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A thin supported Pd-Au based membrane for hydrogen generation and purification: A case study

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ABSTRACT

In this work, a composite membrane based on a thin Pd-Au metallic layer supported on a ceramic substrate was produced by electroless plating deposition with the intent of generating and, meanwhile, purifying hydrogen in a single stage. Permeation tests were performed with pure gases (H$_2$, N$_2$, CO$_2$, CH$_4$) on both of them by varying the temperature between 300 °C and 400 °C and the feed pressure from 150 to 250 kPa to evaluate the hydrogen perm-selectivity characteristics of the membrane.

A reference H$_2$/N$_2$ ideal selectivity around 500 was reached at 400 °C and 50 kPa of transmembrane pressure and it remained stable up to 600 h under operation. The presence of defects on the metallic layer affected negatively the membrane performance in terms of H$_2$ perm-selectivity, probably caused by the absence on an intermediate layer, which did not compensate the mechanical stress due to different thermal dilation coefficients within the metallic layer and the ceramic substrate.

1. INTRODUCTION

The growing attention towards the hydrogen utilization as energy carrier involved a high demand on hydrogen permeable membranes as compact devices for hydrogen separation and purification [1]. Several studies in the open literature demonstrated that composite Pd-based membranes are very effective for the aforementioned purposes, particularly if compared to the utilization of unsupported Pd-based membranes because of their high cost and mechanical limitations [2-3]. Palladium and its alloys possess a particular behavior to be fully hydrogen perm-selective over all of the other gases and this has been extensively studied in the last decades [4].

It is well known that hydrogen permeation through palladium-based membranes follows a solution/diffusion mechanism and many studies were conducted on self-supported thick Pd-based membranes (>5 μm of dense palladium or palladium-alloy layer) because presenting full hydrogen perm-selectivity but low permeability as well as resulting extremely expensive as much as the membrane was thick [5]. In order to improve the hydrogen permeance, meanwhile reducing the amount of palladium utilized and, consequently, the membrane cost, in the last twenty years, much attention was paid for manufacturing thin palladium and palladium-alloy films supported on porous substrates (both ceramic and metallic) [6-10].

However, the hydrogen transport through a dense layer of palladium or palladium-alloy takes place under a driving force (from a high to a low pressure gas region) in a multi-step mechanism involving: (a) the diffusion of molecular hydrogen on the palladium membrane surface, (b) reversible dissociative adsorption on the palladium surface, (c) dissolution of atomic hydrogen into the metal bulk, (d) diffusion of atomic hydrogen

through the bulk metal, (e) association of hydrogen atom on the palladium surface, (f) desorption of molecular hydrogen from the surface, (g) diffusion of molecular hydrogen away from the surface [11].

Commonly, hydrogen permeation through a pd-based membrane is represented by the equation reported below (eq. 1):

$$J_{H_2} = \frac{P\left(p_{hps}^n - p_{lps}^n\right)}{\delta} \tag{1}$$

J_{H2} represents the hydrogen flux permeating through the dense layer of palladium or palladium-alloy, P is the hydrogen permeability, δ the thickness of the palladium/palladium alloy layer, p_{hps} and p_{lps} the hydrogen partial pressures on the high pressure (feed) and low pressure (permeate) sides, respectively, while "n" is the pressure exponent. n-value can vary from 0.5 to 1 depending on the rate-determining step among the hydrogen permeation steps reported above. In case of bulk diffusion through the palladium layer controlling the hydrogen permeation mechanism, n is 0.5 (Eq. 1 becomes the Sieverts-Fick) and, consequently, the Pd-based membrane shows fully hydrogen perm-selectivity. On the contrary, in case of mass transport to or from the surface, dissociative adsorption or associative desorption are the rate determining stage, n is 1 since the processes depend linearly on the concentration of molecular hydrogen.

