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NEW SYNTHESIS METHOD OF Pd MEMBRANES OVER TUBULAR PSS SUPPORTS VIA “PORE-PLATING” FOR HYDROGEN SEPARATION PROCESSES

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ABSTRACT

A new synthesis method to prepare Pd membranes by novelty modified electroless plating over tubular porous stainless steel supports (PSS) has been developed. This new pore plating method basically consists on feeding both plating solution and reducing agent from opposite sides of support, allowing the preparation of totally hydrogen selective membranes with a significantly lower Pd consumption than the corresponding to the conventional electroless plating procedure. In the latter, both reducing agent and plating solution are added simultaneously in one side of the PSS support. This new plating method has been applied over raw commercial PSS supports and air calcined supports in order to generate a Fe-Cr oxide intermediate layer.

A completely dense Pd membrane with a thickness in the range 11-20 μm directly over tubular porous stainless steel tubes with a high roughness has been achieved. The permeation properties of the membranes have been tested at different operating conditions for pure feed gases: retentate pressure (1 – 4 bar) and temperature (350 – 450°C). All membranes present good permeance reproducibility after several thermal cycles and a complete hydrogen ideal selectivity, since complete retention of nitrogen is maintained for all tested experiment conditions, ensuring 100% purity in the hydrogen permeate flux. The permeance of both membranes is maintained in the range of $1\text{-}3 \cdot 10^{-4} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$.

Keywords: Hydrogen separation, PSS, palladium, electroless plating, pore-plating.

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1. INTRODUCTION

Hydrogen production, separation and purification have been receiving growing attention in recent years due to the necessity of high purity hydrogen for applications in petrochemical, refining and semiconductor industries as well as the development of hydrogen economy for a sustainable technological advancement [1]. In this way, palladium or palladium alloy membranes are especially suitable for hydrogen separation and membrane reactor applications. The good mechanical and thermal stability as well as the potential to reach a complete permselectivity for hydrogen are the major goals of this kind of membranes [2]. Nevertheless, they may suffer some important operation drawbacks such as hydrogen embrittlement [3], relatively low fluxes [4] or limited mechanical stability when ultra-thin Pd layers are used [5]. Moreover, high investment costs and the volatility of the palladium prices are making difficult their commercialization on a large scale [6].

The most efficient way to decrease the overall cost of the membrane and to increase the hydrogen permeate flux is to reduce the thickness of the palladium selective layer. This objective can be reached by using membrane supports that contributes to increase both thermal and mechanical stability [7-8]. There is a wide variety of successfully employed porous supports although stainless steel porous supports (PSS) show some advantages such as high thermal resistance, simplicity for the construction of permeation module and use of fittings, resistance to handling and thermal expansion coefficient similar to palladium [9-11]. However, as relevant drawbacks, the presence of large pores, high roughness of the surface and the atomic inter-diffusion phenomena of some metals from the stainless steel support to the palladium film can be mentioned. All these issues make difficult the preparation of completely defect-free membranes and reduce both permeate flux and hydrogen selectivity [12]. To overcome these problems, several authors have modified the surface of the PSS support by adding different inorganic intermediate layers between the PSS and the Pd layer. Among them, some can be mentioned such as silica [13], alumina [14], aluminum hydroxide [15], cerium hydroxide [16] or zirconium oxide [17]. The intermediate layer facilitates to obtain a smoother palladium surface, with a smaller pore mouth, and also prevents the intermetallic diffusion between stainless steel of the support and the Pd selective layer. This last phenomena is an undesirable process that takes place at high temperature since reduces the permeate flux and hydrogen selectivity [17]. However, the use of an interlayer increases the membrane cost in such a way that even the composite support (PSS and inorganic interlayer) outweigh the palladium layer expenses [18].

In the last few years, a large number of methods for palladium film deposition have been developed although the most usual preparation method is the Electroless Plating technique [19-23]. This method is based on the deposition of Pd from aqueous solutions over a porous support on both conducting and non-conducting surfaces with different geometries. The procedure consists of a controlled autocatalytic reduction of a palladium complex, usually $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, with hydrazine or other similar reducing agent on the target surface. The technique is quite easy to carry out, does not require any expensive equipment and neither have high operational cost as compared to than electrical deposition methods, due to the absence of electrodes and external sources of electricity [24].

In addition to all above mentioned it has also to take into account that many membranes are rejected during their manufacturing process due to defects in their preparation, increasing the overall cost of the process for the industry. In this mean, it is important to develop new routes for the preparation of composite membranes with a relatively low cost but in a highly reproducible way in order to minimize the number of rejected membranes. In last years, some authors have developed some Pd deposition methods with the aim to repair palladium layer defects produced during their manufacturing process. In this context, Li and coworkers reported a combination between conventional electroless plating and osmosis for repairing a Pd/ $\alpha\text{-Al}_2\text{O}_3$ composite membrane containing defects. This method ensures a complete disappearance of Pd layer defects and increases considerably the hydrogen selectivity without any reduction of its hydrogen permeation flux or increase in the palladium thickness [25]. Following this pioneer work, Zeng and coworkers developed a new method for defect sealing in palladium membranes via point plating. This method consists of the selective deposition of palladium just over the palladium layer defect by feeding the palladium salt and the hydrazine from opposite sites of a Pd/ceramic composite membrane during the electroless plating [26]. However, these techniques have not been used as unique pore plating method to generate all Pd layer and neither in supports with a wide pore size distribution and higher roughness, such as tubular porous stainless steel supports.

Based on both pioneer methods, in this work a new method is presented to prepare a very reproducible defect free palladium composite membrane by selective deposition of palladium by electroless plating directly over commercial porous stainless steel tubes. Firstly, an original PSS support has been used in order to analyze the palladium incorporation by this technique. Moreover, other membrane has been prepared using a previously modified support by adding an inorganic interlayer of Fe-Cr mixed oxides to study the influence of the surface in the process. The main objective of the present paper is to develop a new alternative plating

method, following named Pore-Plating, with a low Pd consumption and in a quite reproducible way. The Pd deposition is performed directly around both commercial and modified supports pore areas by feeding the Pd complex solution and the hydrazine from opposite sides of the support. Thus, the chemical reaction between Pd²⁺ ions and hydrazine takes place first in the internal porosity of the support, depositing the reduced Pd nuclei there and closing the pores. As these pores come to be closed, chemical reaction between Pd complexes and hydrazine turns difficult and the Pd metallic deposition ends, reducing significantly the preparation costs of these composite membranes. This work reports a complete characterization of prepared composite membranes following the pore-plating method, mainly attending to the morphology of the membrane and its behaviour in hydrogen/nitrogen permeation. All membranes were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), gravimetric analysis and permeation measurements.

2. EXPERIMENTAL SECTION

2.1 Membrane preparation

Tubular porous stainless steel supports (PSS) with a porosity of ca. 20% and media grade of 0.1 µm (which means that 95% rejection of solid particles with a size greater than the grade is guaranteed) were provided by Mott Metallurgical. The supports have a thickness of 1.9 mm, external diameter of 12.9 mm and a length of 150 mm. Original PSS supports were cut to small pieces of 30 mm of length.

Before any further treatment of the commercial supports, they were cleaned to remove surface pollutants, such as oil, dust or grease, as published elsewhere [27]. The process consisted of consecutive immersions in solutions of sodium hydroxide 0.1 M for 5 min, hydrochloric acid 0.1 M for 5 min and pure ethanol for 15 min. All washing steps were performed at 65°C under ultrasonication stirring. After each washing step, supports were rinsed with distilled water. The process was completed with a drying step by air at 110 °C for 8 hours.

After that, an intermediate layer of Fe-Cr oxide over surface of PSS supports was generated by its oxidation in air at high temperature. The cleaned supports were directly introduced into a furnace and were treated at 650°C for 12 h using heating and cooling rates of 1.8 °C/min. These experimental conditions were previously optimized attending to the surface modification and permeation properties of the PSS supports [28].

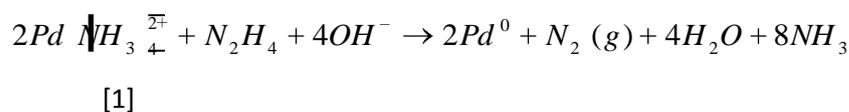
In this work a new process, denoted as pore plating, to develop a dense selective Pd layer directly on commercial PSS supports is presented. In summary, the main difference respect to the classical Electroless Plating is the way to put in contact the two main solutions involved in the plating process. Thus, plating complex (Pd) and reducing agent (hydrazine) are fed from opposite sides of the membrane. Figure 1 shows a scheme of the deposition process. In the first stages, the Pd complexes and hydrazine reacts inside the pores, depositing the metallic Pd particles on this area. While the chemical reaction progresses, the amount of Pd inside the pores increases until the pores eventually get fully closed. At this point, both reactants are maintaining separated and the reaction ends. It is important to emphasize that several recurrences of the “pore-plating” process are necessary in order to close completely all pores of the supports.

The whole process to obtain a dense Pd layer involves two sequential steps: i) surface activation, consisting in the deposition of Pd nuclei in the pore surface, and ii) layer deposition, to generate the Pd dense layer. Both steps are carried out by using the pore plating method.

