

Influence of the selective layer morphology on the permeation properties for Pd-PSS composite membranes prepared by electroless pore-plating: experimental and modeling study

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Abstract

The relationship between permeation behaviour and palladium layer morphology of a composite membrane prepared over a porous stainless steel support by Electroless Pore-Plating is presented in this work. Fully dense membranes were achieved with permeances in the range $7 - 18 \cdot 10^{-5} \text{ mol/m}^2 \text{ sPa}^{0.5}$, although the membrane morphology is clearly influenced by the synthesis conditions, particularly by the concentration of the Pd reducing agent (hydrazine). In this manner, a higher hydrazine concentration provokes the formation of a thicker external Pd film and, consequently, both external porosity and roughness decrease. On the other side, low hydrazine concentration facilitates the penetration of Pd inside the pores of the support. This fact, in turns, introduces an additional permeation resistance, which diminishes the hydrogen permeation flux and also introduces a threshold in the trans-membrane pressure value needed to allow hydrogen flux across the membrane. A new mathematical model, based on the Sieverts' law, is proposed to predict this particular behaviour, obtaining a good accuracy between both predicted and experimental data, including the gap in

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the trans-membrane pressure. In this manner, the presented model can be used in multiple cases to design and optimize membranes modules prepared by Electroless Pore-Plating.

Keywords: Pd membrane, Pd layer morphology, permeation model, Electroless pore-plating, Hydrogen, Hydrazine

1. Introduction

The massive use of fossil fuels for energy generation provokes the emission of large amounts of anthropogenic carbon dioxide that contributes to the global warming, the urban smog, the acid rain and some health problems in humans [1].
5 The continuous grow in population, joined with the economic development, foments an increasing energy demand than makes this situation unsustainable for the future [2]. In this sense, great efforts are being made to mitigate this problem directed towards the substitution of fossil fuels as primary energy resource (i.e. renewable resources, hydrogen economy or nuclear fusion) and developing
10 effective carbon capture processes [3]. In both cases, separation processes are critical for real industrial applications in favourable economic terms. Particularly, the development of a membrane technology for hydrogen separation has been of great interest in the last years. This technology is call to be a major contributor to the establishment of a hydrogen economy [4].

15 Accordingly to the United States Department of Energy, dense metallic membrane materials have to meet the following technical targets for competitive commercialization: i) H_2 selectivity close to 100% , ii) high permeability ($> 680scfh/ft^2/atm^{0.5}$) at $T = 400^\circ C$ and $\Delta P = 20$ psi, iii) long-term stability at operating conditions (mechanical and thermal resistance) and iv) tolerance
20 to typical pollutants (i.e. carbon, CO or H_2S) [5]. In order to achieve all these requirements, different strategies are used to prepare the membranes. The incorporation of a palladium (or alloys) thin film over a porous support by electroless plating is one of the most suitable due to the uniformity and hardness of deposits, simplicity of the technique and good permeability [6]. However, the high

25 investment cost is still one of the main drawbacks for the use of these mem-
branes on a large scale [7]. This elevated cost is mainly due to the palladium
and the support prices, as well as the amount of membranes rejected during the
material synthesis. The main strategy to save costs is based on the prepara-
tion of ultrathin palladium layers, reducing the metal amount and maximizing
30 the permeation capacity of the membrane. Different alternatives have been pro-
posed in the literature, such as the use of vacuum to fill the pores of the support
with palladium by Zhang et al. [8], the combination of electroless plating with
osmosis to facilitate the Pd incorporation around the pore area by Souleimanova
et al. [9] or the preparation of pore-filled membranes in which the palladium
35 is incorporated as a internal layer on the support cross-section by Yogo et al.
[10]. However, the presence of defects such as wrinkles, cracks and pinholes is
frequent during the synthesis of these really thin films. Thus, the repair of these
defects can be also considered a good strategy to reduce the overall cost of the
membrane preparation. In this way, Li et al. proposed a combination of electro-
40 less plating and osmosis, ensuring a complete disappearance of Pd layer defects
without any reduction of permeability or increase in the metal thickness [11].
Zeng et al. used a defect sealing via point plating by feeding the palladium salt
and the reducing agent from opposite sides of the membrane [12]. Differently,
Lu et al. suggest the use of the intermetallic diffusion bonding to the reparation
45 process [13].

Recently, our group have reported a new alternative, denoted as electroless
pore-plating (ELP-PP) to prepare completely dense membranes directly over
porous stainless steel supports in a unique step, minimizing the generation of
defects. It consists on forcing the reaction between Pd source and reducing agent
50 to take place inside the pores by feeding both reactants from opposite sides of the
support [14]. Even though this methodology has demonstrated the possibility to
obtain completely defect-free composite membranes, the particular conditions
employed during the synthesis procedure is still under study.

On the other hand, not only the membrane preparation has been attracted
55 growing attention but also the hydrogen permeation modelling through these

Pd-based membranes has been also a topic of great interest in the last years. Thus, mathematical models can be a great tool in the design and optimization of membrane modules, particularly when laboratory data must be translated into a commercial unit. Moreover, the use of the membrane as part of a membrane
60 reactor, e.g. for the water gas shift or methane reforming reactions [15, 16], require of adequate permeation models to make a successful coupling between the membrane and the reactor.

