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# Influence of the support on permeation of palladium composite membranes in presence of sweep gas

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ABSTRACT

The influence of the porous support on hydrogen permeation of a Pd-composite membrane in presence of sweep gas has been evaluated. A 20 μm thick palladium membrane has been prepared by electroless plating on a tubular stainless steel support. $H_2$ permeation tests have been performed in a laboratory pilot loop up to 400 °C and 800 kPa; a nitrogen sweep gas in the 0–100 Nl/h flow rate range has been fed to the permeate side. $H_2$ flux through the Pd-membrane has been first measured in absence of sweep gas. Permeation can be described by the Sieverts' law and the best fitting of the pressure exponent (*n*-value) at 400 °C is 0.67. Support resistance, estimated by using dusty-gas model equation, determines an increase of $H_2$ pressure at the interface between Pd-layer and support from 100 to 140 kPa, and a $H_2$ flux reduction of the 9.8%, approximately. While feeding $N_2$ as a sweep gas, a $H_2$ flux much lower than expected by considering Sieverts' law is measured. The difference between experimental results and expected values, calculated by a simple uni-dimensional model is about the 30%, at the higher flow rates. Moreover the increase of *n*-value from 0.68 up to 0.9 suggests a strong increase in the mass transfer resistance of the support. The resistance to $H_2$ diffusion due to presence of stagnant $N_2$ in the support pores has been then estimated by using the dusty gas model equation, which combines Knudsen diffusion, viscous flow and binary diffusion. Results indicate that binary diffusion of $H_2$ in stagnant $N_2$ can be responsible of the observed $H_2$ flux reduction. $H_2$ partial pressure calculated at the interface between Pd-layer and support in presence of sweep gas is always significantly higher than $H_2$ partial pressure measured in the permeate. This difference is progressively increasing while increasing sweep gas flow rate and tends to saturate at high flow rates.

## 1. Introduction

Development of palladium and palladium-alloy membranes for hydrogen separation, since early times, has received a lot of attention, focusing on specific applications in membrane reactors such as methane steam reforming and WGS reactions [1–6].

Development of such membranes, however, has obtained a great impulse in the last decade, in correspondence to growing interest of industry for hydrogen economy and carbon capture in power generation plants. Most of these projects are dealing with development of composite membranes made up of a Pd or a Pd-alloy dense layer, where hydrogen separation occurs, deposited with various methods on cheaper porous support materials [7–11]. Palladium, in fact, is very expensive and its cost is fluctuating a lot. For example palladium cost has increased from about 420 up to 788 US$/flyoz in 2010. Forecast for the near future are possibly for further increase, due to the growing demand from emerging economies (e.g. China and India) for large scale applications, such as catalytic silencers in automotive industry.

Increasing hydrogen flux, while maintaining high permselectivity and physico-chemical stability in the long-term is a key issue for near future developments. According to the Sieverts' law, $H_2$ flux through a palladium membrane can be increased either by the reduction of the palladium layer thickness or with the increase of the driving force of the process, e.g. difference of the partial pressure difference between the two sides of the membrane. At a given feed pressure, therefore, the driving force of $H_2$ permeation can be further increased by feeding a sweep gas (such as nitrogen or steam) in the permeate side. Some literature works [10–12], however, suggest that this gain can be significantly reduced due to the diffusion resistance of the support which leads to an increase of the $H_2$ partial pressure in the pores near the surface of the Pd layer. This phenomenon has been first evidenced by Dittmeyer [12] who compared hydrogen fluxes obtained from experiments with nitrogen sweep gas fed on the different sides of a Pd–Ag composite membrane obtained by electroless deposition on a α-alumina support. The sweep gas was more effective in increasing $H_2$ flux when supplied on the palladium-side of the membrane; moreover when the

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## Nomenclature

| | |
|---|---|
| $B_0$ | viscous flow parameter ($m^2$) |
| $D_{H_2N_2}$ | effective binary diffusion coefficient ($m^2/s$) |
| $D^0_{H_2N_2}$ | binary diffusion coefficient in the porous media (N/s) |
| $D_{Ki}$ | effective Knudsen diffusion coefficient ($m^2/s$) |
| $D_{KA}$ | “mean” effective Knudsen diffusion coefficient ($m^2/s$) |
| $E_a$ | activation energy (J/mol) |
| $F_{He}$ | helium permeance ($mol/m^2/s/Pa$) |
| $F_{KH_2}$ | hydrogen Knudsen diffusion component ($mol/m^2/s/Pa$) |
| $F_{VH_2}$ | hydrogen viscous flow component ($mol/m^2/s/Pa^2$) |
| $F_{KHe}$ | helium Knudsen diffusion component ($mol/m^2/s/Pa$) |
| $F_{VHe}$ | helium viscous flow component ($mol/m^2/s/Pa^2$) |
| $J_{H_2}$ | hydrogen flux ($mol/m^2/s$) |
| $J_{N_2}$ | nitrogen flux ($mol/m^2/s$) |
| $J_S$ | Sieverts’ flux ($mol/m^2/s$) |
| $L$ | Pd-layer thickness ($\mu m$) |
| $M_i$ | molecular weight (kg/kmol) |
| $n$ | pressure exponent |
| $P_{FH_2}$ | $H_2$ partial pressure in the feed (Pa) |
| $P_i$ | total pressure at the interface (Pa) |
| $P_{PH_2}$ | $H_2$ partial pressure in the permeate (Pa) |
| $P_{iH_2}$ | hydrogen partial pressure at the interface (Pa) |
| $P_P$ | total pressure in the permeate side (Pa) |
| $P_F$ | total pressure in the feed side (Pa) |
| $Pe_0$ | pre-exponential factor ($mol/m/s/Pa^n$) |
| Pe | membrane permeability ($mol/m/s/Pa^n$) |
| $P_{av}$ | average pressure (Pa) |
| $P_i$ | partial pressure (Pa) |
| $r$ | pore radius (m) |
| $R$ | ideal gas constant (J/mol/K) |
| $T$ | temperature (K) |
| $x_i$ | molar fraction of the component $i$ |
| $x_{iH_2}$ | hydrogen molar fraction at the interface |
| $x_{PH_2}$ | hydrogen molar fraction in the permeate |
| $z$ | support thickness m |
| i | gas: $H_2$, $N_2$ or He |