Surface activation of the pore area is necessary in order to initiate the homogeneous Pd plating process with a relative low induction period. This activation process is the main responsible to the appropriate deposition of Pd in the next step of electroless pore-plating. In this work we have also used a new method for the activation of the pore area of PSS supports by direct reduction of Pd complexes. The process consists of the reaction between Pd²⁺ ions from an acidic PdCl₂ solution and an ammonia-hydrazine solution at room temperature during 2 h (see composition details in Table 1). The PSS support was vertically introduced into the acidic PdCl₂ solution maintaining the system static while the hydrazine was introduced in the internal side of support. Both ends of support were closed with Teflon tapes to prevent the mixture of these two solutions. Since both solutions are fed from opposite sites of PSS supports, the reduction of Pd²⁺ ions takes place just on the pore area, generating the Pd⁰ species through the action of hydrazine diluted in ammonia for a suitable pH. After that, a gentle rinsing in de-ionized water was carried out. It is noteworthy that in contrast with other conventional activation procedures, Sn precursors have not been used.

Once the support is activated, the bulk palladium layer is deposited by electroless pore-plating. The composition of the electroless plating bath and the main variables of the process are also given in Table 1. The chemicals used for the palladium electroless plating consisted of: palladium chloride (PdCl₂), as palladium source, ammonium hydroxide (NH₄OH, 32%), as complexing agent, and ethylenediamine tetraacetic acid disodium salt (Na₂EDTA), as stabilizer. The activated PSS tubular support, closed with Teflon tapes, was immersed into 70 mL of the

plating solution at controlled temperature in a similar way than activation procedure. Then, hydrazine (N₂H₄) was added from the internal side of the support, producing the following autocatalytic reaction:



This process was repeated several times in order to achieve a totally dense palladium layer (2 h per cycle). Finally the membranes were rinsed with deionized water and dried at 110 °C for 8 hours.

2.2 Membrane characterization

The morphology of the membranes were characterized by a Scanning Electron Microscope (Philips XL30 ESEM) equipped with an energy dispersive analytical system (EDAX) for microprobe analysis. Additionally, the images obtained with SEM were analyzed with two different software packages. DigitalMicrograph™ (Gatan) was used for calculation of pore size distribution from the backscattering electron (BSE) SEM images. Scanning Probe Image Processor (SPIP®, Image Metrology) was used to determine the surface roughness from gas scattering electron (GSE) SEM images.

Moreover, the elemental composition of the surface in the samples was determined by energy dispersive X-ray spectroscopy. This technique indicates quantitatively the element concentration in the sample.

The average Pd layer thickness was estimated by gravimetric analysis (electronic balance Kern & Sohn ABS-4 with a precision of ±0.0001 g) from the data of the weight gained just after the plating step.

2.3 Permeation test

A series of single gas permeation experiments with both pure nitrogen and hydrogen have been carried out in a home-made equipment to determine the permeability and the ideal separation factors of the membranes studied. The Figure 2 shows a schematic diagram of the experimental device and the membrane assembly. The experimental setup basically consisted of a 316L stainless steel cell that contains the palladium membrane module. The membrane is

placed in the module between two graphite O-rings to ensure the seal between the retentate and permeate sides. Finally, two copper O-rings were used for the external sealing of the system. This assembly is placed into a homogeneous heating zone in a tubular electrical furnace in order to maintain the membrane module at the desired temperature for each test. The measurements were performed in the range of 0.5 – 3.0 barg (in the retentate side) at temperatures upper than 300°C (in the range 350 – 450 °C) to avoid the Pd layer embrittlement due to the coexistence of α - β hydrogen-palladium hybrids in the composite membranes prepared.

3. RESULTS AND DISCUSSION.

3.1. Support morphology

Commercial porous stainless steel tubes with a media grade specification of 0.1 μm , provided by Mott Metallurgical, were used as support in this work. Several Pd membranes were prepared directly over these commercial supports while others were made from the oxidized support that incorporates a Fe-Cr oxide interlayer. Figure 3 shows SEM images of both, raw and oxidized supports. As it can be clearly seen in Figure 3a, PSS raw support is formed by agglomeration of heterogeneous particles with sizes in the range of 1-20 μm . The surface presents a non-uniform pore size distribution with presence of large pores, greater than specified grade (0.1 μm). Pore size distribution (see enclosed Figure) and an average pore diameter of ca. 3.55 μm are obtained from the Digital Micrograph analysis, although larger pores can be also detected. The average porosity on the external surface of PSS support was also calculated by this software, with a value of ca. 21.48%. Moreover, an average roughness value of $S_a=5.87 \mu\text{m}$ were obtained by Scanning Probe Image Processor software. The image of the support modified by incorporation of a Fe-Cr oxide intermediate layer is shown in Figure 3b. A continuous oxide intermediate layer maintains a very similar external morphology to that of the original support, although a detailed analysis of the surface with both digital software tools indicate that the porosity was reduced to 14.07 %. On the other hand, the average pore diameter on the surface and the roughness are practically identical between both supports ($D_p=3.81 \mu\text{m}$ and $S_a=5.85 \mu\text{m}$, for oxidized support). In this manner, the results obtained indicate that the incorporation of the Fe-Cr oxide as intermediate layer maintains a similar external morphology on PSS supports, although could prevent the undesirable intermetallic diffusion between the steel support and the Pd selective layer when the membrane works at high temperatures.

3.2. Membrane properties

As mentioned above, the external surface of PSS supports presents a wide pore size distribution, with pores quite higher than the specific grade, 0.1 μm . However, these pores are interconnected with other ones throughout the thickness of the support in such a way that it is not allowed particles in size 0.1 μm to pass from one side to the other. This fact indicates that the retention of the particles takes place mainly in the bulk of PSS samples, where the smallest pore sizes are. According to this fact and related to the pore-plating process developed in this work, it is expected that, at the first stage of the palladium plating, the Pd complexes and hydrazine reacts primarily on the internal pores of the support, depositing palladium metallic particles on the wall of the pore structure until they are completely closed. Figure 4 shows the SEM images of the external surface of the membrane prepared directly over a commercial PSS support without any intermediate layer after several deposition cycles: 5 (Figure 4a), 10 (Figure 4b) and 15 (Figure 4c). As can be observed, several recurrences of pore-plating process were needed to obtain a complete dense membrane (15 cycles, Figure 4.c). It can be seen that palladium is deposited on the external surface of PSS support in spite of the reaction takes place in the internal pores even at the first cycles. EDX analysis evidences this effect, obtaining a Pd surface concentration that varies lightly from 87.42% after 5 recurrences to 92.37% after 15 recurrences of the plating process. This fact is due to the presence of a wide variety of pore diameters in the raw supports that allow the hydrazine to pass from the internal to the external side of supports. Due to the deposition is an autocatalytic process and the supports usually present great pores and defects, it is really difficult to control the deposition of Pd particles only in the pore area, obtaining a Pd layer on the external surface. Anyway, just 15 cycles were necessary in order to achieve a completely dense membrane with a negligible porosity, a very low roughness value ($S_a=0.96 \mu\text{m}$) and relative low thickness of ca. 20 μm (estimated by gravimetric analysis).

A similar procedure was used over a modified PSS support with an intermediate layer of Fe-Cr oxide. In this case, Pd layer was also formed on the external surface of support (Figure 5). However, it was possible to obtain a dense membrane with a lower number of deposition cycles, 12, with also negligible porosity, a bit more roughness ($S_a=1.45 \mu\text{m}$) and less estimated thickness, 11 μm (by gravimetric analysis).

Figure 6 shows the cross-section images obtained by SEM of both final membranes, PSS-Pd (Figure 6a) and PSS-OXI-Pd (Figure 6b). As can be observed, a uniform Pd film was achieved on both supports. In this case, Pd film thickness in the range of 14-18 μm and 6-8 μm were obtained for PSS-Pd and PSS-OXI-Pd, respectively. In general, the average thickness of the external layer of Pd is slightly lower than the values achieved by gravimetric analysis. These

differences can be attributed to the incorporation of Pd in the pores of supports, not considered by gravimetric analysis. This fact can be observed on both figures, in which several pores near to the external side of the membrane are filled with Pd. Conventionally, the thickness of Pd membranes prepared over rough supports (as PSS supports) is not uniform, being thicker on the ridges than in the cavities, most likely because during the plating palladium ions and hydrazine are more easily delivered from the plating bath to exposed surfaces than to surfaces lying behind in the structure. In contrast, using the pore-plating method, the Pd growth starts just in the pore area, facilitating the generation of a totally dense membrane with relative low thickness and roughness. Particularly, the use of an oxide intermediate layer (external thickness of about 1.8 μm) emphasizes this effect due to the incorporation of Fe-Cr oxides in both external and internal surface, modifying the pore structure of commercial PSS supports and, consequently, the diffusion of the hydrazine solution through the pores. In this manner, it is possible to obtain an apparent thinner external palladium layer on the calcined PSS support.