Hydrogen permeation through palladium metal is usually modelled using Sieverts' law, which is based on a solution-diffusion mechanism, with the palla-
65 dium solid diffusion step being the controlling one. According to Sieverts' law, hydrogen permeation flux is proportional to the square root partial pressure gradient $p_{H_2}^{1/2}$. However, when using composite membranes formed by different material layers, other mass transfer resistances (i.3. in gas film, in the mem-
brane support and interphase, etc.) may be of importance and the resulting
70 hydrogen permeation flux is reduced. Most of these mass transfer steps predicts a hydrogen permeation flux proportional to the partial pressure gradient p_{H_2} .

In the literature, there have been two approaches to model this situation with different type of gradients: formulate a transport equation for each indi-
vidual step [17–23] or use only one empirical transport equation with unknown
75 exponent (n) for the partial pressure gradient [4, 24–26]. The later approach corresponds to the so-called Richardsons' law. The value of the exponent indicates the contribution of the different steps to the global process: n close to
1/2 implies that the mass transfer through the bulk palladium is the controlling
step, while n close to 1 can be related to a influence of the mass transfer in the
80 gas phase or support steps [4, 22, 25]. The formulation of a transport equation for each individual step is recommended, particularly when different transport steps are of importance, because this approach is more accurate when the model is used in the scale-up of the membrane.

In the present work the influence of reducing agent concentration to pre-
85 pare composite Pd-Porous Stainless Steel (Pd-PSS) membranes by ELP-PP has been studied. Results have shown that this variable affects to the mor-

phology of Pd layer and to the membrane permeability. The permeation results have been modelled by a rigorous approach, based on the explicit formulation of the individual transport steps. Finally, a modification of Sieverts' law has been
90 proposed and validated to model the specific characteristics of the membranes used in the present work.

2. Methodology

2.1. Membrane preparation

All membranes presented in the present manuscript have been prepared following the general procedure described meticulously elsewhere [14]. Tubular
95 porous stainless steel supports with 0.1 μm grade, provided by Mott Metallurgical Corp., were used. Pieces of 30 mm in length were prepared by cutting the original ones. The membrane preparation procedure basically consists of three successive steps: i) initial cleaning, ii) activation and iii) palladium incorporation by ELP-PP. In the last step, the palladium source (Pd-ammonium
100 complex) and the reducing agent (hydrazine) are fed by opposite sides of support in order to force the chemical reaction into the support pores. Three membranes have been prepared by using different reducing agent concentration: 0.05, 0.20 and 0.20 M. The Pd incorporation was repeated several times for each
105 sample until obtaining a complete dense membrane. Between each cycle, the membrane is rinsed with deionized water and dried overnight at 110°C . The complete density was evidenced by getting a negligible helium permeate flux at room temperature and pressure difference of 3 bar.

2.2. Membrane characterization

110 The characterization of the prepared membranes involves the structural analysis, examining aspects such as surface morphology, coverage uniformity, presence of defects, layer thickness or metal penetration in the pore area, as well as the permeation behaviour.

The morphology of the membranes was analysed by Scanning Electron Mi-
115 croscopy (Philips XL30 ESEM) equipped with an Energy Dispersive Analyti-
cal System (EDAS) for microprobe analysis. Both surface and cross-sectional
analyses were carried out in order to describe in detail the external layer (mor-
phology and thickness) and the Pd incorporation in the pore area (penetration
depth). Moreover, the external roughness has been measured with an optical
120 profiler equipped with a 5x focus lens (Zeta-20 Optical Profiler) and the external
surface porosity was determined by the segmentation of the SEM images with
the software Digital Micrograph©. Finally, the total amount of palladium in-
corporated to the membrane was calculated by gravimetric analysis (electronic
balance Kern & Sohn ABS-4 with a precision of ± 0.0001 g).

125 On the other hand, the permeation behaviour of membranes was studied in
a home-made setup described in previous manuscripts [14] [17]. A scheme of
the equipment is shown in Figure 1. Basically, the membrane is placed in a
permeation cell with graphite o-rings to ensure a correct sealing and the system
is rounded by an electrical furnace to achieve the desired temperature. The feed
130 stream is introduced in the inner side of the membrane, collecting the permeate
flux on the external side. Experiments with pure nitrogen, hydrogen or binary
mixtures of both gases can be analysed. Permeate is maintained at ambient
pressure in all cases, varying the driving force with the retentate pressure in the
range of 0.0 - 3.0 bar.

