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**Citation for published version (APA):**

Fernandez, E., Medrano Jimenez, J. A., Melendez, J., Parco, M., Viviente, J. L., van Sint Annaland, M., Gallucci, F., & Pacheco Tanaka, D. A. (2016). Preparation and characterization of metallic supported Pd-Ag membranes for hydrogen separation. *Chemical Engineering Journal*, 305, 182-190. <https://doi.org/10.1016/j.cej.2015.09.119>

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**DOI:**  
[10.1016/j.cej.2015.09.119](https://doi.org/10.1016/j.cej.2015.09.119)

**Document status and date:**  
Published: 01/01/2016

**Document Version:**  
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

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## Preparation and characterization of metallic supported thin Pd–Ag membranes for hydrogen separation



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### HIGHLIGHTS

- Metallic supported Pd–Ag membranes (5 μm thick) with ceramic barrier layer.
- 2 deposition techniques for ceramic layers: APS and powder suspension deposition.
- Optimized membranes showed very high H<sub>2</sub>/N<sub>2</sub> ideal selectivity (>200,000).

### ARTICLE INFO

#### Article history:

Available online 10 November 2015

#### Keywords:

Palladium membrane preparation  
Metallic support  
Interdiffusion barrier layer  
Zirconia  
Alumina  
H<sub>2</sub> separation

### ABSTRACT

This paper reports the preparation and characterization of thin-film (4–5 μm thick) Pd–Ag metallic supported membranes for high temperature applications. Various thin film membranes have been prepared by depositing a ceramic interdiffusion barrier layer prior to the simultaneous Pd–Ag electroless plating deposition. Two deposition techniques for ceramic layers (made of zirconia and alumina) have been evaluated: Atmospheric Plasma Spraying and dip coating of a powder suspension. Initially, the prepared ceramic layers have been characterized for nitrogen permeation at room temperature and surface roughness for the selection of the appropriate type of ceramic layer. The most promising membranes have been tested at 400–600 °C for single gas permeation (H<sub>2</sub> and N<sub>2</sub>), and have shown extremely high H<sub>2</sub>/N<sub>2</sub> permselectivities (>200,000).

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## 1. Introduction

Nowadays, most of the 50 million tons of hydrogen annually produced is obtained through the methane steam reforming process. Hydrogen is normally produced onsite and immediately used in large chemical or petrochemical plants [1] due to the complexity of hydrogen transportation. Among the different reforming processes, steam methane reforming (SMR) is the most employed process to convert CH<sub>4</sub> into H<sub>2</sub> and it is followed by two water gas shift reactors (high and low *T*) and a separation unit in order to obtain a high purity H<sub>2</sub> stream. The large number of different process steps decreases the system efficiency and makes scale-down uneconomical [2]. Recently, novel reactor concepts have been proposed for the improvement in the efficiencies of the steam methane

reforming process. In particular, the application of membrane reactors has been widely studied using Pd-alloy membranes [3,4] obtaining higher conversion degrees compared with conventional systems. Through this novel concept, it has been reported that complete conversion of methane can be achieved at much lower temperatures (~600 °C), resulting in a much higher overall energy efficiency [5]. In the last decade, a lot of research efforts have been devoted to produce much thinner dense Pd-based membranes for their application in membrane reactors. The development of thinner membranes presents some advantages, and most importantly the increase in hydrogen production and the associated improvement in the reaction efficiencies and cost reduction by decreasing the membrane area for the same H<sub>2</sub> production. Thin Pd-based membranes are generally supported on porous substrates to provide mechanical stability [2]. The most commonly used Pd-based layer deposition techniques are electroless plating (ELP), physical vapor deposition, chemical vapor deposition and electroplating [6]. ELP is the most widely used preparation technology due to

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its ability of covering supports with complex geometries with good adhesion characteristics, the simplicity of the required equipment and its low cost and the easiness to scale up from laboratory to industrial scale [7]. In order to get thin defect-free Pd-based films on top of the membrane, the support should have a smooth surface with a small pore size [2]. Generally two types of porous support materials can be distinguished: metallic and ceramic. Ceramic supports typically have a better surface quality providing membranes with thinner selective layers. However, they are more fragile and they need gas-tight seals (for example, made of graphite) to connect them to dense metal tubes and get a proper integration in reactors [8]. Metallic supports are more robust than ceramic supports and there is no need of sealing when an appropriate welding between the porous and dense parts is performed. However, the surface pore size distribution of commercial metallic supports, mainly tubular shape, is not appropriate for deposition of thin Pd layers ( $\leq 5 \mu\text{m}$ ) [9]. For high temperature applications using metallic supported membranes, it becomes necessary to deposit an inter-metallic diffusion barrier layer between the metallic support and the Pd-based layer in order to avoid the interaction between them. Furthermore, this barrier layer can be used to improve the surface quality of the metallic supports. The materials typically used as inter-diffusion barrier layer are:  $\text{ZrO}_2$  [10,11], YSZ [12,13],  $\text{TiO}_2$  [14],  $\text{TiN}$  [15],  $\text{CeO}_2$  [16],  $\text{Al}_2\text{O}_3$  [17,18], zeolites [19,20] and graphite [21]. It has previously been reported that for high temperature applications ( $\approx 600^\circ\text{C}$ ) the use of alumina as Pd-membrane support is not suitable, because it exhibits a significant hydrogen permeance drop over time, thus alumina cannot be applied as barrier layer. Titania may not be an appropriate inter-diffusion barrier material, since it has been demonstrated that interacts with Pd, thus reducing the hydrogen permeance through the membrane [8]. Moreover, Straczewski et al. observed that  $\text{TiO}_2$  layers are unstable during thermal cycling in air [14]. However, the use of Pd membranes on yttria stabilized zirconia (YSZ) has shown a stable hydrogen permeance at  $650^\circ\text{C}$  [22]. Furthermore, Zhang et al. reported that YSZ is also an effective material for preventing inter-metallic diffusion above  $600^\circ\text{C}$  [23]. Hence, the use of YSZ as barrier seems suitable for Pd-alloy membranes on metallic supports. Among different ceramic depositions techniques, the most commonly used are Atmospheric Plasma Spraying (APS) [12,24,25], wet powder spraying (WPS) [14] and powder suspension deposition (PSD) [10,26]. By PSD, ceramic layers with a tuned pore size can be obtained using ceramic powders with a certain