Among a number of supported palladium-alloy membranes, Pd-Au composite membranes attracted a growing interest because gold ensures higher resistance to the catalytic poisoning and corrosive degradation acted by sulfur compounds, globally enhancing the hydrogen permeability over pure palladium (up to 15% Au content) and reducing the

embrittlement phenomenon [12-13]. In early studies, Pd-Au membranes were prepared by expensive metallurgical processes with a thickness ranging from 25 to 100 μm and using intermediate layers [14]. More recently, supported thin Pd-Au alloy membranes were prepared by electroless plating or electroplating technique on different porous substrates, experimentally analyzing the hydrogen perm-selectivity performance and the chemical-physical resistance [15-19]. The intent of this work is to give an overview about Pd-based membranes, paying special attention to the preparation and characterization of composite Pd-alloyed membranes for hydrogen production (in membrane reactor modules), separation and purification.
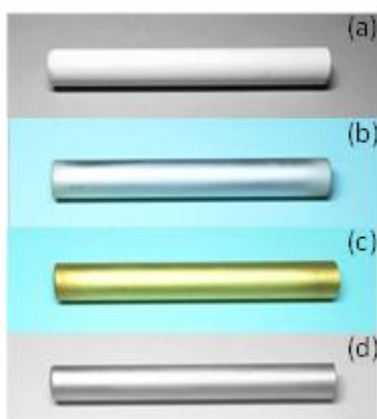

Figure 1. Metallic layers electrodeposition steps for the Pd-Au/Al$_2$O$_3$ membrane, a) ceramic substrate; b) Pd deposition; c) Au deposition; d) Pd-Au/Al$_2$O$_3$ final membrane

As a case study, a new generation of Pd-Au membranes supported on a ceramic substrate (Figures 1,2) is studied considering the absence of an intermediate layer, by varying pressure and temperature, meanwhile evaluating their effects on n-value in the Sieverts' equation and the stability of the membrane in terms of H$_2$/N$_2$ reference selectivity and hydrogen permeating flux with respect to the thermal cycles.
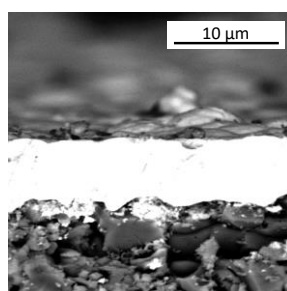

Figure 2. Cross section of the Pd-Au/Al$_2$O$_3$ membrane (Pd-Au metallic layer is around 8 mm)

Furthermore, a comparison among our study and the Pd/Pd-alloyed membranes present in literature is also illustrated.

2. EXPERIMENTAL

The case study of this work considers a not commercial Pd-Au/α-Al$_2$O$_3$ membrane showing an average metallic layer of 8 μm, total length of 7.5 cm (5.0 cm of active length), o.d. 13 mm and i.d. 8 mm. Pd-Au layer was deposited via electroless

plating technique following a multistage process. Indeed, when the Pd deposition was completed, the Pd/Al$_2$O$_3$ sample was soaked with water before Au plating. The plating agent comprises 1 g/L HAuCl$_4$·4H$_2$O, 70 g/L Na$_2$EDTA and 250 mL/L NH$_3$·H$_2$O, the reducing agent is a 0.5 mol/L N$_2$H$_4$ solution. The composite membrane was housed in the membrane module and two graphite gaskets were used to prevent the mixing within permeate and retentate streams. The operating temperature was varied between 300 °C and 400 °C, and feed pressure between 150 kPa (abs.) and 250 kPa (abs.), while the permeate pressure was kept constant at 100 kPa (abs.) in the whole experimental campaign.

The ideal H$_2$ perm-selectivities (Eq. 2) of the supported Pd-Au/α-Al$_2$O$_3$ membrane were experimentally evaluated by permeation tests with pure N$_2$, H$_2$, CH$_4$ and CO$_2$. The volume flow rate of each pure gas permeating through the membrane was measured by means of a bubble-flow meter as an average value of at least 10 experimental points.

$$\alpha_{H2/i} = J_{H2}/J_i \qquad (i = N_2, CO_2, CH_4) \qquad (2)$$

where, J_{H2} and J_i are the H$_2$ permeating flux (Eq. 1) and the permeating flux of another pure gas among CO$_2$, N$_2$ and CH$_4$.