135 2.3. Membrane model

In cylindrical membrane modules, hydrogen permeation takes place through
the module wall and, as a consequence, the concentration of hydrogen in the
retentate decreases along the axial coordinate. Hence, hydrogen partial pressure
gradient at both sides of the membrane also changes along the axial coordinate.
140 To model this accurately, the differential mass balance to the retentate side has
been formulated [17, 27]:

$$\frac{dF_{H_2r}}{dA_m} = -J_{H_2} \quad (1)$$

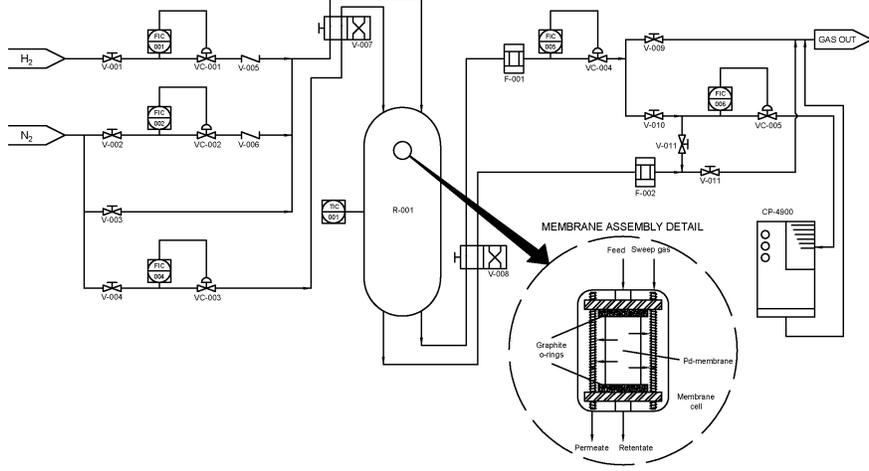


Figure 1: Experimental setup for permeation experiments

where F_{H_2r} is the mole flow rate of hydrogen in the retentate, A_m is membrane external area and J_{H_2} is the local permeation flux.

This ordinary differential equation is solved using the following boundary condition: $F_{H_2r}|_{A_m=0} = F_{H_2r,in}$. The resolution has been done with the help
 145 of a MATLAB code based on function `ode15s`.

The average hydrogen flux for the entire membrane module can be calculated using the following mass balance to the whole membrane. Hydrogen flow rate at the outlet of the retentate side $F_{H_2r,out}$ is obtained after solving the previous
 150 differential equation.

$$J_{H_2av} = \frac{(F_{H_2r,in} - F_{H_2r,out})}{A_m} \quad (2)$$

The local hydrogen flux J_{H_2} is calculated using the permeation model, explained in the following paragraphs, which is evaluated at the corresponding local hydrogen concentration.

The permeation model used in the present work accounts for the different
 155 mass transfer resistances of a cylindrical membrane to calculate the hydrogen

flux. From the retentate side to the permeate side of the membrane the following resistances can be of importance in a palladium-based membrane: gas film, porous support and palladium layer. A mechanistic mass transfer model has been formulated for each resistance and then, the overall mass transfer rate is
 160 calculated by solving the resistances in series.

The gas film resistance appears when the permeability of the membrane is not tested with pure hydrogen. It should be noted that for the case of membranes completely selective to hydrogen, as in the present case, permeate is pure hydrogen, and hence the gas film is not formed at this side. For the retentate
 165 side of the membrane, the following equation is derived from the film theory [17].

$$J_{H_2} = \frac{k_p}{\phi} (p_{H_2r} - p_{H_2s}) \quad (3)$$

where $\phi = \langle 1 - p_{H_2} \rangle_{ln} / P_r$ is the correction factor for unidirectional mass transfer at high concentration (this factor arises when using a linear concentration gradient instead of a logarithmic one), P_r is the absolute pressure in the
 170 retentate, p_{H_2r} and p_{H_2s} are the hydrogen partial pressure in the retentate and in the interface between the gas and internal surface of the support, respectively, and k_p is the gas phase mass transfer coefficient based on partial pressures. This mass transfer coefficient is predicted from Sherwood number for transfer to the inside wall of a tube, $k_p = D_{im} Sh / (RT D_t)$, with $Sh = 3.66$ [28] and D_t is
 175 the membrane internal diameter. The hydrogen diffusion coefficient in the gas mixture (D_{im}) has been calculated using correlations from the literature that takes into account variations in temperature, pressure and composition [28].

The porous support can also contribute with a resistance to mass transfer. The hydrogen flux is proportional to the hydrogen partial pressure gradient:

$$J_{H_2} = \frac{k_h}{L_s RT} (p_{H_2s} - p_{H_2a}) \quad (4)$$

180 where k_h is the hydraulic permeability of the support (m^2/s), p_{H_2a} the hydrogen partial pressure in the interface between the external surface of the support

and the internal surface of the Pd layer and L_S is the support thickness. The hydraulic permeability can be calculated using the dusty-gas-model, which accounts for vand pressure difference of DP=3 iscosus flow (Hagen-Pouisselle) and
185 Knudsen diffusion in porous media [19, 20]:

$$k_h = \frac{\epsilon_p d_{pore}^2 P_r}{32\mu_G\tau} + D_{eK} \quad (5)$$

where d_{pore} is the average pore diameter, ϵ_p is the porosity and τ is the tortuosity of the support, μ_G is the gas viscosity, and $D_{eK} = (2\epsilon_p d_{pore}/3\tau)\sqrt{2RT/\pi M_{H_2}}$ is the effective Knudsen diffusion coefficient of the support, with M_{H_2} being molar weight of hydrogen.