particle size distribution and varying the subsequent sintering process. On the other hand, APS is a widely used commercial technique for ceramic layer deposition due to its process simplicity, low cost, and bulk production. This technique has the advantage that the final layer does not require any post-sintering process. There is also another approach for the formation of inter-diffusion barriers, which consist of obtaining a metal oxide barrier layer through the oxidation of the metallic support [27–29]. For high temperature applications ( $\geq 550^\circ\text{C}$ ), porous supports made of Ni-based alloys (e.g. Hastelloy, Inconel) are needed since common SS316L is not suitable, as also claimed by metal porous tube suppliers such as Mott and GKN [30,31].

In this study two different deposition techniques, Atmospheric Plasma Spraying (APS) and powder suspension deposition (PSD), are used for the development of improved inter-diffusion barriers. High temperature stable Hastelloy X porous tubes have been selected as supports. In this study, first the optimization carried out using nanostructured experimental powders for deposition of YSZ– $\text{Al}_2\text{O}_3$  layers by APS is presented and compared to the ceramic layers deposited by APS using commercial powders. Subsequently, the benefits in terms of surface quality of the YSZ– $\text{Al}_2\text{O}_3$  based layers deposited by PSD are evaluated. Both types of ceramic layers are characterized in terms of surface roughness,  $\text{N}_2$  permeance, and also the  $\text{N}_2$  permeance after Pd–Ag membrane deposition by ELP. The best Pd–Ag supported membranes are tested at  $400\text{--}600^\circ\text{C}$  for single gas permeation ( $\text{H}_2$  and  $\text{N}_2$ ). Finally, the prepared membranes are characterized by SEM–EDX in order to determine the thickness, uniformity and morphology of the deposited layers.

## 2. Experimental

### 2.1. Metallic porous support

Two types of porous Hastelloy X tubes ( $3/8''$  o.d.;  $0.2 \mu\text{m}$  media grade; 125 or 137 mm porous long) supplied by Mott Corporation have been used as membrane supports: surface treated and untreated tubes. The surface treatment consists on ground and reactivated steps (as stated by Mott) in order to reduce the surface pore size and roughness. Both types of porous tubes were welded by Mott to dense Inconel 600 tubes having one closed-end configuration (see the treated tube in Fig. 1 and the untreated tube in Fig. 2a).

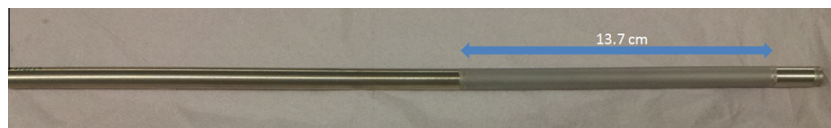


Fig. 1. One closed-end Hastelloy X surface treated porous tube purchased from Mott Corp.

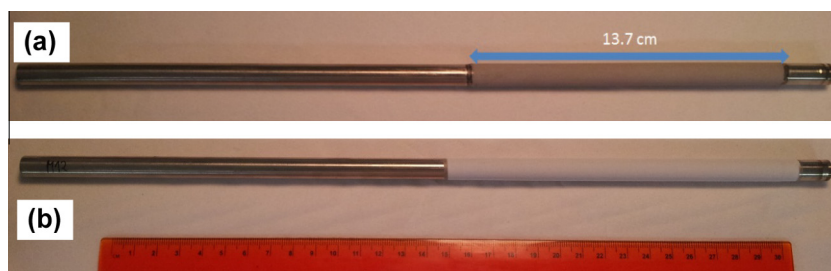


Fig. 2. Untreated Hastelloy X tube before and after coating by APS layer using CERPOTECH powder ( $\text{Al}_2\text{O}_3\text{--}20 \text{ wt.}\% \text{ YSZ}$ ).

## 2.2. Deposition of the ceramic interdiffusion layer

For the untreated supports, two successive deposition techniques were used: first Atmospheric Plasma Spraying (APS) and then dip coating in a powder suspension (PSD). For the treated supports, only the PSD technique was used.