Figure 7 shows the evolution of the weight gain with the “pore-plating” deposition cycles. As it can be seen, in the first stages a great amount of Pd was incorporated to the membrane. As the number of cycles increases, some of the pores are reducing their pore diameter and even getting closed. This makes much more difficult the contact between Pd complexes and hydrazine and thus the Pd deposition rate decreases. When all pores of the support are closed, both reactants, Pd complexes and hydrazine, are completely separated, the chemical reaction is not possible, and the weight gain in following cycles is negligible. In this manner, a marked fall of palladium weight gain at early stages (4-5 first cycles) can be observed for both composite membranes. However, analyzing the evolution of the weight gain for both prepared membranes in detail, some important differences were detected. The weight gain at early stages was lower for the membrane prepared with an intermediate layer of Fe-Cr oxide (PSS-OXI-Pd) and a completely dense membrane was achieved with a minor number of recurrences in the pore-plating process. This fact is due to the modification of the pore structure of the support, reducing both porosity and average pore diameter, so the blockage of pores by palladium becomes easy. Moreover, we have found that Pd complexes of electroless plating solution can be reduced into metallic Pd as the solution was maintained in contact with the Fe-Cr oxides interlayer at temperature of 60°C without any external reducing agent such as hydrazine. In this manner, the combined effect of both hydrazine and oxide intermediate layer could explain the observed results.

The main advantage of this method is to provide an effective and reproducible deposition method in order to obtain totally dense Pd membranes directly over PSS support with a minimum consumption of Pd precursor, i.e. a low theoretical thickness of the Pd layer, avoiding previous treatments of PSS supports and, consequently, saving cost in the production of palladium composite membranes. The pore plating process can be repeated several times until all pores, cracks or defects in a membrane will be closed, ensuring the Pd incorporation only around the pore area without a great increase in the overall Pd thickness.

3.3. Membrane permeation tests

In order to study the permeation properties of the synthesized membranes, a set of single gas permeation experiments with both pure nitrogen and hydrogen have been carried out at temperatures in the range of 350-450°C. From these experiments, the permeability and the ideal separation factor (calculated as the ratio between hydrogen and nitrogen fluxes) have been determined. First at all, it has to be pointed out that both membranes (PSS-Pd and PSS-OXI-Pd) are completely impermeable to nitrogen since nitrogen flux was not detected in the permeate side at any temperature and pressures studied. Therefore, it is concluded that the Pd layer was totally selective to H₂ in both cases.

In order to determine the stability of the membranes under real operation conditions, permeation experiments with both nitrogen and hydrogen gases were repeated at 400°C. Thus, five consecutive cycles of heating and cooling were performed, measuring the permeation properties for each cycle at hydrogen partial pressures differences ($P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5}$) ranged from 73 to 323 Pa^{0.5}. Figure 8 shows the hydrogen permeation fluxes obtained in these experiments for both membranes, PSS-Pd and PSS-OXI-Pd. Only H₂ flux is represented since N₂ was not detected experimentally in any case. Each of data point shown in the graph represents the average value of the five fluxes obtained in each series of experiments carried out. As it can be seen, the reproducibility of the hydrogen fluxes for each driving force (ΔP) and even for each membrane (raw and oxidized PSS) is very high, obtaining random variation of the fluxes and errors below 5% for all cases. These results evidence two facts: i) the high stability of the prepared membranes to thermal cycles and b) the similarity of permeation properties of both membranes. This fact indicates that the incorporation of an iron/chromium oxide intermediate layer is not proving detrimental to the permeability of the palladium composite membrane and the stability of the system to thermal cycles. On the other hand, it can be also observed that the hydrogen flux increases linearly with $\Delta P^{0.5}$ in the range of measurements. This trend is consistent with the solution-diffusion model of permeation through a palladium membrane when the rate-determining step is the diffusion of hydrogen in

the free-pinhole metallic film. The generation of pin-holes after several heating and cooling cycles provokes deviations in the exponential coefficient (0.5) so the results obtained suggest a good stability of the membrane under temperature cycles.

The influence of the temperature in the permeate fluxes was also analysed. Figure 9 shows the permeate flux obtained at 3 different temperatures: 350, 400 and 450 °C. As expected, the temperature of the experiments clearly influences in the permeate flow, obtaining higher flows as the temperature increases. In all cases, the nitrogen gas is blocked and only hydrogen can pass through the membranes, being their hydrogen selectivity infinite. The values of the activation energy were also calculated for both membranes, obtaining values of 15.56 kJ/mol and 15.03 kJ/mol for PSS-Pd and PSS-OXI-Pd membranes, respectively. These values are within the typical range of other palladium membranes from the literature (7-30 kJ/mol) [29].

Table 2 summarizes the results obtained in this work comparing with other experimental data reported in the literature from some different palladium composite membranes. A rigorous comparison between permeation properties of Pd membranes is quite difficult since there are many parameters involved in the permeation process, both the membrane itself as well as operation conditions. We have selected some of these data to carry out a useful comparison. Several parameters are reported in the table: membrane type, preparation method, thickness of the Pd selective layer, and experimental conditions of the permeation experiments (temperature and pressure ranges), apart from hydrogen flux, permeance and ideal selectivity. In most cases, the permeation properties of each membrane are intimately related to their Pd thickness. The thinnest membranes present higher hydrogen fluxes, but their selectivity is far away of the ideal value of infinite, probably due to the presence of Pd defects and pinholes. On contrast, thicker membranes present lower fluxes but the hydrogen selectivity trends to infinite. The membranes presented in this work show hydrogen fluxes in the range of the reported data in literature but with infinite selectivity to hydrogen. For instance, as compared to membranes (rows 4 and 5 of Table 2) prepared by ELP and also with an interlayer of Fe₂O₃, the hydrogen flux of our membranes is quite similar (0.02 – 0.08 versus 0.01 – 0.09 mol/m²·s) but with an infinite selectivity versus 80-900.

4. CONCLUSIONS

A new synthesis method, denoted as “pore-plating”, to prepare Pd membranes by plating over tubular porous stainless steel supports (PSS) has been developed. The main difference respect the conventional procedure is the way to put in contact the plating solution and reducing agent. Whereas in the conventional one, both reducing agent and plating solution are added

simultaneously in one side of the PSS support, in the “pore-plating” method both solutions are added from opposite sides of support. So, the Pd complexes and hydrazine reacts inside the pores, depositing the metallic Pd particles on this area. While the chemical reaction progresses, the amount of Pd inside the pores increases until the pores eventually get fully closed. Moreover, other variation of the proposed method respect the conventional one is that the activation step of the support, previous to the Pd pore plating, has been carried out in the absence of Sn precursors.

Two different PSS supports have been used, raw commercial support and modified support after calcination in air to generate a Fe-Cr oxide interlayer. In both cases, the weight gain of Pd after each deposition decreases for consecutives cycles of the process due to the pore blockage and the formation of a dense Pd layer, stopping the chemical reaction. In this sense, this new method avoids the high consumption of Pd that happens in the conventional electroless plating process. In the latter, it is necessary to carry out multiple cycles with fresh solution in order to minimize the presence of defects or pin-holes, mainly using supports with a high average pore diameter and roughness, increasing significantly the Pd layer. However, using the new pore-plating process the reaction only occurs around the open pores. The oxidation of raw supports makes possible to obtain a complete dense membrane with a lower number of recurrences of the process than the unmodified PSS supports, although their textural properties are similar. This fact could be due to the modification of the internal pore structure of the support, where the narrow pores (in order of 0.1 μm) are placed. All membranes present a complete hydrogen ideal selectivity and good permeance reproducibility after several thermal cycles with values in the range of $1\text{-}3 \cdot 10^{-4} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ with a Pd thickness in the range of 11-20 μm . These values are agree to the typical ones reported in the literature for the majority of Pd composite membranes, additionally improving in a significant manner the purity of the permeate flux (complete ideal selectivity). Moreover, activation energy of ca. 15 kJ/mol has been obtained after tests at different temperatures. Summarizing, this new method allows close all pores of both original and oxidized supports, minimizing the rejection of membranes due to the presence of defects or a significant increase in the Pd thickness.

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REFERENCES

- [1] Bartels J.R., Pate M.B., Olson N.K., An economic survey of hydrogen production from conventional and alternative energy sources. *Int. J. Hydrogen Energy* 35 (2010) 8371-8384.
- [2] Paglieri S.N., Way J.D., Innovations in palladium membranes research. *Sep. Pur. Meth.* 31 (2002) 1-169.
- [3] Mallada R., Menéndez M., *Inorganic membranes: synthesis, characterization and applications*. Ed. El Servier (2008)
- [4] Peters T.A., Tucho W.M., Ramachandran A., Stange M., Walmsley J.C., Holmestad R., Borg A., Bredesen R., Thin Pd-23%Ag/stainless steel composite membranes: Long-term stability, life-time estimation and post-process characterization. *J. Membr. Sci.* 326(2) (2009) 572-581.
- [5] Caravella A., Barbieri G., Drioli E., Modelling and simulation of hydrogen permeation through supported Pd-alloy membranes with a multicomponent approach. *Chem. Eng. Sci.* 63(8) (2008) 2149-2160.
- [6] Ockwig N.W., Nenoff T.M., Membranes for hydrogen separation. *Chem. Rev.* 107 (2007) 4078-4110.
- [7] Basile A., Gallucci F., Tosti S., Synthesis, characterization and applications of palladium membranes, *Membrane Science and Technology Series* 13 (2008) 255-327.
- [8] Tosti S., Supported and laminated Pd-based metallic membranes, *Int. J. Hydrogen Energy* 28 (12) (2003) 1445-1454.
- [9] Mardilovich I.P., Engwall E., Ma Y.H., Dependence of hydrogen flux on the pore size and plating surface topology of asymmetric Pd-porous stainless steel membranes, *Desalination* 144 (2002) 85-89.
- [10] Chi Y-H., Yen P-S., Jeng M-S., Ko S-T, Lee T-C., Preparation of thin Pd membrane on porous stainless steel tubes modified by a two-step method, *Int. J. Hydrogen Energy* 35 (2010) 6303-6310.