190 The palladium layer is the active element of the membrane, being responsible of the separation achieved in the membrane. The mechanism of hydrogen mass transfer in the palladium layer can be simplified into two stages: hydrogen molecule dissociative adsorption and solution in the metal, and hydrogen atom diffusion [4]. The latter, usually the controlling step, is modelled by Ficks' law.
195 Hydrogen molecule dissociation and solution is modelled by the equilibrium expression. By combination, the so-called Sieverts' law is obtained [29]:

$$J_{H_2} = \frac{Q}{L_{Pd}} \left(p_{H_2^a}^{1/2} - p_{H_2p}^{1/2} \right) \quad (6)$$

where Q is the metal permeability, $k_{Pd} = Q/L_{Pd}$ is the metal permeance of the membrane, p_{H_2p} is the hydrogen partial pressure in the permeate and L_{Pd} is the metal layer thickness. Q , and hence k_{Pd} , have an Arrhenius dependence
200 with temperature, $k_{Pd} = Ae^{-E_a/RT}$ with activation energy, E_a .

The membranes used in the present work exhibit important palladium intrusion inside the pores of the support. Hydrogen molecules from the retentate side diffuse in the porous support and are adsorbed in the palladium of the inside of the pores. Then, hydrogen atoms diffuse in the palladium layer and
205 are desorbed in the permeate side of the membrane. The permeate side of the membrane has no support, it is open to the gas phase. Hence, the gas-palladium interphase surface in the retentate side of the palladium layer is lower than in the

permeate side, due to the presence of the porous support. This fact reduces the effective hydrogen partial pressure gradient and hence, the hydrogen flux of the membrane. To account for this effect the Sieverts' law has been modified with the introduction of a novel parameter, η , which is the ratio of the gas–palladium interphase surface in the retentate and permeate sides of the membrane:

$$J_{H_2} = \frac{Q}{L_{Pd}} \left(\eta p_{H_2a}^{1/2} - p_{H_2p}^{1/2} \right) \quad (7)$$

In the appendix, a detailed deduction of the previous equation derived from the mechanism of hydrogen permeation in the palladium metal has been included. This modification of Sieverts' law constitutes a novelty in the modelling approach of palladium–based membranes for hydrogen separation.

The permeation model, formed by equations (3), (4) and (7), has been solved numerically for known p_{H_2r} and p_{H_2p} to determine the J_{H_2} , p_{H_2a} and p_{H_2s} . The resulting local hydrogen permeation flux (J_{H_2}) is substituted in equation (1) to calculate the retentate flow rate and concentration axial gradients.

The average hydrogen flux (J_{H_2av}) obtained in the permeation experiments has been fitted to the membrane model with two main objectives: determine the controlling mass transfer steps and the unknown membrane properties (k_h , Q and η). The fitting has been carried out using a MATLAB code based on the least-square method (function `lsqcurvefit`).

3. Results and discussion

3.1. Membrane morphology

As it has been previously indicated, commercial porous stainless steel tubes with a grade 0.1 μm were used as support for the membrane preparation. Figure 2 shows the surface morphology of the support (PSS, Figure 2a), obtained from scanning electron microscopy, as well as the surface of the membranes prepared with an hydrazine concentration of 0.05 M (PSS–Pd–01, Figure 2b), 0.20 M (PSS–Pd–02, Figure 2c) and 1.00 M (PSS–Pd–03, Figure 2d). The average

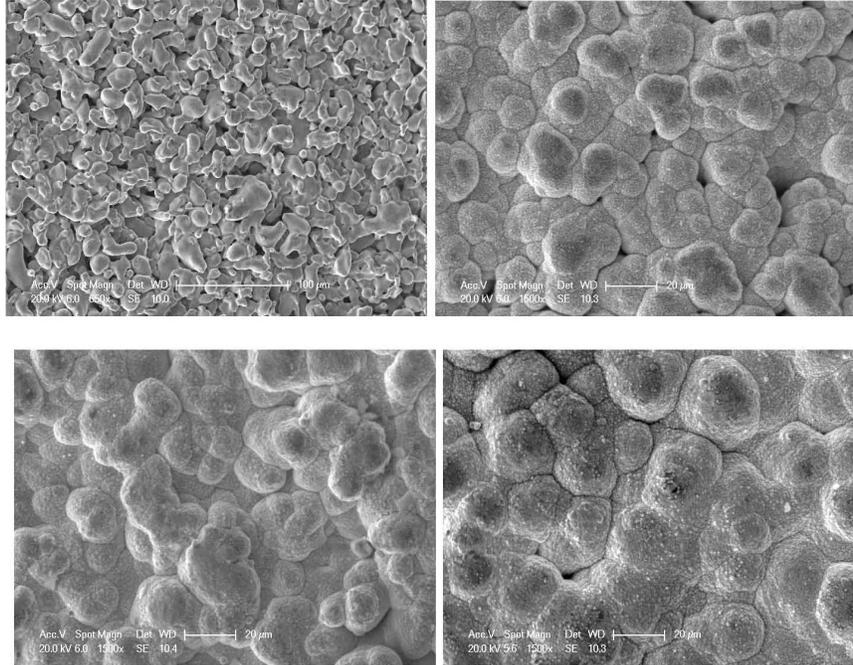


Figure 2: SEM images of the PSS support surface (a) and membranes obtained after Pd incorporation with diverse hydrazine concentration: 0.05 M (b), 0.20 M (c) and 1.00 M (d).

porosity (ε) and surface roughness (R_a) values for each sample are summarized
 235 in Table 1.