### 2.2.1. Atmospheric Plasma Spraying

Porous ceramic layers have been deposited onto untreated Mott tubes by APS using a commercial system from Sulzer Metco (F4 gun). With this technique, a feedstock material in powder form is introduced into the core of a plasma plume emanating from a d. c. torch. The powder is fully or partially melted, and accelerated towards the work piece (the membrane support in our case). When impacting on the substrate, the powder is flattened and quenched, thus forming a coating with a layered microstructure containing pores, splat boundaries and microcracks [32]. An experimental powder supplied by CERPOTTECH ( $\text{Al}_2\text{O}_3$ -20 wt.% YSZ, 2–20  $\mu\text{m}$  particle size) was used for the optimization of the APS layer. The morphology and particle size distribution of this experimental powder was selected based on results collected in a previous stage using commercial powders [12,24]. Prior to the coating deposition, all supports were cleaned first with acetone and later with ethanol using an ultrasonic bath. The optimized APS process conditions in order to obtain a porous coating structure are: 600 A, 45 NL/min of argon, 10 NL/min of hydrogen, 4 NL/min of carrier gas, a ceramic powder feeding rate of 25–30 g/min and a surface velocity of 13 cm/s. The optimized APS allows producing ceramic layers with a gas permeance at room temperature of  $1 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a surface roughness below 1 and 10  $\mu\text{m}$  in Ra and in Rt, respectively.

In a previous work when using microstructured powders as AMDRY 6660 [8], low helium permeances were obtained ( $2.7 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ). Then, a nano-sized powder (Nanox™ Powder S4007, 63–90 microns particle size) with a very high internal porosity was used obtaining YSZ layers with helium permeances close to the target ( $9 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ) [19]. However, these layers have high surface roughness ( $\approx 10 \mu\text{m}$  in Ra) for deposition of thin Pd-based layers. In the present work, the deposited layers using a nanosized powder with a smaller particle size than Nanox (2–20  $\mu\text{m}$ , supplied by CERPOTTECH) exceeded the  $\text{N}_2$  permeance target ( $3\text{--}4 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ) with roughness of 5–6 microns in Ra. The APS process parameters were adjusted (optimized) to have a largest un-melted ceramic part with a sufficient mechanical stability in order to obtain the highest nitrogen permeance. The final coating thickness is around 40  $\mu\text{m}$ . A picture of the coated tube is shown in Fig. 2b. While good adherence was obtained with APS layers deposited onto the untreated Hastelloy X tubes, for the treated Hastelloy X tubes the ceramic layers underwent a delamination failure as result of the poor mechanical anchoring to the support surface, hence this last option was ruled out.

### 2.2.2. Powder suspension deposition

For both treated and untreated supports, ceramic top layer(s) were deposited by PSD. This method consists of three main steps: (a) powder suspension preparation, (b) deposition of powder suspension onto the metallic tube by vacuum-assisted dip coating and (c) sintering. Two ceramic powders were used:  $\alpha$ -alumina (AKP-30) provided by SUMITOMO [33] and yttria-stabilized zirconia (YSZ) (TZ-8Y, 8 mol%  $\text{Y}_2\text{O}_3$ ) provided by TOSOH [34]. The preparation of the aqueous suspensions containing ceramic powder(s) and other additives (PVA, PEG) and the dip coating of the ceramic layers onto metallic porous supports were carried out following a similar procedure reported before [35]. Different numbers (from 2 to 5) of layers combining  $\text{Al}_2\text{O}_3$ -YSZ or pure YSZ powder based

suspensions were deposited. After each dip coating process, the samples were sintered at 750 °C for 2 h into a quartz tube that was placed in a cylindrical furnace from Termolab. The temperature was increased at 2–3 °C  $\text{min}^{-1}$  under helium to the desired temperature and then maintained at the sintering temperature. A mixture of hydrogen flow of 50  $\text{cm}^3 \text{ min}^{-1}$  and a helium flow of 450  $\text{cm}^3 \text{ min}^{-1}$  was fed into the furnace at temperatures higher than 400 °C. Helium was used for the subsequent cooling step.

## 2.3. Pd-based layer deposition

Thin Pd-Ag layers were deposited on top of the ceramic coated metallic tubes by using the simultaneous (Pd and Ag) electroless plating technique reported in the literature [36]. All the membranes have at least a base plating process (210 min). For selected membranes a second Pd-Ag sequential plating step was carried out in order to have a thicker final membrane to close any possible pin-hole still present in the first plated layer. After each plating step, the membrane layers were annealed at 650 °C for 2 h, by exposure to a 10%  $\text{H}_2$ /90% He gas mixture with the same heating rate and gas flows reported previously [37]. This annealing treatment allows to alloy the Pd and Ag, and to eliminate the remaining undesired compounds of the electroless plating process. The preparation conditions of the membrane samples prepared in this work are listed in Table 1, and a picture of two membranes is shown in Fig. 3.

## 2.4. Physico-chemical characterization of the membranes

In order to evaluate the quality of the ceramic layers onto different metallic supports, two characterization methods have been applied before and after the deposition of the Pd-Ag layers: profilometry of the surface layer and the single gas  $\text{N}_2$  permeation tests. The surface roughness of the ceramic layers was analyzed by Veeco DEKTAK 150 contact profilometer using a 2  $\mu\text{m}$  radius stylus tip. The measurements were carried out following the standard ISO 4287-4288 (at least 5 measurements were carried out along the surface of each deposited layer) and the results are given in Ra and Rt (see Table 1). Ra is the arithmetic average of the absolute values of the roughness profile ordinates. "Rt", peak-to-valley height, is the difference between the highest peak and lowest valley in each sample on the evaluated length.

The cross-section of some membranes samples was analyzed by JEOL JSM-6330F SEM-EDX equipment. Before the analysis, metallographic specimens were prepared mounting pieces of membrane in bakelite and polishing them in order to have each part of the membrane in same level for a suitable imaging.