- [11] Tong J., Suda H., Haraya K., Matsumura Y., A novel method for the preparation of thin dense Pd membrane on macroporous stainless steel tube filter. *J. Membr. Sci.* 260 (2005) 10-18.
- [12] Zhang K., Gao H., Rui Z., Liu P., Li Y., Lin Y.S., High-Temperature stability of palladium membranes on porous metal supports with different intermediate layers. *Ind. Eng. Chem. Res.* 48 (2009) 1880-1886.
- [13] Calles J.A., Sanz R., Alique D., Influence of the type of siliceous material used as intermediate layer in the preparation of hydrogen selective palladium composite membranes over a porous stainless steel support. *Int. J. Hydrogen Energy* 37 (2012) 6030-6042.
- [14] Yepes D., Cornaglia L.M., Irusta S., Lombardo E.A., Different oxides used as diffusion barriers in composite hydrogen permeable membranes. *J. Membr. Sci.* 247 (1-2) (2006) 92-101.
- [15] Tong J., Suda H., Haraya K., Matsumura Y., A novel method for the preparation of thin dense Pd membrane on macroporous stainless steel tube filter. *J. Membr. Sci.* 260 (2005) 10-18.
- [16] Tong J., Su C., Kuraoka K., Suda H., Matsumura Y., Preparation of thin Pd membrane on CeO₂-modified porous metal by a combined method of electroless plating and chemical vapor depositions. *J. Membr. Sci.* 269 (2006) 101-108
- [17] Wang D., Tong J., Xu H., Matsumura Y., Preparation of palladium membrane over porous stainless steel tube modified with zirconium oxide. *Catal. Today* 93-95 (2004) 689-693.
- [18] Hu X., Yu J., Song J., Wang X., Huang Y., Towards low-cost Pd/ceramic composite membranes for hydrogen separation: A case study on reuse of the recycled porous Al₂O₃ substrates in membrane fabrication. *Int. J. Hydrogen Energy* 36 (2011) 15794-15802.
- [19] Cheng Y.S., Yeung K.L., Effects of electroless plating chemistry on the synthesis of palladium membranes. *J. Membr. Sci.* 182 (2001) 195-203.
- [20] Shi Z., Wu S., Szipunar J.A., Roshd M., An observation of palladium membrane formation on a porous stainless steel substrate by electroless deposition. *J. Membr. Sci.* 280 (2006) 705-711

- [21] Li A., Grace J.R., Lim C.J., Preparation of thin Pd-based composite membrane on planar metallic substrate. Part II. Preparation of membranes by electroless plating and characterization, *J. Membr. Sci.* 306 (2007) 159-165.
- [22] Mardilovich P.P., She Y., Ma Y.H., Rei M.H., Defect-free palladium membranes on porous stainless-steel support, *Separations* 44(2) (1998) 310-322.
- [23] Gade S.K., Thoen P.M., Way J.D., Unsupported palladium alloy foil membranes fabricated by electroless plating, *J. Membr. Sci.* 316 (2008) 112-118.
- [24] Mallory O., Hajdu J.B., *Electroless plating. Fundamentals and applications.* American Electroplaters and Surface Finisher Society (2002).
- [25] Li A., Liang W., Hughes R., Repair of a Pd/ α -Al₂O₃ composite membrane containing defects. *Sep. Pur. Tech.* 15 (2) (1999) 113-119.
- [26] Zeng G., Goldbach A., Xu H., Defect sealing in Pd membranes via point plating. *J. Membr. Sci.* 328 (1-2) (2009) 6-10.
- [27] Sanz R., Calles J.A., Alique D., Furones L., Ordoñez S., Marín P., Corengia P., Fernández E., Preparation, testing and modelling of a hydrogen selective Pd/YSZ/SS composite membrane. *Int. J. Hydrogen Energy* 36 (2011) 12783-15793.
- [28] Calles J.A., Sanz R., Alique D., Furones L., Development of interphase layers of Fe-Cr oxides and silicalite-1 in Pd-based membranes for hydrogen separation. 10th International Conference on Clean Energy, North Cyprus (2010)
- [29] Ryi S.K., Xu N., Li A., Lim C.J., Grace J.R., Electroless Pd membrane deposition on alumina modified porous hastelloy substrate with EDTA-free bath. *Int. J. Hydrogen Energy* (6) (2010) 2328-2335.
- [30] Basile A., Pinacci P., Iulianelli A., Broglia M., Drago F., Liguori S. et al., Ethanol steam reforming reaction in a porous stainless steel supported palladium membrane reactor. *Int. J. Hydrogen Energy* 36 (2011) 2029-2037.
- [31] Pinacci P., Broglia M., Valli C., Capannelli G., Comité A., Evaluation of the water gas shift reaction in a palladium membrane reactor. *Catal. Today* 156 (2010) 165-172.
- [32] Lee DW., Lee YG., Nam SE., Ihm SK., Lee KH., Study on the variation of morphology and separation behavior of stainless steel supported membranes at high temperature. *J. Membr. Sci.* 220 (2003) 137-153.

[33] Yun S., Ko JH., Oyama ST., Ultrathin palladium membranes prepared by a novel electric field assisted activation. *J. Membr. Sci.* 369 (2011) 482-489.

FIGURE CAPTIONS

Figure 1. Scheme of the Pd pore-plating process.

Figure 2. Schematic diagram of the experimental setup.

Figure 3. SEM images of: a) raw PSS support (grade 0.1 μm) and b) PSS support modified after calcinations in air (PSS-OXI) with pore size distributions calculated by DigitalMicrograph™.

Figure 4. SEM images of external surface in PSS-Pd sample after: a) 5, b) 10 and c) 15 cycles of the Pd pore-plating process.

Figure 5. SEM image of the external Pd layer obtained by pore-plating over calcined support (PSS-OXI-Pd).

Figure 6. SEM micrographs depicting cross-sections of: a) PSS-Pd and b) PSS-OXI-Pd composite membranes.

Figure 7. Evolution of the weight gain in PSS-Pd and PSS-OXI-Pd composite membranes after different Pd “pore-plating” cycles.

Figure 8. Hydrogen flux vs hydrogen partial pressure for permeation experiments with pure H_2 .

Figure 9. Hydrogen flux vs hydrogen partial pressure for permeation experiments at different temperatures (350, 400 and 450°C).

