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Development of highly permeable ultra-thin Pd-based supported membranes

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HIGHLIGHTS

- Preparation of ultra-thin ($\sim 1 \mu\text{m}$ thick) Pd-based supported membrane.
- Membrane prepared by PVD magnetron sputtering and electroless plating.
- Membrane has very high hydrogen flux and good perm-selectivity ($\text{H}_2/\text{N}_2 \approx 500$).

GRAPHICAL ABSTRACT

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ABSTRACT

This paper reports the preparation and characterization of ultra-thin ($\sim 1 \mu\text{m}$ thick) Pd-based supported membranes for hydrogen purification. Ultra-thin membranes have been prepared by a combination of PVD magnetron sputtering and electroless plating techniques. The membranes have been characterized for single gas and mix gas permeation at temperatures between 350 and 500 °C and they have shown to exhibit very high hydrogen fluxes combined with a good perm-selectivity ($\text{H}_2/\text{N}_2 \approx 500$). These results have been compared with the performance of highly permeable membranes reported in the literature. The influence of the morphology of the deposited Pd-based layers on the membrane performance has been investigated and discussed.

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1. Introduction

Hydrogen is an attractive energy carrier alternative to fossil fuels because it is clean and environmentally sustainable. The current use of high purity hydrogen include micro/nano-electronics, fuel cells, transport and small stationary energy conversion

devices, chemical industry and metallurgical applications, and large stationary energy installations [1]. One way to produce high purity hydrogen is by separation from hydrogen containing gas mixtures produced by catalytic or chemical manufacturing processes. Conventional hydrogen separation techniques, such as pressure swing adsorption and cryogenic distillation, are energy intensive processes. Membrane technology seems to be a promising alternative to more conventional processes thanks to the reduced energy requirements. The expanding domain of membrane operations demands tailored materials with unprecedented performances in terms of separation efficiency and resistance to

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high temperature at affordable costs. Among the membranes for H_2 separation, Pd-based membranes show the highest permeability and permselectivity for H_2 due to the unique permeation mechanism. Most of the commercially available palladium alloy membranes are above 20–30 μm thick [2,3], and therefore have higher costs and low hydrogen permeation fluxes. When palladium film thicknesses approach 2 μm , the cost of the palladium become a small fraction of the total cost of the module and the membrane support becomes the bulk of the membrane costs [4]. Thin Pd-based membranes are generally supported on porous substrates including stainless steel and ceramic planar or tubular supports [5]. In order to avoid the hydrogen embrittlement phenomenon, alloying of Pd with Ag is generally performed which also allows up to 70% higher H_2 permeability compared to pure Pd. An optimal value for the hydrogen permeability is reached for a silver content around 23 wt.% Ag ($\text{Pd}_{77}\text{Ag}_{23}$) [6]. There are several technologies reported in the literature for deposition of Pd and Pd-alloy layers such as physical vapor deposition (PVD) including magnetron sputtering (PVD-MS), thermal evaporation or pulsed laser evaporation, chemical vapor deposition (CVD) or metal organic chemical vapor deposition (MO-CVD), electroless plating (ELP), electroplating and diffusion welding [7]. The electroless plating (ELP) method is the most used method for the preparation of thin Pd based membranes [8–10], particularly with respect to the operational flexibility, simple equipment, cost performance and applicability to non-conductive materials of any shape. The minimum thickness of the Pd membrane required to achieve a dense layer by ELP is more than three times the diameter of the largest pores in the support [10]. As an example, Pacheco et al. prepared a 0.9–1.0 μm thick $\text{Pd}_{92}\text{-Ag}_8$ membrane onto 5–10 nm pore size $\text{YSZ-}\gamma\text{-Al}_2\text{O}_3$ coated 200 nm pore size $\alpha\text{-Al}_2\text{O}_3$ porous tube by simultaneous Pd/Ag deposition [11].