A X-ray diffraction (XRD) analysis was carried out on a Siemens D8 Bruker-Axs III diffractometer with Cu-K$_\alpha$ radiation operating at 40 kV and 30mA.

SEM analyses were done using a Phenom ProX desktop.

3. DISCUSSION

XRD patterns of Pd-Au membrane before and after heat treatment are illustrated in Figure 3. The higher intensity of Au signals is because the outer layer of the membrane precursor is Au.

After heat treatment, both palladium and gold with a cubic crystallinity were completely transferred into Pd-Au alloy with a cubic crystallinity. As shown in Figure 3, the peak of the Pd-Au alloy is closer to that of palladium, probably because of the much larger content of palladium.
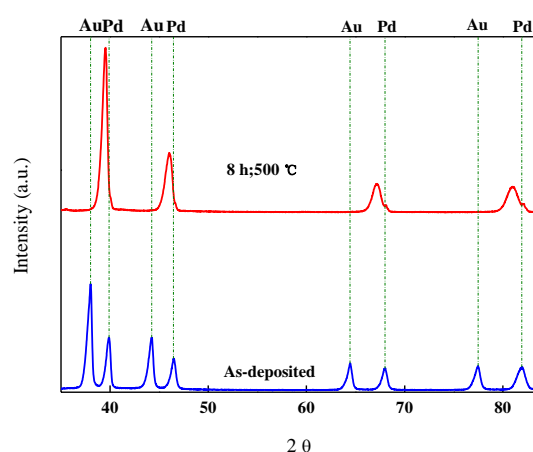

Figure 3. XRD Patterns of Pd-Au membrane

The H$_2$ hydrogen flux permeating through the composite membrane at various temperatures and by varying the transmembrane pressure between 150 and 250 kPa is reported in Figures 4-6, where the graphical assessment of "n-value" indicated that the best fitting is reached at n=0.5.
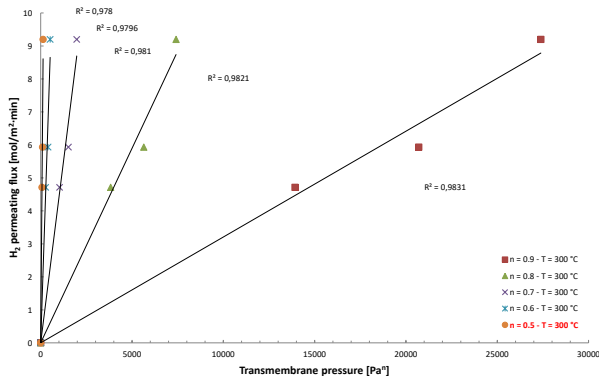
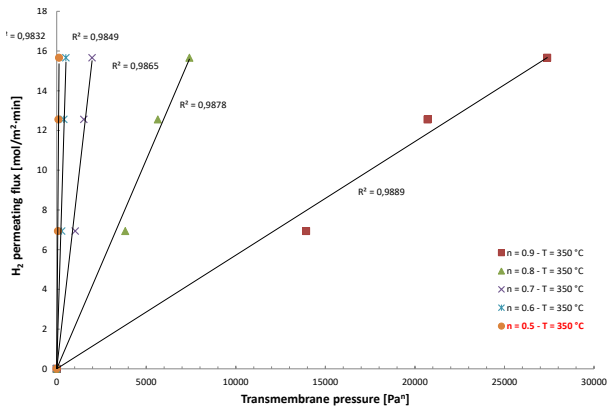**Figure 4.** Graphical assessment of H_2 permeating flux vs transmembrane pressure at 300 °C for the Pd-Au/a-Al$_2$O$_3$ membrane

