = \kappa P^{0.5}_{H_2} \quad (2)$$

where C is the hydrogen concentration in palladium, κ a proportionality constant and P_{H_2} is the hydrogen pressure. However, at 200 °C, the hydrogen absorption isothermal

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Nomenclature

E_p	activation energy for hydrogen permeation (J mol^{-1} or kJ mol^{-1})
F_{H_2}	hydrogen permeance derived from a single point ($m^3\ m^{-2}\ h^{-1}\ bar^{-0.5}$)
F_n	hydrogen permeance derived from the least squares analysis adjusting the n-value ($m^3\ m^{-2}\ h^{-1}\ bar^{-n}$)
$F_{0.5}$	hydrogen permeance derived from the least squares analysis assuming $n = 0.5$ ($m^3\ m^{-2}\ h^{-1}\ bar^{-0.5}$)
J	gas flux (mol $m^{-2}\ s^{-1}$ or $m^3\ m^{-2}\ h^{-1}$)
L	palladium membrane thickness (m or μm)
M_i	molecular weight for i compound (kg mol^{-1})
n	n-value or hydrogen pressure exponent
P_{H_2hp}	hydrogen partial pressure in retentate, shell or high pressure side (Pa or bar), also noted as P_{shell}
P_{H_2lp}	hydrogen partial pressure in permeate, tube or low pressure side (Pa or bar), also noted as P_{tube} or P_0
Q_0	permeability of pure palladium (mol $m^{-1}\ s^{-1}\ Pa^n$)
r	contribution of Knudsen flow to the total leak
R	universal gas constant (8.314 J $mol^{-1}\ K^{-1}$)
T	membrane temperature (at the permeate side) (K)

Greek symbols

α	Knudsen component coefficient of He leak ($m^3\ m^{-2}\ h^{-1}\ bar^{-1}$)
β	viscous component coefficient of He leak ($m^3\ m^{-2}\ h^{-1}\ bar^{-2}$)
η_i	viscosity of gas i (Pa s^{-1})

($P^{0.5}$, hydrogen loading (H/Pd)) starts to curve as the miscibility gap is approached, i.e. >0.5 bara. Therefore, determining the hydrogen pressure exponent in the 1.1–2 bara pressure range would certainly lead to $n > 0.5$ even though bulk diffusion may still be the rate-limiting step. The permeation of hydrogen through thick palladium foils was studied by Morreale et al. [17] at very high pressures, and n-values were calculated based on permeation data from four pressure ranges (1.01–1.75, 1.01–7.75, 1.0–16.00, 1.01–26.00 bara). They reported an increase in the n-values from 0.53 (the limit value) to 0.65 as the pressure range was increased.

For thick films, deviations from the Sieverts' law can also be due to a decrease in the surface reaction rate after absorption of contaminants, such as C, CO, CO_2 or hydrocarbons, on the palladium surface [18–21]. Heat treatment in air was used for contaminant removal and also led to the increase of surface area of the palladium surface [22–24]. The palladium grain size is also believed to have an important effect on the hydrogen flux or n-value [13,25,26] but this dependence has not yet been fully explored or characterized. Finally, n-values greater than 0.5 are expected in palladium membranes with defects where a large fraction of the hydrogen permeates through pinholes and dislocations via a combined Knudsen-viscous mechanism.

The primary objective of the present study was to investigate the physical significance of the exponent n in the Sieverts' equation and show experimental evidence on the relationship between the palladium surface activity and the n-value for relatively thick membranes (20–30 μm). The effects of leaks on the hydrogen flux were also studied. In addition, the effect of temperature on the n-value was experimentally examined to elucidate the change in the permeation mechanism as a function of temperature.

2. Experimental

2.1. Membrane preparation

Composite palladium-porous stainless steel (PSS) membranes were prepared using the electroless deposition method. 0.1 and 0.2 μm grade PSS supports (1.27 cm in diameter) were purchased from Mott Metallurgical Corporation. The supports were cleaned in an alkaline solution (NaOH, 45 g/l; Na_2CO_3, 65 g/l; $Na_3PO_4\cdot12H_2O$, 45 g/l) for grease and dirt removal, thoroughly rinsed with de-ionized water (Di-water), rinsed with acetone and dried overnight at 120 °C. After cleaning, the supports were oxidized in stagnant air at the desired temperature (400–500 °C) to produce an oxide layer as the intermetallic

Table 1
List of membranes studied in this work

Membrane	Grade (μm)	Surface (cm^2)	Oxidation temperature (°C)	Oxidation time (h)	Thickness[a] (μm)	Use
M1	0.1	8	400	10	33	Measure n-value vs. temperature (no surface modification)
M2	0.1	8	500	10	40	Palladium seeded membrane
M3	0.1	23	500	10	19	Palladium seeded surface; reactivated surface in air at 350 °C for 48 h
M4	0.2	17	500	10	37	Effect of membrane defects on the n-value
M5	0.2	17	–	–	37	Effect of membrane defects on the n-value

[a] From weight gain.