The original PSS support presents $\varepsilon = 18.6\%$ and $R_a = 11.8\mu\text{m}$. External
 porosity drastically reduces after the palladium incorporation through ELP-PP,
 independently of the hydrazine concentration. Thus, an average porosity of $\varepsilon =$
 3.2% for PSS-Pd-01 and $\varepsilon = 2.0\%$ for PSS-Pd-03 were obtained, while a negli-
 240 ble porosity was detected for PSS-Pd-02. In this manner, a very homogeneous
 deposition is observed and only some remaining pores are detected.

It is important to emphasize that an external palladium layer was obtained
 in all cases, in spite of the chemical reaction between palladium source and
 hydrazine takes place preferentially in the internal pores of the support. This
 245 fact, apparently contrary to the electroless pore-plating method, has been ex-
 plained in detail in our previous paper [14]. In summary, this behaviour can be

Table 1: Pd layer properties of support and membranes.

Sample	C_H (M)	ε (%)	R_a (μm)	t (μm)
PSS	–	18.6	11.8	–
PSS-Pd-01	0.05	3.2	10.8	16.2
PSS-Pd-02	0.20	0.9	11.3	8.8
PSS-Pd-03	1.00	2.0	6.8	22.0

C_H : Hydrazine concentration; ε : porosity;

R_a : Roughness; t : Pd averaged weight thickness.

explained by the wide pore size distribution of the raw support. The smallest pores can be easily closed with Pd particles, while hydrazine can pass through the larger pores, partially covered, generating an external layer. This external Pd layer makes the surface slightly smoother, decreasing the average roughness until values in the range of $R_a = 6 - 11 \mu\text{m}$. This reduction can be also related to the Pd amount incorporated in the membrane. In this manner, the smoother surface ($R_a = 6.80 \mu\text{m}$) was obtained for the thick Pd layer ($t=22.0 \mu\text{m}$), when a higher hydrazine concentration is employed ($C_{N_2H_4} = 1.00 \text{ M}$, PSS-Pd-03). In other cases, the estimated Pd thickness, obtained by gravimetric analysis, was reduced until $t = 16.2 \mu\text{m}$ for PSS-Pd-01 ($C_{N_2H_4} = 0.05 \text{ M}$) and $t = 8.8 \mu\text{m}$ for PSS-Pd-02 ($C_{N_2H_4} = 0.20 \text{ M}$). In both cases a roughness around $R_a \approx 10 \mu\text{m}$ is observed.

In this point, it is important to emphasize that remaining surface porosity obtained in some samples does not imply gas leaks due to the nature of the palladium deposition method. It is possible to obtain a completely dense membrane when most of the internal pores of the PSS support are filled with palladium, independently of the continuity in the external layer. In this sense, the performance of these membranes have to be evaluated through permeation measurements.

3.2. Membrane permeation

In order to evaluate the permeation behaviour of the prepared membranes, diverse tests with pure gases and mixtures have been carried out in a temperature range of 350-450 °C and pressure difference interval of 0.25 - 2.50 bar. First
270 of all, it has to be pointed out that no nitrogen was detected in the permeate flux and thus all membranes were completely selective to hydrogen. Figure 3 and Figure 4 shows the permeation fluxes obtained at different conditions for membranes PSS-Pd-01 and PSS-Pd-02, respectively. The membrane prepared with a higher hydrazine concentration ($C_{N_2H_4} = 1.00$ M, PSS-Pd-03) shows a
275 Pd thickness very close to the obtained with pure hydrazine and is described in detail in previous paper [14]. Since the permeation behavior of both membranes are very similar, the results obtained for these conditions have been omitted in this manuscript.