## 2.5. Gas permeation

Pure hydrogen permeance has been measured at five different temperatures between 400 and 600 °C and pressure difference between 0 and 3 bar in a permeation setup [8]. Although industrial relevant conditions would require higher pressures (>20 bar) the present setup only allows these low pressure for highly permeable membranes due to safety restrictions. The feed flow rate was controlled by digital mass flow controllers and the pressure in the reactor was controlled with a back pressure regulator. The flow rate of permeate and retentate was monitored by Brooks mass flow meters. The  $\text{N}_2$  leakage was monitored after each of the experiments using a Bronkhorst flowmeter (model F-110C-002; Nominal flow: 0.014–2 Nml/min Air).

**Table 1**  
Sample preparation conditions and physico-chemical and permeation characterization results.

Membrane preparation					Membrane characterization		
Sample	Metallic support	APS layer	PSD layer	Pd–Ag layer	“Ra” roughness parameter ( $\mu\text{m}$ )	“Rt” roughness parameter ( $\mu\text{m}$ )	$\text{N}_2$ permeance at RT ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ )
Mott untreated		–	–	–	$6.09 \pm 0.29$	$40.04 \pm 2.65$	$4.90 \cdot 10^{-5}$
Mott treated		–	–	–	$0.98 \pm 0.07$	$9.37 \pm 0.70$	$3.54 \cdot 10^{-5}$
#1	Untreated	$\text{Al}_2\text{O}_3$ –YSZ layer by APS	–	–	$5.86 \pm 0.30$	$42.12 \pm 1.93$	$3.74 \cdot 10^{-5}$
		–	2 dip coated layers/standard sintering	–	$3.97 \pm 0.46$	$33.47 \pm 3.62$	$2.14 \cdot 10^{-5}$
		–	–	1 Pd–Ag layer/annealing	–	–	$4.40 \cdot 10^{-6}$
#2	Untreated	$\text{Al}_2\text{O}_3$ –YSZ layer by APS	–	–	$5.98 \pm 0.40$	$42.16 \pm 0.90$	$4.09 \cdot 10^{-5}$
		–	2 dip coated layers/standard sintering	–	$4.52 \pm 0.44$	$33.37 \pm 2.43$	$3.13 \cdot 10^{-5}$
		–	–	1 Pd–Ag layer/annealing	–	–	$1.79 \cdot 10^{-5}$
#3	Untreated	$\text{Al}_2\text{O}_3$ –YSZ layer by APS	–	–	$5.51 \pm 0.08$	$39.26 \pm 0.81$	$3.85 \cdot 10^{-5}$
		–	2 dip coated layers/standard sintering	–	$3.13 \pm 0.60$	$27.54 \pm 0.37$	$2.35 \cdot 10^{-5}$
		–	–	1 Pd–Ag layer/annealing	–	–	$7.54 \cdot 10^{-6}$
#4	Untreated	$\text{Al}_2\text{O}_3$ –YSZ layer by APS	–	–	$4.65 \pm 0.20$	$34.90 \pm 3.68$	$3.64 \cdot 10^{-5}$
		–	2 dip coated layers/standard sintering	–	$3.22 \pm 0.11$	$25.05 \pm 0.18$	$2.05 \cdot 10^{-5}$
		–	–	1 Pd–Ag layer/annealing	–	–	$1.34 \cdot 10^{-7}$
#5	Treated	No	2 dip coated layers/standard sintering	–	$1.19 \pm 0.06$	$8.66 \pm 1.77$	$7.43 \cdot 10^{-6}$
			–	2 Pd–Ag layers/annealing	–	–	$1.30 \cdot 10^{-9}$
#6	Treated	No	2 dip coated layers/standard sintering	–	$0.41 \pm 0.04$	$5.16 \pm 0.36$	$1.82 \cdot 10^{-5}$
			–	2 Pd–Ag layers/annealing	–	–	$9.30 \cdot 10^{-10}$
#7	Treated	No	3 dip coated layers/standard sintering	–	$0.47 \pm 0.03$	$3.46 \pm 0.43$	$7.72 \cdot 10^{-6}$
			–	2 Pd–Ag layers/annealing	–	–	$1.38 \cdot 10^{-10}$
#8	Treated	No	4 dip coated layers/standard sintering	–	$0.44 \pm 0.02$	$5.01 \pm 1.16$	$1.34 \cdot 10^{-5}$
			–	2 Pd–Ag layers/annealing	–	–	$<8.35 \cdot 10^{-11}$
#9	Treated	No	5 dip coated layers/standard sintering	–	$0.46 \pm 0.03$	$4.49 \pm 0.95$	$8.22 \cdot 10^{-6}$
			–	2 Pd–Ag layers/annealing	–	–	$6.55 \cdot 10^{-10}$
#10	Treated	No	5 dip coated layers/standard sintering + extra sintering	–	$0.45 \pm 0.02$	$4.08 \pm 1.85$	$8.50 \cdot 10^{-6}$
			–	2 Pd–Ag layers/annealing	–	–	$<8.37 \cdot 10^{-11}$
			–	–	–	–	–
#11	Treated	No	5 dip coated layers/standard sintering + extra sintering	–	$0.35 \pm 0.03$	$2.95 \pm 0.82$	$6.12 \cdot 10^{-6}$
			–	2 Pd–Ag layers/annealing	–	–	$<7.94 \cdot 10^{-11}$

NA: not available data.

RT: room temperature.