Figure 1

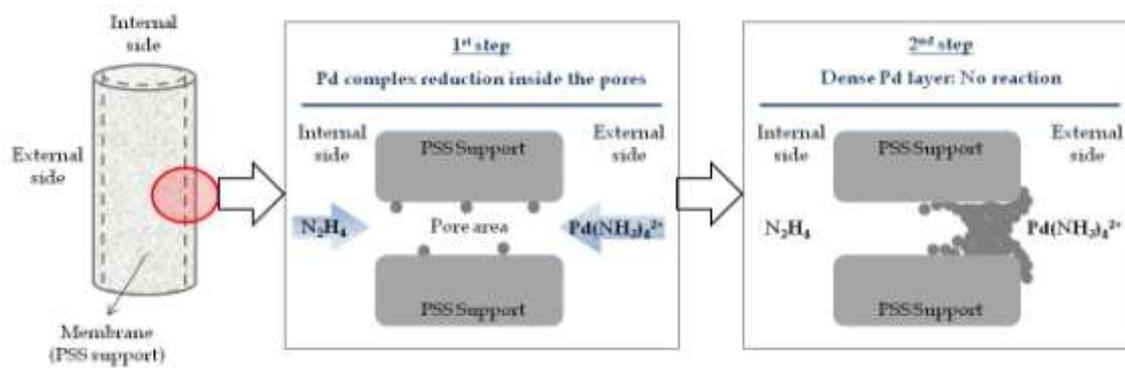


Figure 2

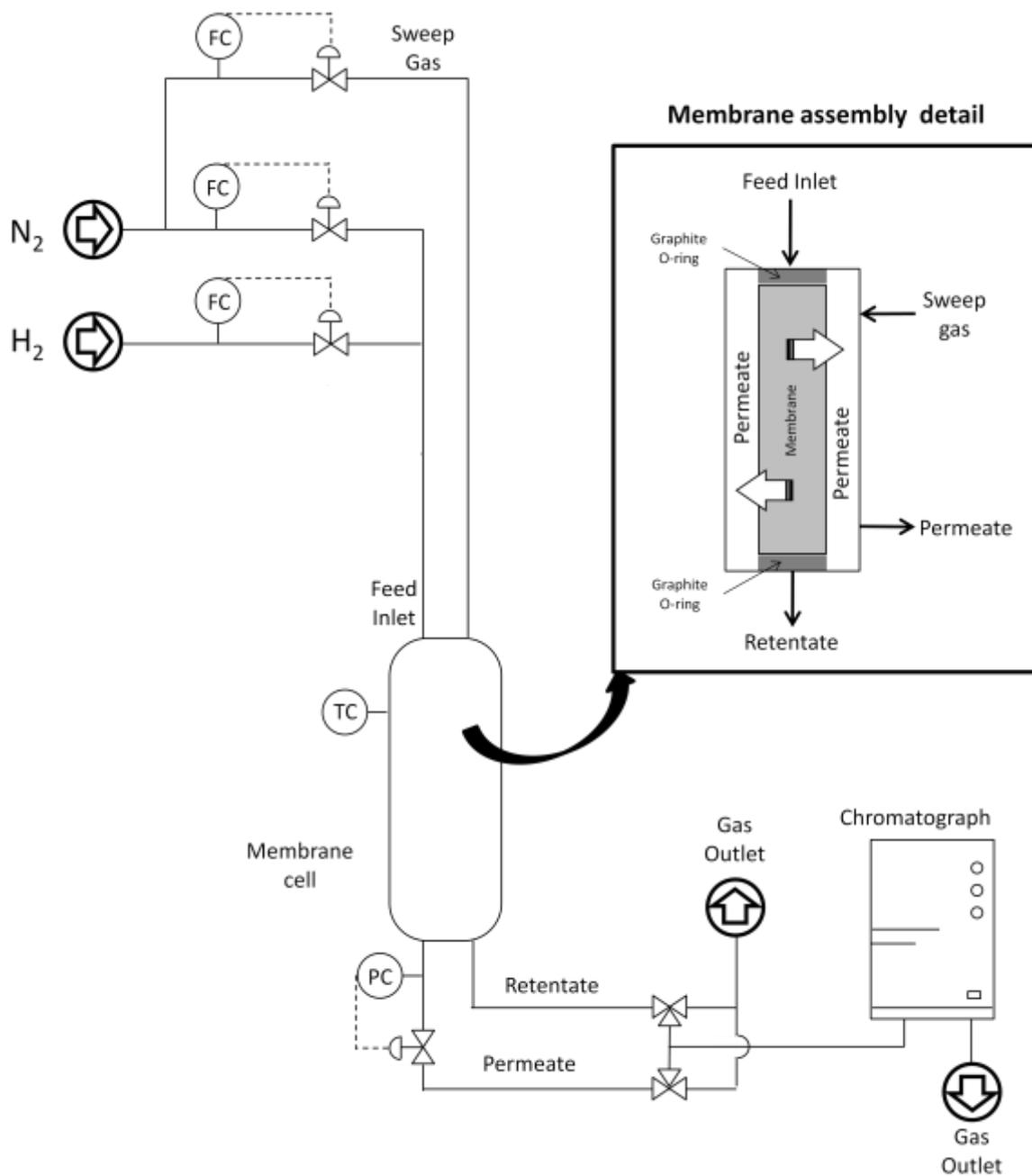


Figure 3

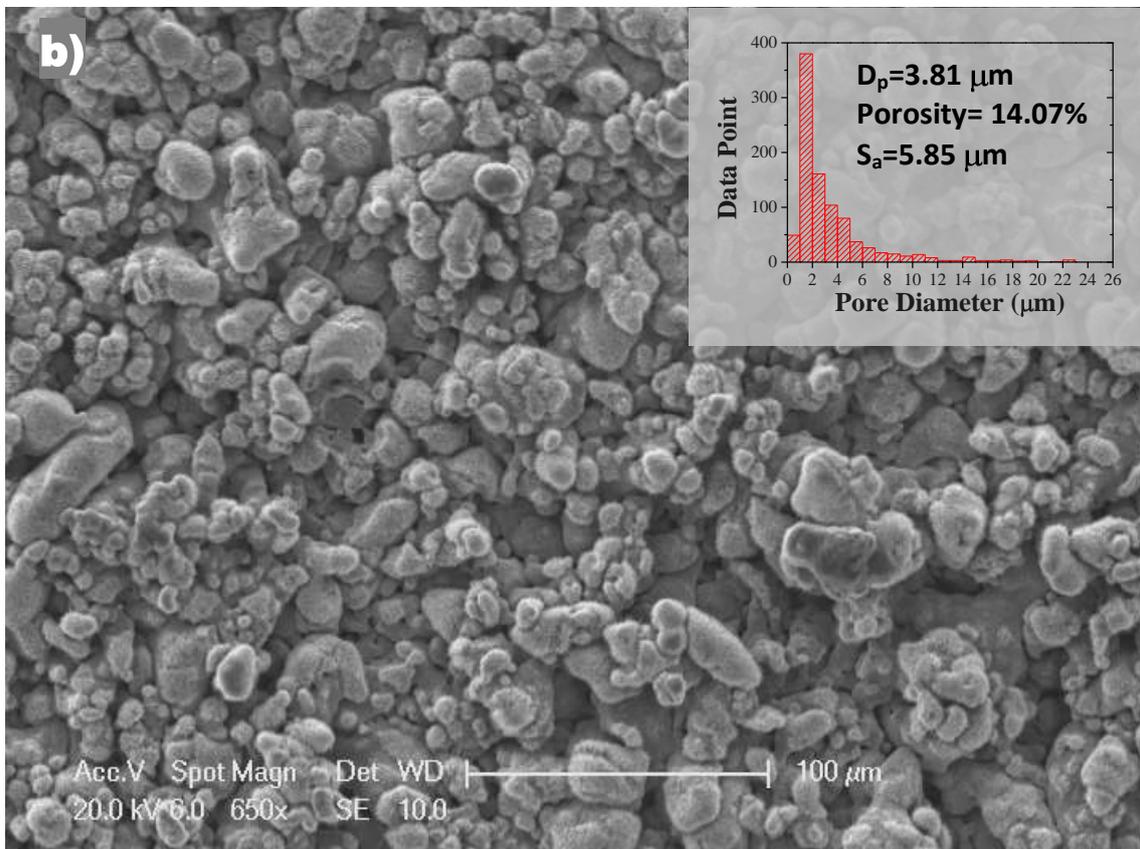
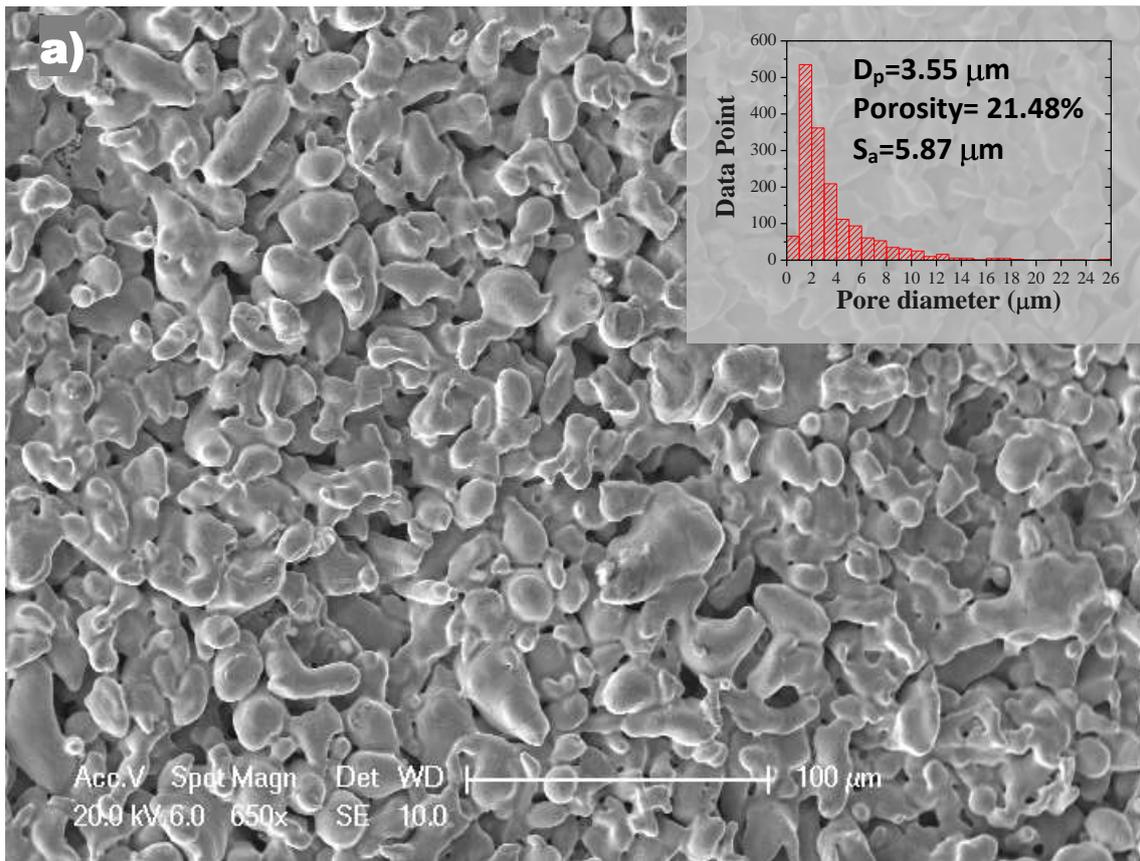