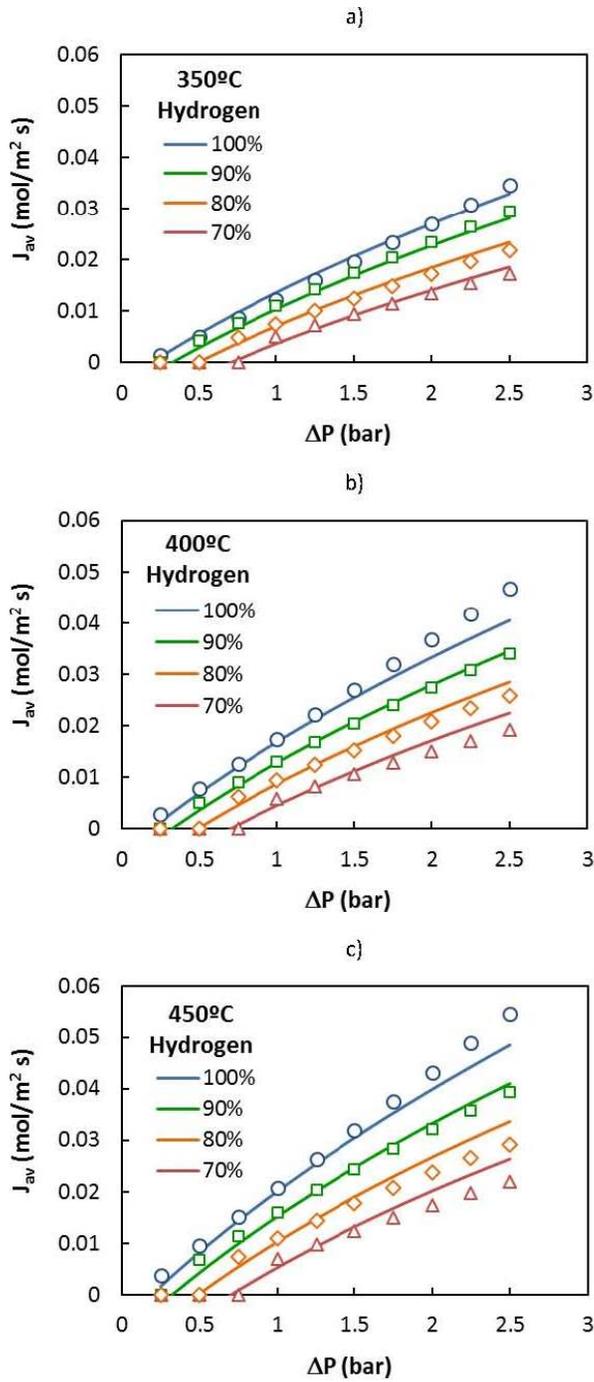


Figure 3: Membrane-averaged permeation flux of membrane MB02. Influence of total pressure gradient (0.5–2.5 bar), temperature, 350°C (a), 400°C (b) and 450°C (c), and hydrogen concentration, 100 (○), 90 (□), 80 (◇), 70 (△). Symbols: experiments. Lines: model fitting.

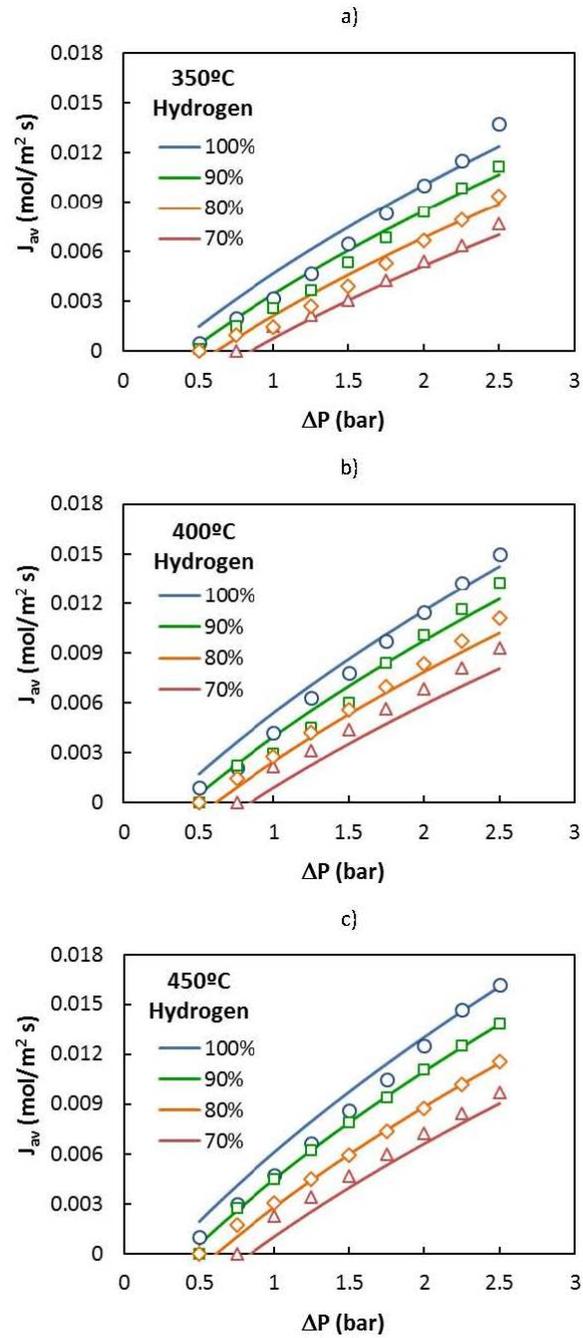


Figure 4: Membrane-averaged permeation flux of membrane MB05. Influence of total pressure gradient (0.5–2.5 bar), temperature, 350°C (a), 400°C (b) and 450°C (c), and hydrogen concentration, 100 (○), 90 (□), 80 (◇), 70 (△). Symbols: experiments. Lines: model fitting.