Figure 5. Graphical assessment of H_2 permeating flux vs transmembrane pressure at 350 °C for the Pd-Au/a-Al$_2$O$_3$ membrane
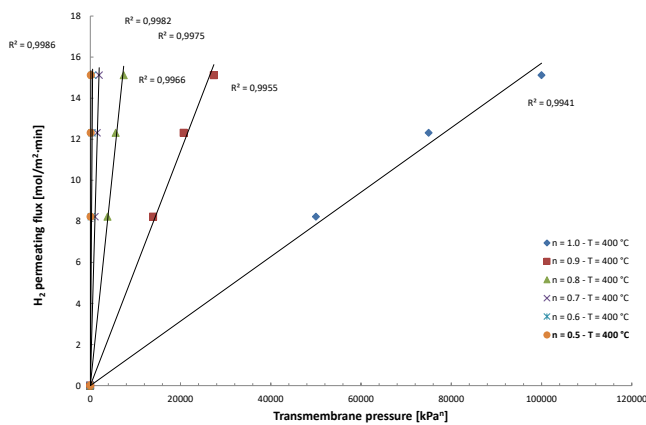

Figure 6. Graphical assessment of H_2 permeating flux vs transmembrane pressure at 400 °C for the Pd-Au/a-Al$_2$O$_3$ membrane

Consequently, being n=0.5 for all the temperatures investigated in this work, the mechanism regulating the H_2 transport through the Pd-Au/Al$_2$O$_3$ membrane can be described by the Fick-Sieverts law (Eq. 3).

$$J_{H_2} = \frac{P(p_{hps}^{0.5} - p_{lps}^{0.5})}{\delta} \tag{3}$$

The resulting H_2/other gas selectivities are then reported in Table 1 (at 400 °C).

Table 1. Perm-selectivity characteristics of the Pd-Au/Al$_2$O$_3$ membrane at 400 °C

Ideal selectivity - T = 400 °C				
J_{H_2} [mol/m^2·min]	Δp [kPa]	$\alpha_{H2/N2}$	$\alpha_{H2/CO}$	$\alpha_{H2/CH4}$
8.2	50	500	~ 630	350

As stated above, the hydrogen transport mechanism through the membrane is the Fick-Sieverts law and, consequently, higher H_2 perm-selectivities were expected. However, the low H_2 perm-selectivity values reported in Table 1 can be justified by the possible presence of defects in the separative metallic layer, which favored the transport of other gases besides hydrogen with a different mechanism from diffusion. The defects in the metallic film could be related to the absence of an intermediate layer, responsible of a not uniform metallic thickness distribution on the porous ceramic support. Indeed, this probably made possible local imperfections in the Pd-Au film. It was also reflected in the decreasing trend of the perm-selectivities at higher transmembrane pressures, which favored higher pure gas flow rates in the defects of the metallic layer.

Generally speaking, an intermediate layer plays a crucial role when H_2 selective metallic films are deposited on porous metallic supports. Indeed, it acts as a barrier limiting the intermetallic diffusion. On the contrary, for porous ceramic supports, in which its roughness should favor a better adhesion of the deposited metallic layer, the intermediate layer is useful to compensating the effect of the thermal dilatation of the two different materials constituting the composite membrane, avoiding the formation of defects and, consequently, the membrane failure.

The negative role of the absence of the intermediate layer was checked by analyzing the effects of the thermal cycles on the perm-selectivity performance of the composite membrane. After almost 650 h under operation, the membrane module was cooled down at room temperature and heated up once again at 400 °C to observe the effect of the thermal cycle. At this temperature and $\Delta p = 50$ kPa, a dramatic decrease of H_2/N_2 ideal selectivity was observed, inducing to stop the experimental tests and confirming that the different thermal dilation/contraction coefficients the of Pd-Au layer and ceramic support were responsible of local cracks in th separative layer, consequently making possible low H_2 perm-selectivity values.

4. CONCLUSIONS

A H_2/N_2 ideal selectivity around 500 was reached at 400 °C and 50 kPa of transmembrane pressure and it remained stable up to 600 h under operation. The presence of defects on the metallic layer affected the H_2 perm-selectivity of the membrane and it was probably caused by the absence of an intermediate layer, useful for compensating the mechanical stress due to different thermal dilation coefficients of the two materials constituting the composite membrane.

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