Figure 4

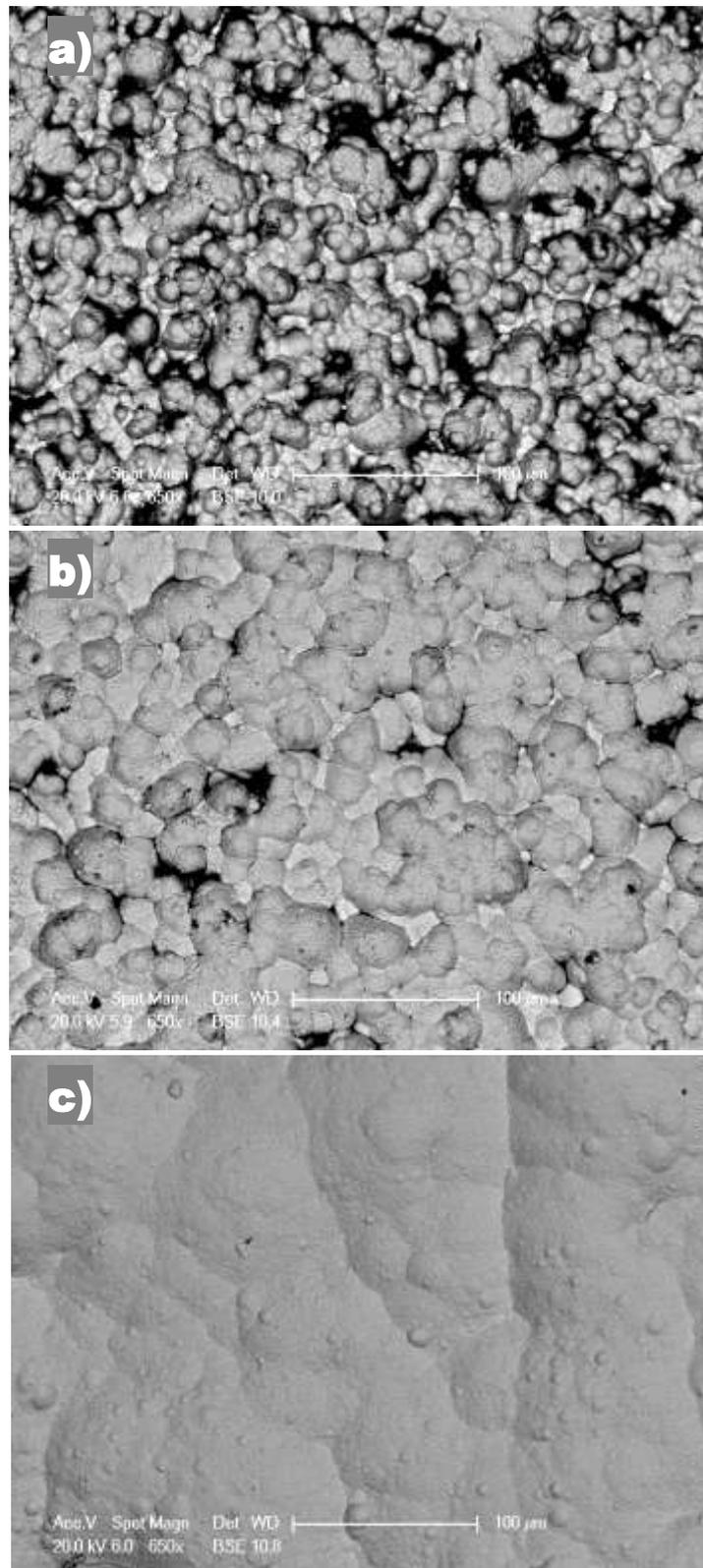


Figure 5

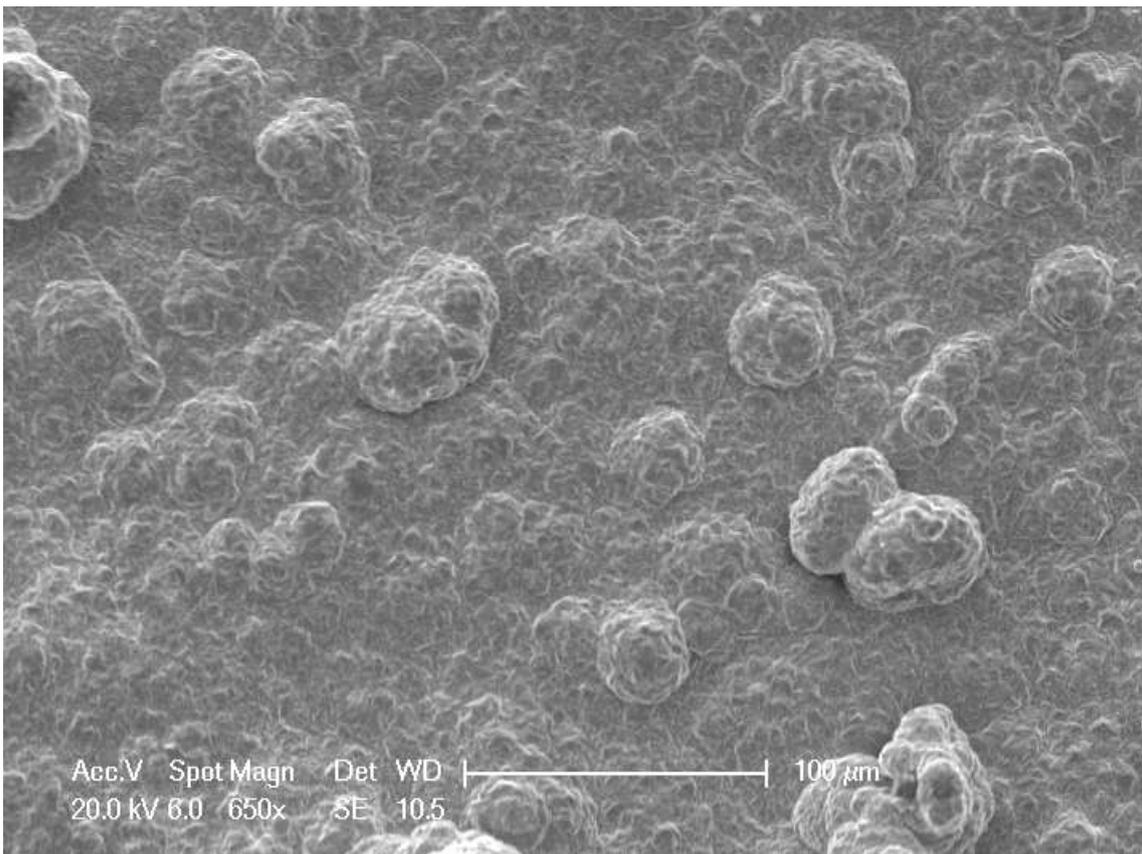


Figure 6

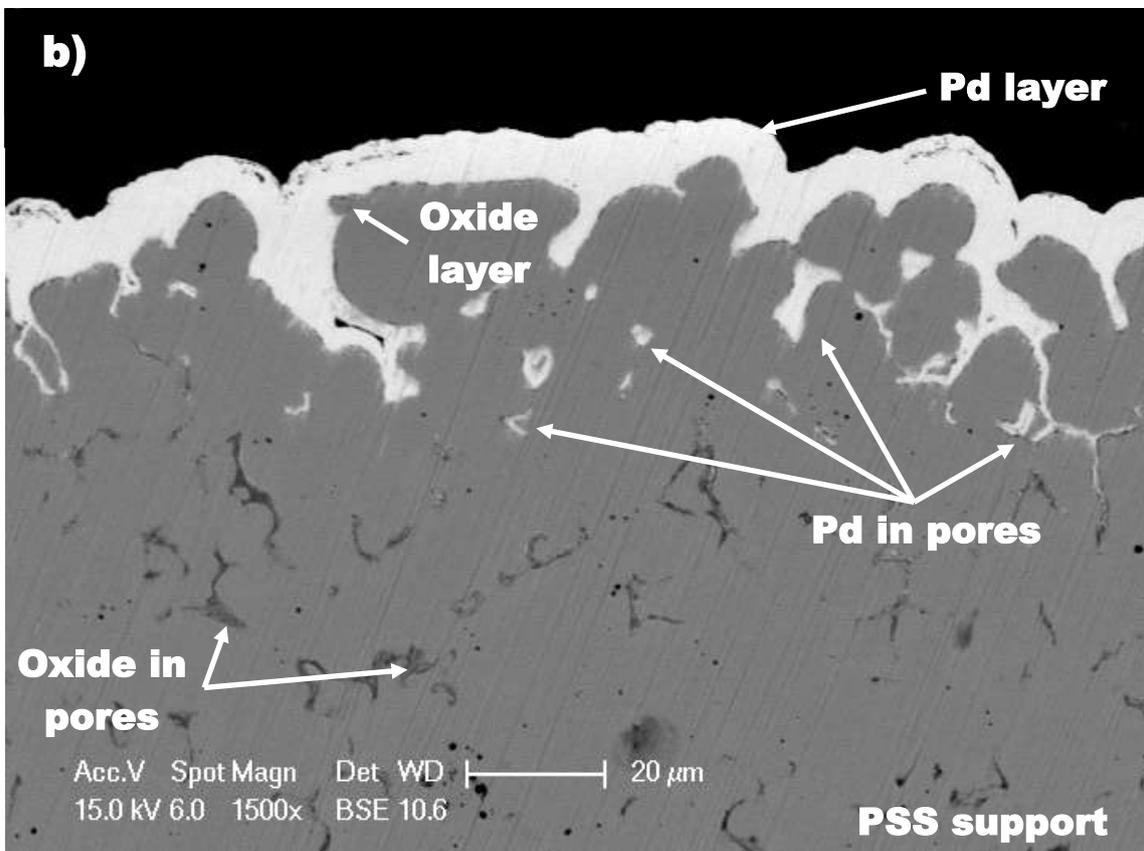
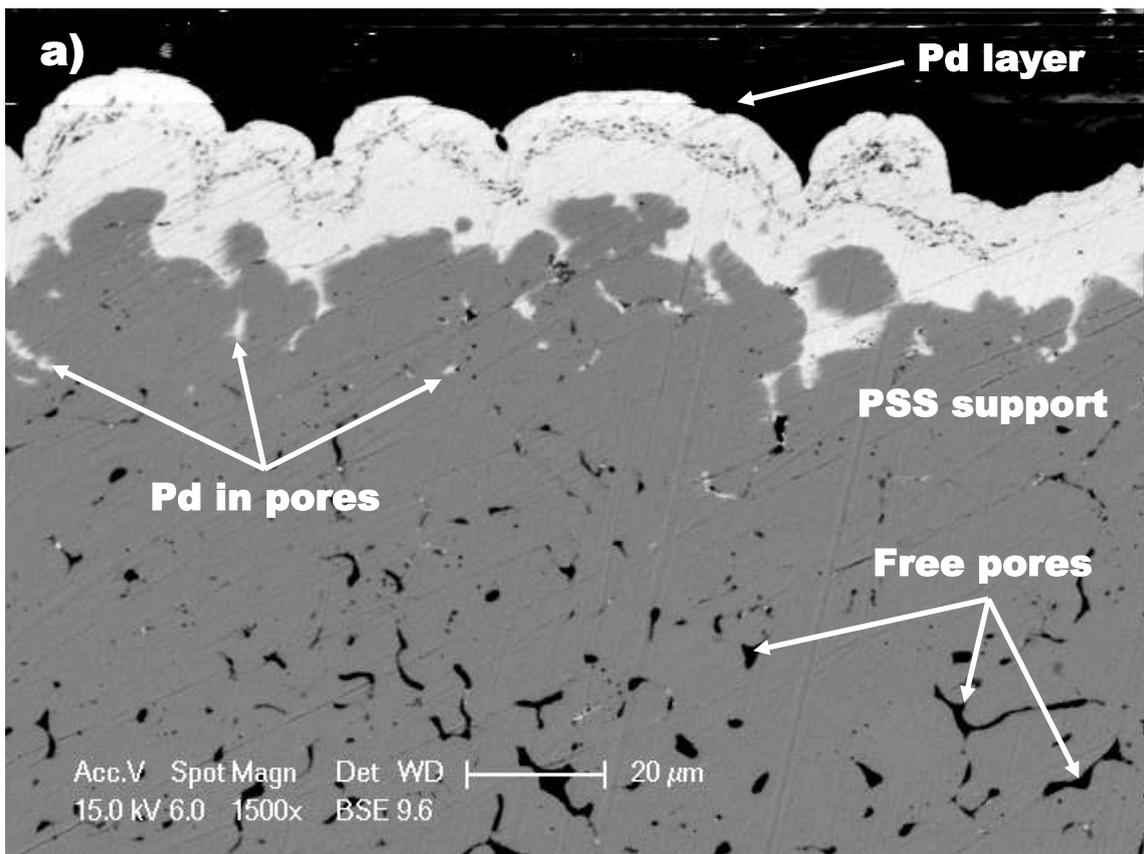