Focusing on the permeation fluxes obtained for the PSS-Pd-01 and PSS-
280 Pd-02 membranes, a better permeation capacity was obtained as pressure dif-
ference and temperature increase. These results agree with the performance of
conventional Pd membranes that predicts the Sieverts' law. However, in both
cases, a particular behaviour differs with this theoretical equation. As it can be
clearly seen, a deviation is obtained when experimental data are extrapolated to
285 the origin since there is a minimum pressure difference below which the hydro-
gen permeation through the Pd membrane will not occur. A similar behaviour
is observed for both membranes, although the initial threshold for hydrogen
permeation processes increases as the hydrazine concentration decreases. This
fact suggests the existence of an additional resistance which is function of the
290 hydrazine concentration used during the ELP-PP and the conditions of the per-
meation tests (mainly, hydrogen content in feed stream and temperature). This
effect was analysed carefully through the modelling to adequate the predicted
model in the following section.

3.3. Model fitting

295 The experimental permeation data have been fitted to model proposed in the
methodology. As discussed previously, this phenomenological model considers
the existence of three possible mass transfer resistances in series. The data have
been processed in two groups as explained in the following paragraphs.

Firstly, the experiments carried out with pure hydrogen have been used to
300 fit the parameters of the porous support and palladium layer steps. Note that
with pure hydrogen there is an absence of concentration gradients, and hence of
gas film resistance. It was found that the resistance of the porous support was
negligible for both membranes. This is in agreement with the characteristics
of the membranes, with palladium intrusion inside the pores of the support.
305 Secondly, the fitting of the parameters of the palladium layer resistance was
repeated, but now using all the experimental data. For the case of experiments
with hydrogen/nitrogen mixtures, the gas film resistance was entirely predicted
using a correlation from the literature, as explained in the methodology section.

Table 2: Model parameters obtained by least-square fitting of the experimental data.

	PSS-Pd-02	PSS-Pd-01
Permeance (673 K) 10^5 (mol/m ² s Pa ^{1/2})	17.9 ± 0.8	7.0 ± 0.3
Activation energy (kJ/mol)	14.5 ± 1.7	9.7 ± 1.8
Parameter η	0.916 ± 0.01	0.88 ± 0.01
R_{adj}^2	0.974	0.968

The results of the fitting are presented in Table 2 for both membranes.

310 The goodness of the fitting can be evaluated by means of the regression coefficients, displayed in Table 2, and the model prediction curves of Figure 3 and 4. In general, the accuracy of the model fitting is good. The mayor discrepancies are observed for membrane PSS-Pd-02 at the highest pressure and temperature. Overall, the proposed model, based on a modified Sieverts' law, is
 315 able to predict the reduced hydrogen partial pressure gradient observed in these membranes and the initial trans-membrane pressure threshold. These results can be extrapolated to the design and optimization of commercial membrane modules.

The permeance is given at the reference temperature of 673 K. It can be
 320 observed that membrane PSS-Pd-02 has a permeance which is more than twice the permeance of the membrane PSS-Pd-01. This is due to the lower palladium layer thickne of membrane PSS-Pd-02 with respect to PSS-Pd-01 (8.8 μm and 16 μm , respectively). To compare both membranes, regardless of their different palladium content, the metal permeance can be used, $Q = k_{Pd}L_{Pd}$. A value of
 325 $1.58 \cdot 10^{-9}$ and $1.12 \cdot 10^{-9}$ mol/m s Pa^{1/2} are obtained, respectively, for membranes PSS-Pd-02 and PSS-Pd-01. The metal permeance of both membranes is not the same, but it is similar, and the discrepancy can be attributed to a different distribution of the palladium between the external layer and the pores.

Activation energy is also similar for both membranes, obtaining 14.5 and 9.7

330 kJ/mol, respectively, for membrane PSS-Pd-02 and PSS-Pd-01, respectively. These values are in agreement with the typical activation energy for permeation in dense palladium, 15.5 kJ/mol [30].

Finally, the parameter η is slightly different for both membranes. This value is a measurement of the ratio of the gas-palladium interphase surface at both sides of the palladium layer. Values of η equal to 1 means that the adsorption positions at one side of the layer and the other are the same. In this case, the membrane PSS-Pd-01 has the lowest value, which is an indication that more palladium has intruded inside the pores of support of this membrane.

Figure 5 shows the SEM cross-section images of both membranes. As it can be clearly seen, the hydrazine concentration determine the relationship between the external Pd film and the penetration inside the pores. In this manner, an external Pd film of about 5 microns and a penetration of around 20-30 microns in depth was obtained for the membrane PSS-Pd-02, while the Pd incorporation inside the pores significantly increases as the hydrazine concentration decreases (CN₂H₄ = 0.05 M, PSS-Pd-01). Accordingly to this behaviour, a hydrazine concentration of 0.2 M was selected as best conditions in order to prepare Pd-composite membranes by Electroless Pore-Plating.