On the other hand, PVD magnetron sputtering is a very attractive deposition technology, because it could provide sub-micron uniform layers with a controlled microstructure and composition across these coatings, with a required Ag contents up to 23%, which is very difficult to obtain with the ELP technique. Other important advantages of PVD are its environmental friendly operation without producing waste liquids from chemical baths [12] and its versatility for binary, ternary and multi-component film deposition [13]. However, an initial costly equipment investment has to be made for PVD magnetron sputtering, that is not the case for ELP. SINTEF (Norway) has developed a two-step technique for the manufacture of very thin (with very high H_2 permeation flux) defect free palladium-based membranes. First, a defect-free Pd-alloy thin film is prepared by PVD magnetron sputtering onto a silicon wafer and then, the thin film (1–2 μm thick) is removed from the wafer and placed onto a porous support [14]. Although there are some works on the direct deposition by sputtering techniques of Pd-based layers onto porous supports the results are not completely satisfactory. Pd–Ag membranes with a thickness between 0.2 and 0.5 μm were prepared by McCool by direct PVD onto a γ -alumina planar support (top layer pore size of 4 nm) using a target composed of 75% Pd and 25% Ag, but the H_2 permeance is low for these membrane thicknesses (maximum in the order of $1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) [15]. Recently, Pereira et al. [16] prepared Pd–Ag alloy supported membranes by direct PVD using two separate targets of Pd and Ag, and the resulting Pd–Ag membranes showed a H_2/N_2 selectivity of ~ 10 , not enough for ultrapure hydrogen production, and a H_2 permeance of $7.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 300 kPa pressure difference. The combination of PVD and ELP techniques for the preparation of Pd-based membranes was reported by Dittmar et al. [17], where the PVD layer was used as an activation step, however, for 11–13 μm thick membranes. The activation by this method would be more environmentally friendly compared

to the commonly used method based on the reduction of Sn–Pd chloride [18] or Pd acetate [19].

In this paper we will present the preparation and characterization of ultra-thin composite Pd-based membranes ($\sim 1 \mu\text{m}$ thick) prepared by combining PVD-MS and ELP techniques onto commercially available asymmetric ceramic tubes. The results show higher permselectivities compared with PVD membranes reported in the literature, as well as high permeation fluxes.

2. Experimental

2.1. Membrane preparation

Alumina tubes (10/7 mm o.d/i.d., 200–250 mm long) with an outer ZrO_2 top layer (3 nm mean pore size) were used as membrane supports (provided by Rauschert Kloster Veilsdorf). Firstly, a thin Pd–Ag layer ($\sim 0.5 \mu\text{m}$ thick) was deposited directly onto this ceramic support by a DC-Magnetron sputtering technique using a “Cemecon CC800/8” apparatus equipped with a turbomolecular pump reaching pressures lower than $1 \times 10^{-5} \text{ Pa}$. Pd–Ag alloy (23 wt.% Ag) rectangular plates (200 mm height $\times$ 88 mm width $\times$ 5 mm depth) were used as target materials and high purity Ar ionized gas was fed at the working pressure of 500 mPa. The sample holder was maintained at room temperature and -140 V self-bias voltage was applied, with a target-substrate distance set to be 80 mm. The power of the Pd–Ag targets was set to 1500 W. The thickness of Pd–Ag alloy film was controlled by adjusting the sputtering time. For comparison purposes, in the same batch, six identical supports were deposited. To one of them, an additional thin Pd layer was deposited by electroless plating technique onto the PVD layer following a procedure reported before (30 min of plating) [19].

After the ELP step, the membrane was thermally treated at 450°C for 4 h; by exposing the membrane to a 10% $H_2/90\%$ N_2 gas mixture with the same heating rate (3°C min^{-1}) and gas flow rates as reported before ($50 \text{ cm}^3 \text{ min}^{-1}$ of H_2 and $450 \text{ cm}^3 \text{ min}^{-1}$ of N_2) [20].

2.2. Physico-chemical characterization of Pd-based membranes

The outer surface morphology and cross-section analysis of the membrane layers were performed using an Environmental Scanning Electron Microscope (ESEM) (FEI Quanta 250 FEG). This technique has also been used to measure the thickness of the different Pd alloy layers.

The change of the surface roughness after deposition of each layer was analyzed with a Veeco DEKTAK 150 contact profilometer using a 50 nm radius stylus tip. The measuring conditions used are: scan length of 100 μm , scan duration of 100 s, measuring range of 6.5 μm and cut-off of 10 μm . The results are given in R_a and R_q , R_a represents the arithmetic average of the absolute values of the roughness profile ordinates and R_q the root mean square average between the height deviations and the mean line/surface taken over the evaluation length.