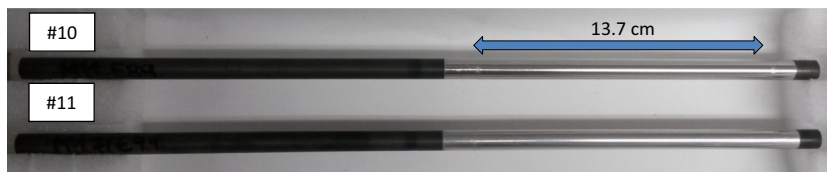


Fig. 3. Metallic supported Pd–Ag membranes (the characteristics of the membranes are listed in Table 1).

### 3. Results and discussion

#### 3.1. Physico-chemical characterization of prepared membranes

A composite 80%Al<sub>2</sub>O<sub>3</sub>–20%YSZ (wt) powder (supplied by CER-POTECH) was selected for the manufacture of the ceramic layers by APS onto treated Mott tubes. This powder is based on nano-structured spherical granules with particle sizes between 2 and 20 microns in order to obtain a ceramic layer with low roughness but with enough gas permeance. The composite Al<sub>2</sub>O<sub>3</sub>–YSZ powder has a better thermo-mechanical performance than each material separately and the resulting composite layer would be used as intermediate layer deposited before the PSD top layer. The APS process parameters were optimized (as reported in Section 2.2.1) based on the thickness homogeneity, nitrogen permeance at room temperature and surface roughness of the resulting coatings.

The influence of the number of ceramic layers prepared by PSD was evaluated. The aim was to cover the whole porous surface of the treated metallic support with the thinner interdiffusion layer avoiding the contact between the metallic support and the selective layer as well as reducing the surface roughness of the metallic support.

Finally, the two interdiffusion barrier layer approaches based on APS and on PSD deposited onto untreated and treated Hastelloy X, were evaluated in terms of surface roughness, nitrogen permeance of the resulting ceramic layer and the nitrogen permeance of 3–5 microns thick Pd–Ag deposited onto each type of ceramic layers. In Table 1 the preparation conditions used together with the physico-chemical and permeation characterization results for each membrane sample prepared by the two approaches are detailed.

As can be concluded from Table 1 the untreated Mott tube has a high surface roughness (around 6 μm in Ra) and after deposition of the Al<sub>2</sub>O<sub>3</sub>–YSZ layer deposited by APS layer the surface roughness did not decrease much (around 5–6 μm in Ra). Then, after depositing several PSD layers onto the APS layer the surface roughness decreased (down to 3–4 μm in Ra) but still it has a high surface roughness (the target is to achieve <<1 μm in Ra or <<10 μm in Rt). The variation on the roughness values of the layers is due to the differences in surface quality of the metallic support samples. Afterward, Pd–Ag layers were coated onto these surfaces but the

N<sub>2</sub> permeance of the membrane was too high (very far from the target of a N<sub>2</sub> permeance of 1.0 × 10<sup>−9</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup> at room temperature). A smooth surface for defect-free thin Pd layer deposition was thus not obtained using this approach. Fig. 4 shows the Al<sub>2</sub>O<sub>3</sub>–YSZ deposited by APS onto Hastelloy X. With a thickness of ~40 μm, these APS layers can already cover homogeneously the rough metallic support, featuring N<sub>2</sub> permeance values at room temperature in the order of 3–4 × 10<sup>−5</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>; their roughness (around 5–6 μm in Ra) is, however, still too high for a well-functioning interdiffusion layer, although it is lower than as-sprayed YSZ layers using commercial powders (around 10 μm in Ra).

The treated Mott tube has a low surface roughness (close to 1 μm in Ra) as can be seen in Table 1. After the deposition of 3–5 Al<sub>2</sub>O<sub>3</sub>–YSZ or YSZ layers by PSD the surface roughness was reduced to 0.3–0.5 μm in Ra (e.g. #7–#11 membranes) and the N<sub>2</sub> permeance ranged between 6.12 × 10<sup>−6</sup> and 8.50 × 10<sup>−6</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>, that is much lower than of the treated support (3.54 × 10<sup>−5</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>). Afterward, Pd–Ag layers were coated onto these surfaces and the nitrogen permeance of the membrane achieved the targets on N<sub>2</sub> permeance at room temperature (<1.0 × 10<sup>−9</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>). The surface quality of the ceramic layer prepared by PSD is suitable for deposition of thin Pd layers when 3 or more depositions are carried out, since the N<sub>2</sub> permeance target for the Pd-based layer is achieved. Fig. 5 shows the SEM cross-section images of #11 membrane after the permeation tests. In Fig. 5a, a homogeneous Pd–Ag layer (white) can be seen deposited onto the ceramic coated treated Hastelloy X support (grey). By comparing this figure with previous Fig. 4, it is observed that the treated support has a smoother surface compared to the untreated one, but in any case it has big open pores (>10 μm) that may hinder the preparation of thin defect-free Pd-based membranes. In the same zone at higher magnifications (Fig. 4b), the Pd–Ag layer is around 4–5 microns thick, and most importantly the ceramic layer is a continuous layer even if there is a big pore in the metallic support. The filling of the big pores in order to obtain a continuous layer penalizes the gas permeance through the ceramic layer (6.12 × 10<sup>−6</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>). In another zone (Fig. 5c) again the Pd–Ag layer is 4–5 microns thick and big metallic pores are filled with the ceramic acting as an interdiffusion barrier and