Figure 7

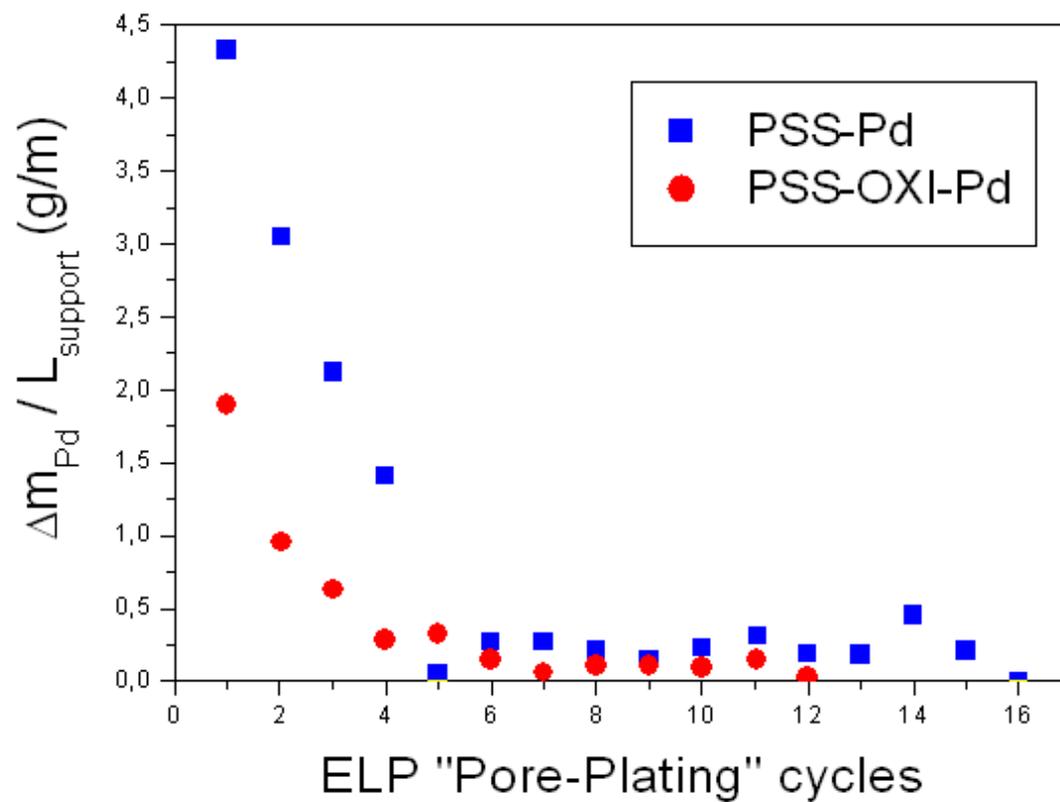


Figure 8

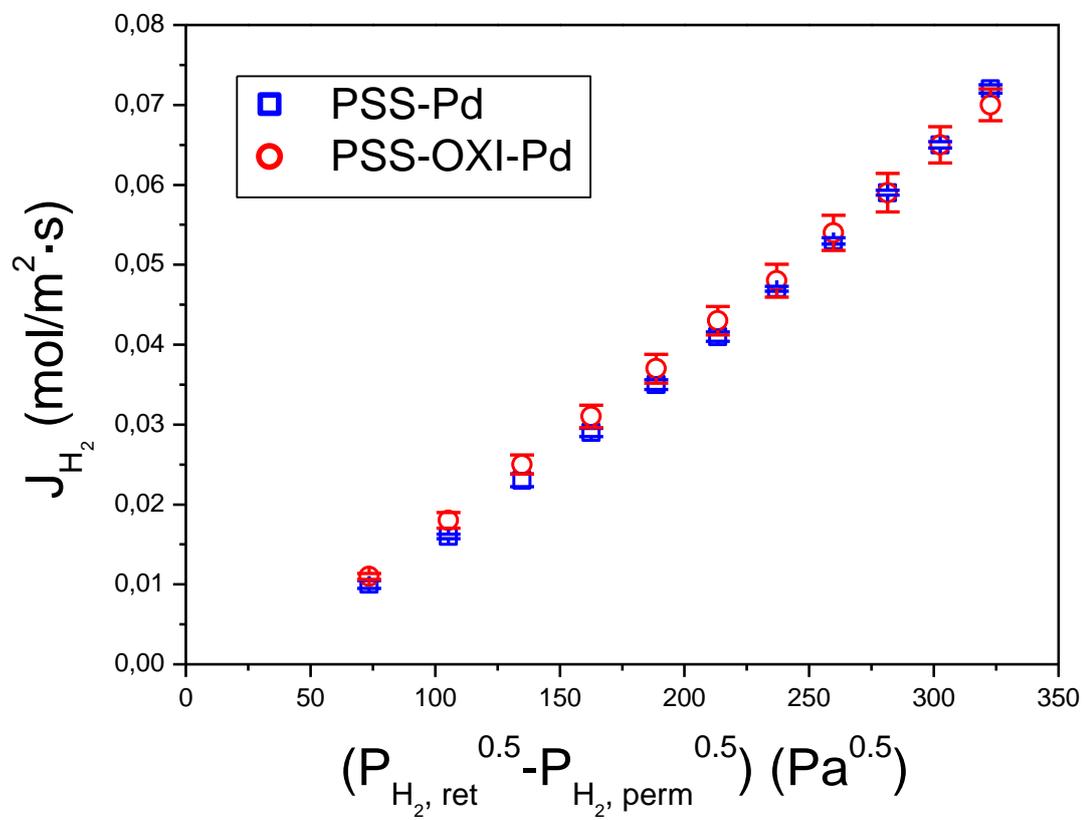


Figure 9

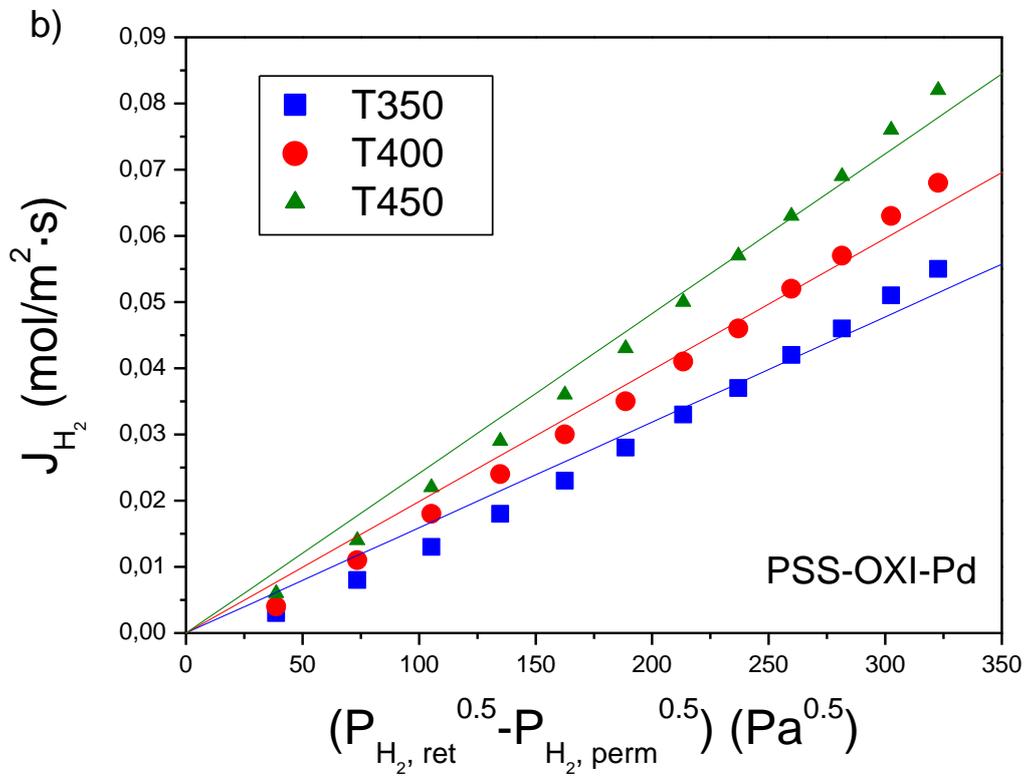
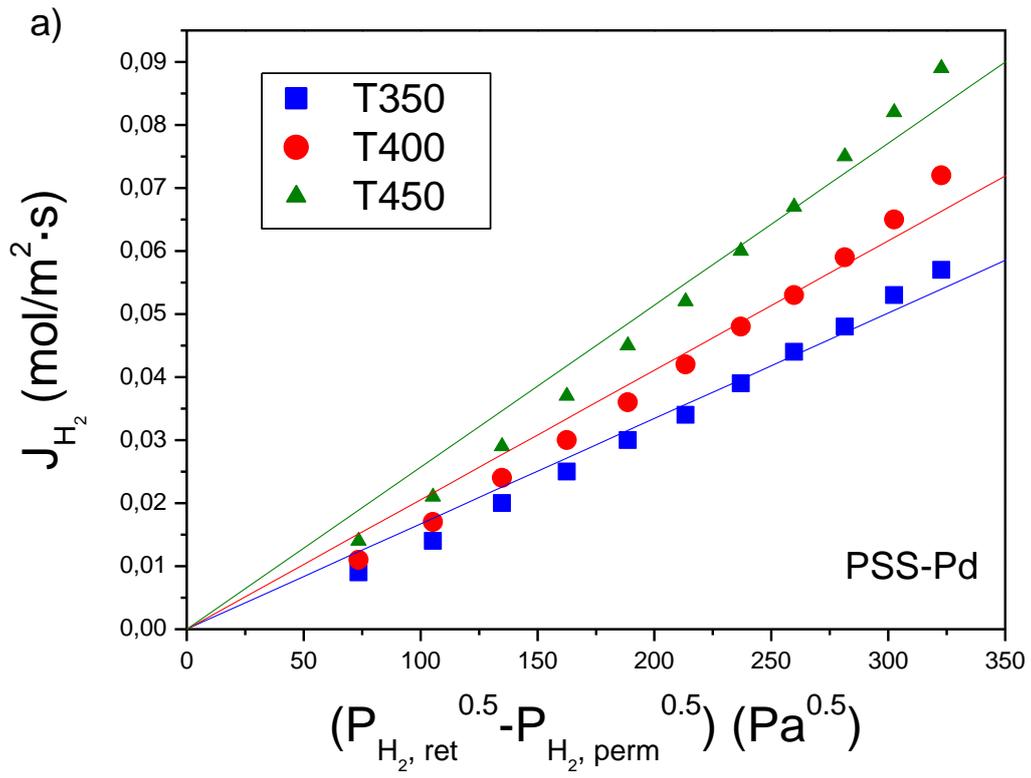


TABLE CAPTIONS

Table 1. Composition and conditions of the activation and electroless Pd pore-plating baths.

Table 2. Permeation data of Pd composite membranes reported in the literature.

Table 2

| Components and conditions | Activation baths ^a | | Plating Pd-bath ^a |
|--------------------------------------|-------------------------------|-------|------------------------------|
| PdCl ₂ (g/L) | 0.1 | - | 5.4 |
| NH ₄ OH 32% (mL/L) | - | 119.6 | 390 |
| HCl 35% (mL/L) | 1.0 | - | - |
| Na ₂ EDTA (g/L) | - | - | 70 |
| N ₂ H ₄ (mL/L) | - | 10 | 10 |
| Temperature (°C) | 25 | 25 | 60 |

^a $V_{\text{solution}}/S_{\text{plating area}} (\text{cm}^3/\text{cm}^2) = 5.76$

Table 3

| Membrane type | Preparation method | Pd thickness (μm) | Experimental conditions | | H_2 flux ($\text{mol}/\text{m}^2\cdot\text{s}$) | H_2 permeance ($\text{mol}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$) | Ideal selectivity (α) | Reference |
|--|--------------------|--------------------------------|-------------------------|------------------------|--|---|--------------------------------|-----------|
