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 \(7 \times 10^{-5} \text{mol/m}^2\text{sPa}^{0.5}\), 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

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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]. The continuous grow in population, joined with the economic development, foment 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 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].

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 (> 680 scfh/ft\(^2\)/atm\(^{0.5}\)) at T = 400° C and \(\Delta P = 20\) psi, iii) long-term stability at operating conditions (mechanical and thermal resistance) and iv) tolerance to typical pollutants (i.e. carbon, CO or H\(_2\)S) [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
The investment cost is still one of the main drawbacks for the use of these membranes 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 preparation of ultrathin palladium layers, reducing the metal amount and maximizing the permeation capacity of the membrane. Different alternatives have been proposed 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 is incorporated as an 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 electroless 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 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 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 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 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 palladium solid diffusion step being the controlling one. According to Sieverts’ law, hydrogen permeation flux is proportional to the square root partial pressure gradient $\frac{p_{H_2}}{2}$. However, when using composite membranes formed by different material layers, other mass transfer resistances (i.e. in gas film, in the membrane support and interphase, etc.) may be of importance and the resulting 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 individual step [17, 23] or use only one empirical transport equation with unknown 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 gas phase or support steps [1, 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 prepare 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 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 porous stainless steel supports with 0.1 \( \mu \)m 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 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 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

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 Microscopy (Philips XL30 ESEM) equipped with an Energy Dispersive Analytical System (EDAS) for microprobe analysis. Both surface and cross-sectional analyses were carried out in order to describe in detail the external layer (morphology and thickness) and the Pd incorporation in the pore area (penetration depth). Moreover, the external roughness has been measured with an optical 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 incorporated to the membrane was calculated by gravimetric analysis (electronic balance Kern & Sohn ABS–4 with a precision of ± 0.0001 g).

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 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.

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. To model this accurately, the differential mass balance to the retentate side has been formulated [17] [27]:

\[
\frac{dF_{H_2r}}{dA_m} = -J_{H_2} \tag{1}
\]
Figure 1: Experimental setup for permeation experiments

where $F_{H_2 r}$ 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: $F_{H_2 r}|_{A_m=0} = F_{H_2 r, in}$. The resolution has been done with the help 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 $F_{H_2 r, out}$ is obtained after solving the previous differential equation.

$$J_{H_2 av} = \frac{(F_{H_2 r, in} - F_{H_2 r, out})}{A_m}$$ (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 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 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 side of the membrane, the following equation is derived from the film theory [17].

$$J_{H_2} = \frac{k_p}{\phi} (p_{H_2r} - p_{H_2s})$$  \hspace{1cm} (3)

where \(\phi = \frac{1}{1 - \frac{p_{H_2}}{P_r}}\) 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 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, \(k_p = D_{im} Sh/(RT \delta)\), with \(Sh = 3.66\) [28] and \(\delta\) is 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:

$$J_{H_2} = \frac{k_h}{L_s RT} (p_{H_2s} - p_{H_2a})$$  \hspace{1cm} (4)

where \(k_h\) is the hydraulic permeability of the support (m²/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 Darcy pressure difference of $DP=3$ isocur flow (Hagen-Pouiselle) and Knudsen diffusion in porous media [19, 20]:

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

(5)

where $d_{pore}$ is the average pore diameter, $\epsilon_p$ is the porosity and $\tau$ is the tortuosity of the support, $\mu_G$ 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.

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. 

Hydrogen molecule dissociation and solution is modelled by the equilibrium expression. By combination, the so-called Sieverts’ law is obtained [29]:

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

(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 with temperature, $k_{pd} = A e^{-E_a/RT}$ 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 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, $\eta$, which is the ratio of the gas–palladium interphase surface in the retentate and permeate sides of the membrane:

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

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 $\eta$). 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 $\mu$m 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 ($\varepsilon$) and surface roughness ($R_a$) values for each sample are summarized in Table I.

The original PSS support presents $\varepsilon = 18.6\%$ and $R_a = 11.8 \mu m$. 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 negligible 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 fact, apparently contrary to the electroless pore–plating method, has been explained in detail in our previous paper [14]. In summary, this behaviour can be
Table 1: Pd layer properties of support and membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_H$ (M)</th>
<th>$\varepsilon$ (%)</th>
<th>$R_a$ (µm)</th>
<th>$t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSS</td>
<td>–</td>
<td>18.6</td>
<td>11.8</td>
<td>–</td>
</tr>
<tr>
<td>PSS–Pd–01</td>
<td>0.05</td>
<td>3.2</td>
<td>10.8</td>
<td>16.2</td>
</tr>
<tr>
<td>PSS–Pd–02</td>
<td>0.20</td>
<td>0.9</td>
<td>11.3</td>
<td>8.8</td>
</tr>
<tr>
<td>PSS–Pd–03</td>
<td>1.00</td>
<td>2.0</td>
<td>6.8</td>
<td>22.0</td>
</tr>
</tbody>
</table>

$C_H$: Hydrazine concentration; $\varepsilon$: 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 $R_a = 6 - 11$ µm. This reduction can be also related to the Pd amount incorporated in the membrane. In this manner, the smoother surface ($R_a = 6.80$ µm) was obtained for the thick Pd layer ($t=22.0$ µm), when a higher hydrazine concentration is employed ($C_{N_2H_4} = 1.00$ M, PSS–Pd–03).