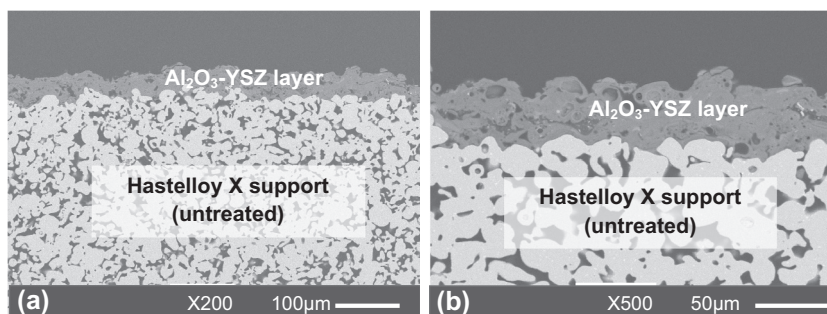
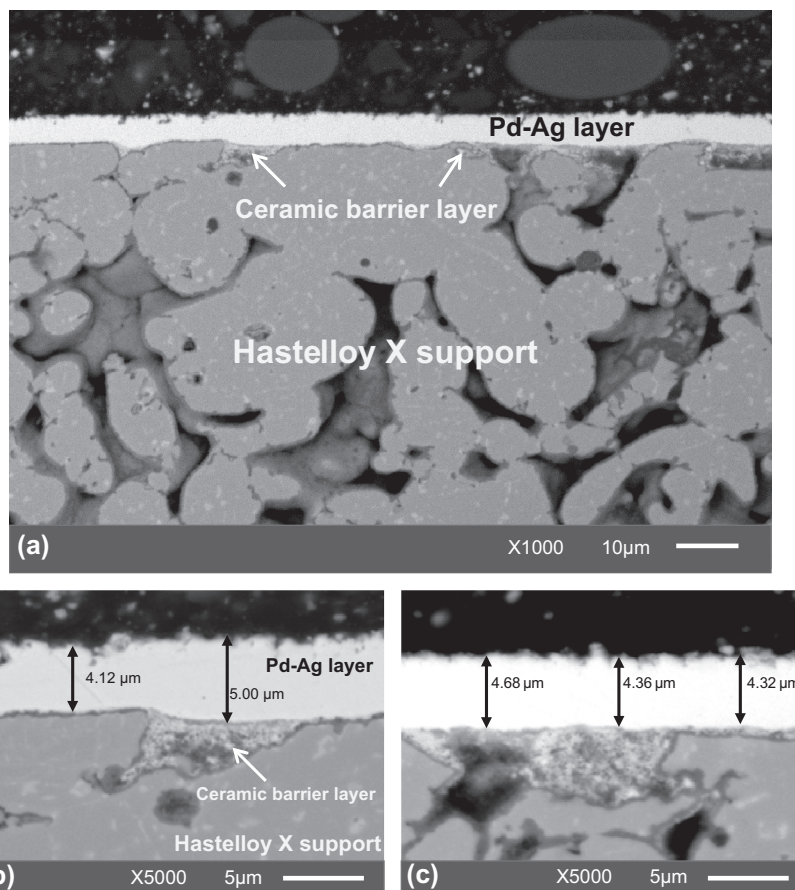


Fig. 4. Cross sectional SEM images of Al<sub>2</sub>O<sub>3</sub>–20 wt.% YSZ interdiffusion layer (CERPOTECH powder) deposited by APS onto untreated Hastelloy X Mott tube (a) at 200× and (b) at 500× magnifications.



**Fig. 5.** Cross sectional SEM images of #11 membrane (Pd–Ag/YSZ–Al<sub>2</sub>O<sub>3</sub>/treated Hastelloy X): (a) “Zone 1” at 1000×, (b) “Zone 1” at 5000×, (c) “Zone 2” at 5000×.

support for Pd–Ag layer. The ceramic layer is 0.5–2 μm thick when it is deposited onto a surface treated metallic particle as shown in Fig. 5c (right part). However, this thin layer can be a weak part for high temperature and reactive long-term operation.