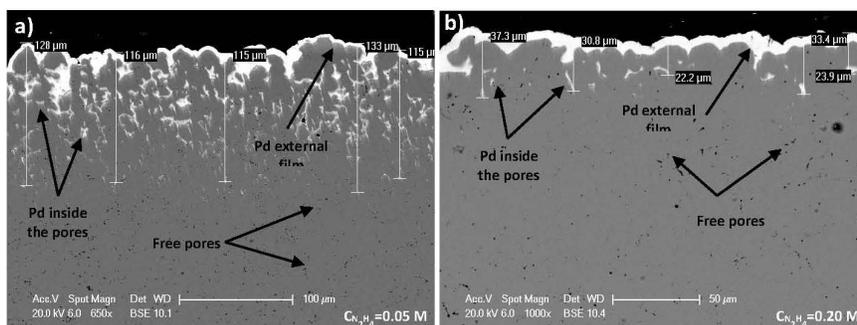


Figure 5: Cross sectional SEM images of membranes prepared with diverse hydrazine concentration: a) CN₂H₄ = 0.05 M (PSS-Pd-01) and b) CN₂H₄ = 0.20 M (PSS-Pd-02).

4. Conclusions

Three different membranes were prepared through the electroless pore-plating
350 method varying the hydrazine concentration, obtaining in all cases totally dense
membranes in spite of the observation of external pores. This fact can be ex-
plained by the nature of the Pd incorporation method in which the closing of
the support pores does not imply a continuous metal layer on the surface. From
all experiments can be extracted that hydrazine concentration clearly deter-
355 mines the membrane morphology. In this way, a higher concentration makes
the generation of an external film easy, decreasing the external porosity and
roughness, while lower concentrations facilitate the penetration of Pd inside
the pores of PSS. A particular permeation behaviour is observed with these
membranes, obtaining a threshold of pressure difference while no hydrogen per-
360 meation occurs. At lower pressures differences, the driving force for the perme-
ation process was insufficient to overcome the material resistance. This effect
increases as the hydrazine concentration decreases during the membrane prepa-
ration step. From these minimum values, a conventional permeation behaviour
accordingly to Sieverts' law was obtained. All these effects have been modelled
365 with a really good accuracy. In this manner, the model provides a powerful tool
for designing and optimizing a wide variety of commercial membrane modules.
Finally, accordingly to the experimental data obtained in this work, the mem-
brane PSS-Pd-02, prepared by using $\text{CN}_2\text{H}_4 = 0.20 \text{ M}$, must be selected due
to accomplish a complete hydrogen selectivity with limited Pd thickness and
370 initial permeation threshold.

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Appendix A. Deduction of the palladium permeation model

The permeation model in the palladium has been deduced from the follow-
375 ing mechanism of permeation. In the retentate side of the membrane, hydrogen

from the gas adsorbs and dissociates on the palladium surface. Then, the hydrogen atoms diffuse through the solid palladium, which includes diffusion in the palladium inside the porous support and in the dense layer coated to the support. Finally, in the permeate side of the membrane hydrogen molecule is
 380 formed and desorbs into the gas phase. The diffusion step is considered the rate-limiting step of this mechanism, because of the thickness of the palladium layer of the membranes used in this work.

Hydrogen adsorption and desorption

Hydrogen adsorbs and dissociates on specific points of the palladium surface
 385 (σ), according to the following reaction:



This step is fast in comparison with the diffusion step, hence hydrogen concentrations can be considered in equilibrium. The adsorption equilibrium constant relates hydrogen gas partial pressure (p_{H_2}) and hydrogen fractional adsorption (Θ_{H}):

$$K_{ads} = \frac{\theta_{\text{H}}^2}{p_{\text{H}_2}(1 - \theta_{\text{H}})^2} \quad (9)$$

390 Since hydrogen dissolves and diffuses into the palladium, hydrogen fractional adsorption is maintained low, so $(1 - \Theta_{\text{H}}) \approx 1$, and hence [18]:

$$\theta_{\text{H}} = (K_{ads} p_{\text{H}_2})^{1/2} \quad (10)$$

Hydrogen diffusion

The diffusion of the hydrogen atom into the palladium metal is modelled by Ficks law, where mass transfer *flux* (J_{H_2}) is proportional to the concentration

395 difference of dissolved hydrogen (X_H) at both sides of the palladium layer [19]:

$$J_{H_2} = \frac{D_H}{L_{Pd}} (X_H^{(1)} - X_H^{(2)}) \quad (11)$$

The concentration of dissolved hydrogen is related to the hydrogen fractional adsorption, $X_H = \Omega\theta_H$, where Ω is the total molar concentration on the palladium surface. The Ω parameter is proportional to the gas-palladium interphase surface. In the membranes of the present work, the intrusion of palladium inside
400 the pores of the support determines different interphase surfaces at both sides of the palladium layer, and hence $\Omega^{(1)} < \Omega^{(2)}$. By substituting into the flux expression:

Considering now equation 10 to relate fractional adsorption and partial pressure, and making the definition of the parameter $\eta = \Omega^{(1)}/\Omega^{(2)} < 1$, the flux
405 expression is simplified into the following expression:

$$J_{H_2} = \frac{D_H\Omega^{(2)}K_{ads}^{1/2}}{L_{Pd}} \left(\eta \left(p_{H_2}^{(1)} \right)^{1/2} - \left(p_{H_2}^{(2)} \right)^{1/2} \right) \quad (12)$$

Where $Q = D_H\Omega^{(2)}K_{ads}^{1/2}$ is the metal permeability of the membrane.

Notation

Decidir si poner o quitar

Greek letters

410 *Superscript*

Subscript

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