In other cases, the estimated Pd thickness, obtained by gravimetric analysis, was reduced until $t = 16.2$ µm for PSS–Pd–01 ($C_{N_2H_4} = 0.05$ M) and $t = 8.8$ µm for PSS–Pd–02 ($C_{N_2H_4} = 0.20$ M). In both cases a roughness around $R_a \approx 10$ µm 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 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 \( C_{N_2H_4} = 1.00 \text{ M} \), PSS–Pd–03) shows a 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–Pd–02 membranes, a better permeation capacity was obtained as pressure difference 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 the origin since there is a minimum pressure difference below which the hydrogen 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 hydrazine concentration used during the ELP-PP and the conditions of the permeation 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

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 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.

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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PSS–Pd–02</th>
<th>PSS–Pd–01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeance ((673,\text{K})10^5) (mol/m(^2) s Pa(^{1/2}))</td>
<td>(17.9 \pm 0.8)</td>
<td>(7.0 \pm 0.3)</td>
</tr>
<tr>
<td>Activation energy (kJ/mol)</td>
<td>(14.5 \pm 1.7)</td>
<td>(9.7 \pm 1.8)</td>
</tr>
<tr>
<td>Parameter (\eta)</td>
<td>(0.916 \pm 0.01)</td>
<td>(0.88 \pm 0.01)</td>
</tr>
<tr>
<td>(R^2_{adj})</td>
<td>0.974</td>
<td>0.968</td>
</tr>
</tbody>
</table>

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

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 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 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 \(\mu\)m and 16 \(\mu\)m, 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 \(1.58 \cdot 10^{-9}\) 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
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 $\eta$ 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 $\eta$ 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 (CN$_2$H$_4$ = 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) CN$_2$H$_4$ = 0.05 M (PSS-Pd-01) and b) CN$_2$H$_4$ = 0.20 M (PSS-Pd-02).
4. Conclusions

Three different membranes were prepared through the electroless pore-plating method varying the hydrazine concentration, obtaining in all cases totally dense membranes in spite of the observation of external pores. This fact can be explained 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 determines 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 permeation occurs. At lower pressures differences, the driving force for the permeation process was insufficient to overcome the material resistance. This effect increases as the hydrazine concentration decreases during the membrane preparation step. From these minimum values, a conventional permeation behaviour accordingly to Sieverts’ law was obtained. All these effects have been modelled 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 membrane PSS–Pd–02, prepared by using CN$_2$H$_4$ = 0.20 M, must be selected due to accomplish a complete hydrogen selectivity with limited Pd thickness and 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 following mechanism of permeation. In the retentate side of the membrane, hydrogen
from the gas adsorbs and dissociates on the palladium surface. Then, the hy-
drogen 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
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
(σ), according to the following reaction:

\[
H_2 + 2\sigma \rightleftharpoons 2H - \sigma
\]  

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 \((\Theta_H)\):

\[
K_{ads} = \frac{\theta_H^2}{p_{H_2}(1 - \theta_H)^2}
\]  

Since hydrogen dissolves and diffuses into the palladium, hydrogen fractional
adsorption is maintained low, so \((1 - \Theta_H) \approx 1\), and hence [13]:

\[
\theta_H = (K_{ads}p_{H_2})^{1/2}
\]  

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
difference of dissolved hydrogen \( (X_H) \) at both sides of the palladium layer:  

\[
J_{H_2} = \frac{D_H}{L_{Pd}} (X_H^{(1)} - X_H^{(2)})
\]  

(11)

The concentration of dissolved hydrogen is related to the hydrogen fractional adsorption, \( X_H = \Omega \theta_H \), where \( \Omega \) is the total molar concentration on the palladium surface. The \( \Omega \) parameter is proportional to the gas-palladium interphase surface. In the membranes of the present work, the intrusion of palladium inside 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 \( \eta = \Omega^{(1)}/\Omega^{(1)} < 1 \), the flux expression is simplified into the following expression:

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

(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
- Superscript
- Subscript

**References**

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