| | | | T ($^\circ\text{C}$) | ΔP (bar) | | | | |
| PSS-Pd | PP-ELP | 20 | 350-450 | 0.3-4.0 | 0.01-0.09 | $1.0\text{-}3.0\cdot 10^{-4}$ ^a | ∞ | This work |
| PSS-OXI-Pd | PP-ELP | 11 | 350-450 | 0.3-4.0 | 0.01-0.09 | $1.0\text{-}2.0\cdot 10^{-4}$ ^a | ∞ | This work |
| PSS-YSZ-Pd | ELP | 27.7 | 350-450 | 0.3-4.0 | 0.01-0.06 | $4.05\cdot 10^{-4}$ ^a | ∞ | [27] |
| PSS- Fe_2O_3 -Pd | ELP | 25 | 350 | 0.5-1.5 | 0.02-0.08 | - | 887-698 | [30] |
| PSS- Fe_2O_3 -Pd | ELP | 29 | 400 | 1.0-5.0 | - | $4.2\cdot 10^{-7}\text{-}3.7\cdot 10^{-7}$ | 550-80 | [31] |
| PSS-Pd | ELP | 3.5 | 500-550 | 0.0-3.5 | 0.06-0.33 | - | ∞ | [20] |
| PSS-YSZ-Pd | ELP | 10 | 350-550 | 0.0-0.2 | 0.01-0.09 | - | - | [17] |
| PSS-Ni-SiO ₂ -Pd | CVD | - | 450 | 0.2-0.7 | - | $6.4\cdot 10^{-6}$ | 6100 | [32] |
| PSS-CeO ₂ -Pd | ELP-CVD | 6-10 | 500 | 1.0 | 0.18-0.24 | - | 14-108 | [16] |
| α -Al ₂ O ₃ -Pd | ELP | 1 | 450 | 0.3-1.2 | 0.05-0.45 | $4.0\text{-}5.0\cdot 10^{-6}$ | 3000-9000 | [33] |

^a This value is given in $\text{mol}/\text{m}^2\cdot\text{s}\cdot\text{Pa}^{0.5}$ accordingly to the infinite selectivity of the membrane verified in the experiments (Sieverts' Law)