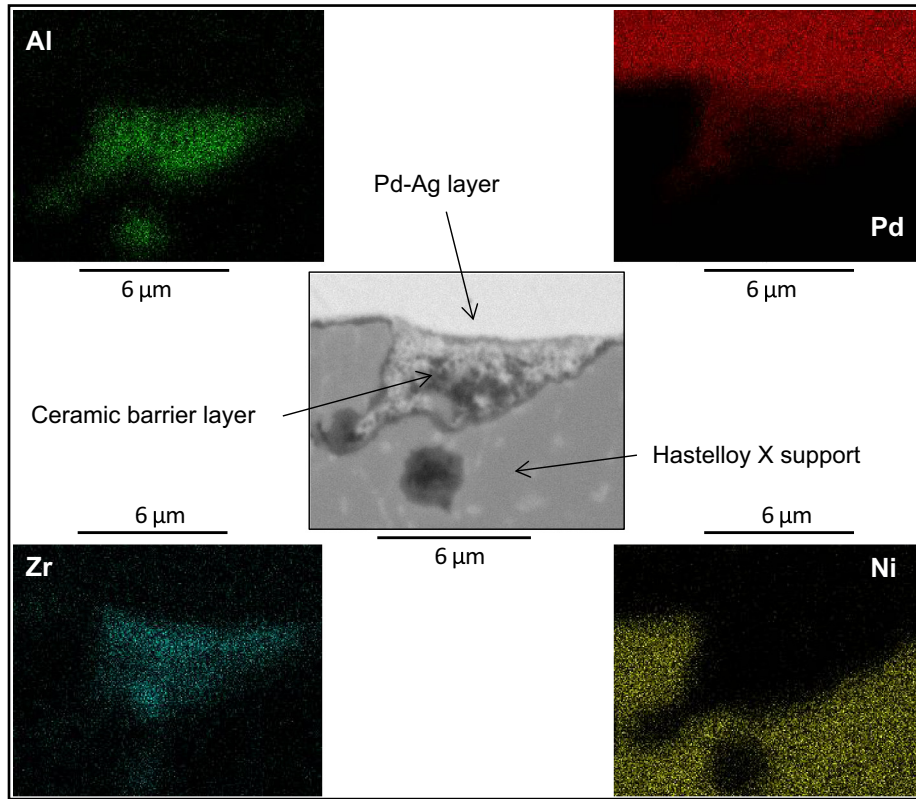
In order to confirm the presence of the YSZ–Al<sub>2</sub>O<sub>3</sub> layer deposited by PSD, an EDX mapping of the area was performed for the following elements: aluminum in green colour (from Al<sub>2</sub>O<sub>3</sub>), zirconium in blue colour (from YSZ), Pd in red colour (selective layer) and Ni in yellow colour (the major component of Hastelloy X support). The results are presented in Fig. 6. Al and Zr were detected in the ceramic interdiffusion barrier layer, therefore YSZ–Al<sub>2</sub>O<sub>3</sub> depositions are able to fill the big pores of the Hastelloy X tube. Besides, the Zr is detected in the top part of the ceramic layer and thus the presence of YSZ in contact with Pd-based layer would avoid the Pd–Al alloying during long-term operation at temperatures above 600 °C [22]. The Pd-based layer and the Ni-based support part are well separated and it is thus expected that the ceramic layer will play the role of interdiffusion barrier for metallic components.

### 3.2. Permeation of membranes

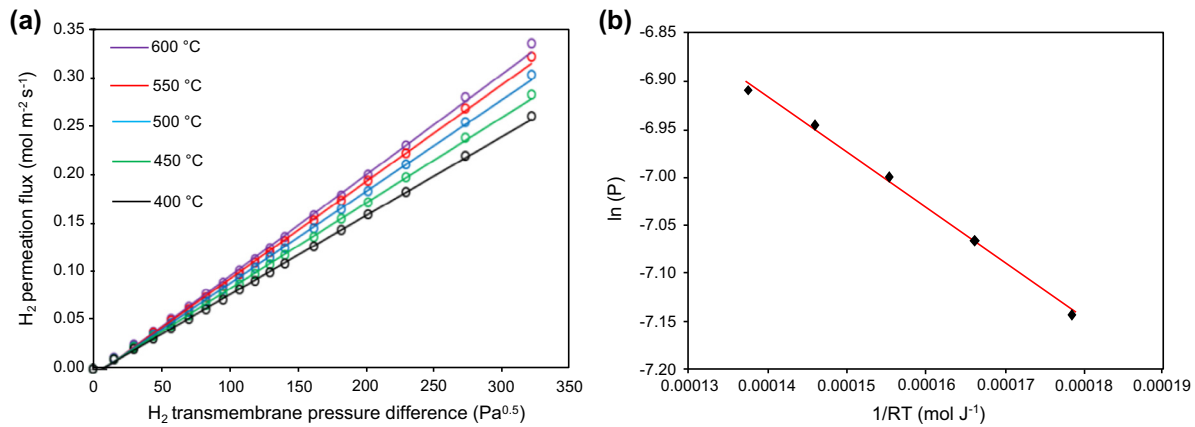
According to the properties listed in Table 1, membrane #11 was selected for the permeation tests at high temperature since it has very low N<sub>2</sub> permeance at room temperature ( $<8 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ). In Fig. 7a the hydrogen flux for this membrane at different hydrogen partial pressure and different temperatures between 400 and 600 °C is shown. The hydrogen permeation is increasing with increasing transmembrane partial pressure difference and temperature. The tested membrane shows a perfect

linear behavior for the pressure exponential factor  $n = 0.738$ , which differs from the typical for Pd-alloy membranes at low pressures, if bulk-diffusion through the membrane is the rate limiting step according to Sieverts Law ( $n = 0.50$ ) [38]. This difference may be due to the influence of the metallic support and/or ceramic layer on the H<sub>2</sub> transport through the entire membrane. The membrane parameters for the tested membrane have been determined at  $5.8 \text{ kJ mol}^{-1}$  for the activation energy ( $\Delta E_{\text{act}}$ ) and  $1.01 \times 10^{-8} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$  for the pre-exponential factor ( $P_0$ ) using the plot of the logarithm of the permeance against the reciprocal temperature with  $R^2 = 0.997$ , as shown in Fig. 7b.

The H<sub>2</sub>/N<sub>2</sub> ideal perm-selectivity of this membrane was  $>200,000$  at the testing temperature range, since the N<sub>2</sub> permeance was  $<5.7 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . The extremely low N<sub>2</sub> permeance of the membrane also indicates that the welding of the porous and dense tube is leak-tight. This was also confirmed by an ethanol-helium leak test [39] in which no bubbles were found on the membrane surface and welding when membrane #11 is immersed in ethanol and a pressure of 0.5 bars of helium is applied inside of it. This very high perm-selectivity is maintained at the same value after 100 h of operation. Table 2 compares the metallic supported Pd–Ag membrane tested in this work with other membranes reported in the literature. The ideal H<sub>2</sub>/N<sub>2</sub> permselectivity of this membrane is extremely high being one of the highest reported in the literature and its H<sub>2</sub> permeance is lower than that of the supported membranes reported with a similar Pd-based layer thickness. The low H<sub>2</sub> permeance is caused by the gas resistance through the ceramic interdiffusion barrier layer and the low porosity of the treated metallic support.