*Greek symbols*

| | |
|---|---|
| $\varepsilon$ | porosity |
| $\mu_i$ | viscosity of pure gas (Pa s) |
| $\bar{\mu}$ | mean viscosity of a gas mixture (Pa s) |
| $\tau$ | tortuosity |

sweep gas was supplied on the support side, at high flow rates no real increase of $H_2$ flux was observed, although $H_2$ partial pressure in the permeate decreased substantially with increasing sweep gas flow. This behavior was attributed to the diffusion resistance of the support which determines an increase of the partial pressure in the pores of the support towards the surface of the palladium layer.

More recently Zeng, while studying the impact of the mass transfer resistance of the support on $H_2$ permeation of a Pd/Ag composite membrane, suggested that $H_2$ transport out of the ceramic support was slowed down by counter-diffusion of $N_2$ into the support pores [13].

This effect has been also detected by Li, during bench scale test of a ultrathin supported Pd-membranes in syngas mixtures at 400 °C and up to 35 bar [14].

Such a phenomenon, however, has not been yet systematically investigated.

The scope of this work, therefore, is to develop a methodology which can be applied to evaluate the influence of any type of porous support on the hydrogen permeation of a Pd-composite membrane in presence of sweep gas in the support side.

## 2. Experimental

### 2.1. Membrane preparation

A palladium composite membrane has been prepared by electroless plating on a tubular macroporous support.

The support is an AISI 316L porous tube, O.D.10 mm and 2 mm thick, with a nominal pore size of 0.1 μm, supplied by Mott Corporation. The effective mean pore size, however, of such a material, measured by mercury intrusion is about 2 μm [15]. Two non porous AISI 316 L tubes were welded at the ends of the porous support in order to allow a gas tight sealing when introducing the membrane in the reactor. The total length of the support is 20 cm and the active length of the porous support is 7.5 cm. The active surface of the membrane is 23.5 $cm^2$.

The porous support has been machine polished for 8 h with a diamond paste in order to reduce surface rugosity and minimize the thickness of the deposited palladium layer. At the end of the mechanical treatment the surface mean rugosity has been reduced from 3.4 μm down to 0.65 μm.

Membrane has been prepared according to a procedure similar to the one developed by Ma [16] and described in detail in [17]. It consists of the following steps:

- Cleaning of the support in an ultrasonic bath with acetone, followed by successive rinsing in water, diluted hydrochloric acid, de-ionized water up to a neutral pH, and acetone.
- Oxidation of the support in a oven with static air at the temperature of 500 °C, for two successive cycles of 10 h.
- Activation of the oxidized support by dipping into a stannous chloride solution and a palladium chloride solution, alternately, for many times.
- Deposition in successive bath of palladium by electroless plating on the shell side of the tube.

At the end of each bath, membrane thickness has been estimated by gravimetric measurements and, thereafter, helium permeance as a function of pressure has been determined, at room temperature.

Fig. 1 shows He permeance of the support, as received and machine polished, and of the membrane, after successive Pd-depositions. Machine polishing determines an occlusion of support

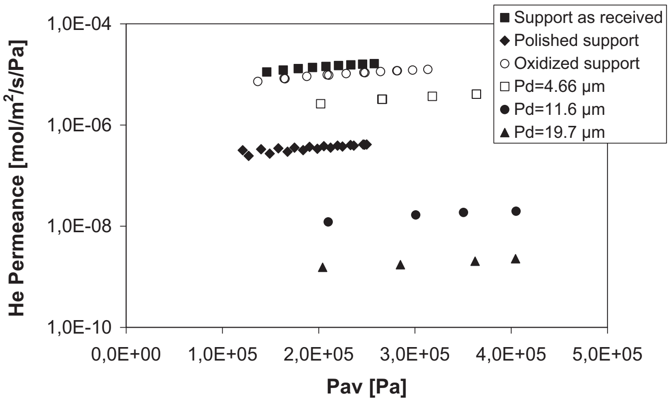

**Fig. 1.** He permeance at room temperature of the support and of the Pd-composite membrane for different Pd-layer thicknesses.