The XRD patterns of the Pd-based films were examined with an X-ray Bruker D8 Advance diffractometer, with a $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. The scan rate was $0.02^\circ/\text{s}$ in the range $2\theta = 30\text{--}50^\circ$. In addition, XRD was used to determine the Ag content of the layer and the alloy condition.

2.3. Permeation characterization of Pd-based membranes

One of the composite Pd-based membranes supported onto ZrO_2 3 nm (pore size) was cut and sealed following the procedure

Fig. 1. Pd–Ag membrane deposited (34.8 mm long) by combined ELP/PVD supported onto ZrO_2 3 nm and sealed with graphite based seals.

reported previously [20]; the final membrane length was 34.8 mm (see Fig. 1). This membrane was characterized in a membrane permeation test equipment. A shell and tube module configuration was used to test the membrane. The feed gases enter through the shell side and hydrogen permeates to the tube side. The module pressure in the shell side is controlled by a back pressure regulator installed at the retentate side. The membrane is heated under a fixed flow of N_2 . The hydrogen permeation flow rate was monitored with a Brooks mass flow meter and the N_2 leakage was measured using a Bronkhorst flowmeter (model F-110C-002; Nominal flow: 0.014–2 N ml/min air). A process flow diagram (PFD) of the experimental setup is given in Fig. 2. Single gas tests (H_2 and N_2) at temperatures between 350–500 °C and mix gas tests (H_2/N_2 , H_2/CO_2 , $\text{H}_2/\text{CO}/\text{N}_2$) at 400 °C have been performed.

3. Results and discussion

3.1. Physico-chemical characterization results of Pd–Ag membranes

3.1.1. SEM analysis results

Fig. 3 shows the cross-section (a) and surface (b) SEM images of the Pd–Ag coated by PVD. The thickness of the Pd–Ag layer deposited by PVD is $\sim 0.5 \mu\text{m}$. The membrane surface looks like a close

structure with small grains in the order of a few nanometers. Fig. 3c and d show the cross-section and surface SEM images of the composite membrane layer consisting of the Pd layer by ELP deposited onto the Pd–Ag PVD layer after thermal treatment. The thickness of the whole membrane is in the order of $\sim 1 \mu\text{m}$. By comparing the Fig. 3b and d, it can be seen that the layer grown by ELP has bigger grains and the surface seems much rougher and less dense, even when the ELP layer picture (d) was taken at lower magnifications than the PVD layer picture (b).

In order to confirm the change on the surface roughness presented in Fig. 3, the PVD and the ELP/PVD layers were analyzed by contact profilometry. According to Table 1 and Fig. 4, the PVD layer reproduces the surface profile of ZrO_2 3 nm pore size support (no significant roughness change is indeed observed). However, the roughness of the ELP layer increased more than double compared to the previous PVD layer (R_a and R_q), confirming the change seen by SEM surface analysis.

3.1.2. XRD analysis results

The formation of thin film Pd-based layers by PVD and ELP was analyzed by XRD. Fig. 5 shows the XRD patterns of the Pd–Ag layer grown by PVD-MS onto the $\text{ZrO}_2/\alpha\text{-Al}_2\text{O}_3$ (red line) and the XRD pattern after deposition of the Pd-layer by ELP on top of the previous PVD layer (black line). The same figure also shows the (104), (110) and (113) reflections from $\alpha\text{-Al}_2\text{O}_3$ at 35.13°, 37.78° and 43.36° angle positions respectively. Since the outer ZrO_2 layer deposited onto the Al_2O_3 support is very thin, it was not detected by XRD. After layer deposition by PVD, a peak at 39.90° was found, between the Pd and Ag reflections, which is characteristic of the lattice spacing of the fcc Pd–Ag alloy. In addition, a very small Ag peak was detected suggesting that some Ag was not alloyed. The average lattice constant for the Pd–Ag alloy is 3.9345 Å. This value is between the Pd lattice ($a = 3.8890 \text{ Å}$) and the Ag lattice ($a = 4.0861 \text{ Å}$) constants. The Ag content in the metallic layer, for the sample prepared after PVD deposition, was calculated from the lattice constant [21]. The Pd–Ag solid phase forms a continuous solid solution. These Pd–Ag alloys, which have the face-centered

Fig. 2. Process flow diagram (PFD) of the single membrane permeation setup for membrane permeation characterization.