**Fig. 6.** EDX mapping results of “Zone 1” (center) of #11 membrane (Pd–Ag/YSZ–Al<sub>2</sub>O<sub>3</sub>/treated Hastelloy X) at 10000× for the elements: Al (green); Zr (blue); Pd (red) and Ni (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 7.** (a) H<sub>2</sub> flux vs. H<sub>2</sub> partial pressure difference at different temperatures for #11 membrane (Pd–Ag/YSZ–Al<sub>2</sub>O<sub>3</sub>/treated Hastelloy X), (b) linear regression to determine membrane parameters (intercept value is  $\ln P_0$  and slope is  $-\Delta E_{act}$  in J/mol).

**Table 2**

Comparison of different Pd based membranes reported in the literature.

Membrane material (method)	Selective layer thickness ( $\mu\text{m}$ )	Support	Interdiffusion barrier layer (method)	T ( $^{\circ}\text{C}$ )	H <sub>2</sub> permeance [ $10^{-8}$ (mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> ) <sup>a</sup> ]	Ideal permselectivity	Refs.
Pd–Au (ELP)	2.3	PSS	YSZ (not specified)	400	710	82,000 (H <sub>2</sub> /N <sub>2</sub> )	[13]
Pd–Ag (PVD)	2.8	PSS	No	400	1500	2900 (H <sub>2</sub> /N <sub>2</sub> )	[40] <sup>b</sup>
Pd (ELP)	7.5	316L	$\alpha$ - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (PSD)	400	158	3770 (H <sub>2</sub> /He)	[26]
Pd (PVD + EP)	10–12	Fe–Cr alloy	YSZ (PSD, 50 $\mu\text{m}$ thick)	400	112	400–4000 (H <sub>2</sub> /N <sub>2</sub> )	[4]
Pd (ELP)	20	SS316L	Fe–Cr oxide (oxidation)	390	43	200–300 (H <sub>2</sub> /N <sub>2</sub> )	[41]
Pd–Au (ELP)	12	PSS	ZrO <sub>2</sub> (PSD)	400	120	>10,000 (H <sub>2</sub> /N <sub>2</sub> )	[10]
Pd–Au (ELP)	2–3	Al <sub>2</sub> O <sub>3</sub>	NA	500	620	1400 (H <sub>2</sub> /N <sub>2</sub> )	[42]
Pd–Ag (ELP)	3.2	Al <sub>2</sub> O <sub>3</sub>	NA	400	310	8000–10,000 (H <sub>2</sub> /N <sub>2</sub> )	[37]
Pd–Ag (ELP)	~4–5	Hast X	YSZ–Al <sub>2</sub> O <sub>3</sub> /YSZ (PSD, 1 $\mu\text{m}$ thick)	400	100	>200,000 (H <sub>2</sub> /N <sub>2</sub> )	This work

NA, not applicable.

<sup>a</sup> Permeance values have been calculated for a H<sub>2</sub> partial pressure of 1 bar.

<sup>b</sup> Self-supported membranes.



Long-term stability studies of the metallic supported Pd–Ag membranes will be performed at high temperatures (>600 °C) in order to evaluate their use as high temperature purifiers and/or for reforming membrane reactors. Moreover, the resistance to attrition by catalysts of these thin Pd-based supported membranes in fluidized bed assisted membrane reactors will be evaluated.

#### 4. Conclusions

Intermetallic diffusion barrier layers were successfully deposited by two techniques onto Hastelloy X tubes: by APS onto untreated tubes and by PSD onto surface treated tubes. Al<sub>2</sub>O<sub>3</sub>–YSZ layers were deposited by APS using an experimental powder but they showed a high surface roughness not suitable for deposition of thin Pd–Ag membrane layers without defects. On the other hand, a ~4–5 μm thick Pd–Ag membrane that includes a ceramic layer prepared by several dip coatings (PSD) onto a treated Hastelloy X tube (#11 membrane) showed an ultra-high H<sub>2</sub>/N<sub>2</sub> permselectivity (>200,000), one of the highest reported for supported membranes, and a somewhat lower H<sub>2</sub> permeance compared to the supported membranes reported in the literature ( $1 \times 10^{-6}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> at 400 °C and 100 kPa). This ceramic layer is continuous, has a low surface roughness and covers homogeneously the metallic porous support, but since big surface metallic pores were filled by the ceramic material the gas resistance through it is significantly increased. In any case, this ceramic layer acts as an interdiffusion barrier layer between the metallic support and the Pd-based layer, rendering this metallic supported membrane a good candidate for high temperature applications. Long-term stability tests and reactive tests using these metallic supported Pd–Ag membranes are in progress.

#### Acknowledgements

The presented work is funded within ReforCELL project as part of the European Union's Seventh Framework Programme (FP7/2007–2013) under Grant agreements n° 278997 (for the Fuel Cells and Hydrogen Joint Technology Initiative). *Note:* "The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein". Also NWO/STW is acknowledged for the financial support through the VIDJ project number 12365.

The authors would like to thank CERPOTECH and SUMITOMO for providing the ceramic powders. Finally, the authors would like to thank the University of Basque Country (UPV-EHU) for Zabalduz scholarship program and Prof. Pedro Luis Arias.

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