Fig. 3. SEM images of Pd-Ag layer by PVD (cross section (a) at 30,000 $\times$ and surface (b) at 50,000 $\times$) and of Pd ELP/Pd-Ag PVD (cross section (c) at 30,000 $\times$ and surface (d) at 20,000 $\times$) deposited on ZrO_2 3 nm pore size asymmetric porous tube.

Table 1
Surface roughness of the support and the deposited Pd-based layers.

	Ra (nm)	Rq (nm)
ZrO_2 3 nm support	15.1 ± 0.6	20.1 ± 0.4
Pd-Ag PVD layer on ZrO_2 3 nm	20.0 ± 0.8	29.9 ± 2.9
Pd-based layer (PVD + ELP) on ZrO_2 3 nm	44.2 ± 5.4	59.5 ± 3.9

Fig. 4. Surface roughness profile of ZrO_2 , PVD/ ZrO_2 and ELP/PVD/ ZrO_2 .

cubic (fcc) phase, vary only in composition but not in crystal structure. Ayrtuk et al. [22] discussed that the only effect of a change in the composition is the shift in the diffraction line positions in

Fig. 5. XRD patterns of the Pd-Ag/ ZrO_2 / $\alpha\text{-Al}_2\text{O}_3$ membrane growth by PVD (red line) and Pd/Pd-Ag/ ZrO_2 / $\alpha\text{-Al}_2\text{O}_3$ growth by PVD + ELP (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

accordance with the change in the lattice parameter, which varies continuously from that of pure Ag to that of pure Pd. Therefore, it is possible to assume a linear relationship between the lattice constant of the alloy and the Pd content. From the lattice constant of the Pd-Ag by PVD, a Ag content of near to 23 wt.% was determined. Note that this concentration is representative of complete 0.5 μm

Table 2N₂ permeance of the ZrO₂ 3 nm support tube and the Pd-based layers onto this support at 25 °C.

Sample	Thickness of the Pd–Ag measured by SEM (μm)	N ₂ permeance × 10 ^{−9} (mol m ^{−2} s ^{−1} Pa ^{−1}) at 25 °C
ZrO ₂ 3 nm	NA	24,600 ± 430 [*]
PVD layer on ZrO ₂ 3 nm	~0.5	15,140 ± 1290 [*]
Pd–Ag (PVD + ELP) on ZrO ₂ 3 nm	~1	8.5 ± 4.8 ^{**}

NA: not applicable.

^{*} 5 samples.^{**} 3 samples. **Fig. 6.** H₂ flux versus pressure difference of the Pd-based supported membrane prepared by PVD + ELP at 350–500 °C feeding pure H₂.

film in depth because in the diffractograms the peaks corresponding to α -Al₂O₃ also appear. Ayturk et al. [22] estimated that the information recorded on the diffraction pattern comes from the X-rays that penetrate 2.0–2.2 μm deep for Pd and Ag. On the other hand, the XRD analysis results of the ELP/PVD layer after the thermal treatment (black curve) represents a combination of the Pd–Ag layer by PVD (shoulder) and the Pd layer by ELP. The asymmetry of this curve indicates that the Pd top layer by ELP and the Pd–Ag layer by PVD were not completely alloyed after the thermal treatment, since the formation of the alloy is more difficult in less dense membranes and the low temperature of annealing. Again, since Al₂O₃ is detected, the XRD curve is representative of the composite layer.

Table 3

Comparison with different highly permeable Pd-based supported membranes reported in the literature.

Membrane/support	Pd-layer thickness (μm)	Preparation method	T (°C)	H ₂ permeance × 10 ^{−8} (mol m ^{−2} s ^{−1} Pa ^{−1}) ^a	Ideal permselectivity	References
Pd–Ag/SiO ₂ –Al ₂ O ₃	0.15	Pulsed laser deposition (PLD)	300	140	600–900	[23]
Pd–Ag/γ-Al ₂ O ₃	0.2–0.5	PVD	300	3–10	4–4000 (H ₂ /He)	[15]
Pd–Ag/PSS	2.8	PVD (two steps)	400	1500	2900 (H ₂ /N ₂)	[14] ^b
Pd–Ag/γ-Al ₂ O ₃ –YSZ	0.71	PVD	300	71	10 (H ₂ /N ₂)	[16]
Pd/α-Al ₂ O ₃	1.5	ELP	450	240	3115 (H ₂ /N ₂)	[24]
Pd–Cu/ZrO ₂	1.3	ELP	365	310	127 (H ₂ /N ₂)	[4]
Pd/TiO ₂	0.4	Photocatalytic deposition (PCD)	450	330	4.7 (H ₂ /N ₂)	[25]
Pd–Ag/α-Al ₂ O ₃	3.2	ELP	400	310	8000–10,000 (H ₂ /N ₂)	[20]
Pd–Ag/γ-Al ₂ O ₃ –YSZ	0.9–1.0	ELP	400	650	1200 (H ₂ /N ₂)	[11]
Pd–Ag/ZrO ₂	1.0	PVD + ELP	400	800	500 (H ₂ /N ₂)	This work

^a Permeance values have been calculated for a H₂ partial pressure of 1 bar.^b Self-supported membranes.

3.2. Permeation results of Pd–Ag supported membranes

Firstly, the N₂ permeance of five membranes prepared during the same batch of PVD was measured before and after the deposition of the ELP layer at 25 °C. The average results are shown in Table 2.

From Table 2 it can be concluded that the 0.5 μm thick Pd–Ag coated film by PVD has a high N₂ permeance, indicating that the layer is not completely closing the porous structure of the ZrO₂ 3 nm support. This relatively high N₂ permeance value makes this Pd–Ag membrane prepared by PVD supported onto ZrO₂ 3 nm not suitable for ultrapure hydrogen production applications. Similar results were obtained by Pereira et al. [16] on nanoporous YSZ/γ-Al₂O₃. After plating the Pd layer by ELP, the N₂ permeance decreased dramatically down to an acceptable order for this application, enabling a good ideal H₂/N₂ permselectivity; the ELP close most of the pores on the surface of the PVD layer.

Fig. 6 shows the hydrogen flux for the sealed composite membrane at different partial pressure differences of hydrogen and various temperatures between 350 and 500 °C. In general the hydrogen flux increased with increasing transmembrane partial pressure difference and temperature. However, the hydrogen permeation values at 450 °C and 500 °C are similar. The reduction of hydrogen permeation may be caused by gas resistance of the nanoporous top ceramic layers of the support. This effect was also reported before [11].

Table 3 compares the separation properties of the membrane in this work, in terms of permeance and selectivity, with the ones reported in the literature. The H₂ permeance of this membrane is the highest found in the literature for supported membranes (8 × 10^{−6} mol m^{−2} s^{−1} Pa^{−1} at 400 °C and 100 kPa pressure difference) and around half of the permeance value of the self-supported membrane prepared by SINTEF [14]. Moreover, this hydrogen permeance is higher than the dense Pd–Ag membrane with similar film thickness measured prepared by ELP (6.5 × 10^{−6} mol m^{−2} s^{−1} Pa^{−1} for 0.9–1.0 μm thick membrane [11] at the same

Fig. 7. Hydrogen permeate flux of the membrane at different $H_2:N_2$ feed compositions (400 °C) and total gas flow rate up to 3000 ml/min.

Fig. 8. Hydrogen permeate flux of the membrane at different $H_2:CO_2$ feed compositions (400 °C) and total gas flow rate up to 3000 ml/min.

temperature and pressure), since the PVD part of the composite PVD + ELP membrane is porous. Therefore, the whole composite membrane behaves as a dense membrane with a thickness of 0.7–0.8 μm .

The effect of other gases on the hydrogen permeation of the membrane is investigated and discussed; the gases present in the WGS reaction were selected [20]. Firstly, various tests were carried out at different H_2/N_2 ratios in order to investigate the presence of mass transfer limitations (concentration polarization) for this highly permeable membrane. The results for the hydrogen flux at different H_2/N_2 mixtures at 400 °C and different H_2/CO_2 mixtures at 400 °C are shown in Figs. 7 and 8, respectively. The hydrogen flux through the membrane is plotted as a function of the partial pressure difference of hydrogen (inlet conditions). At the same partial pressure difference the driving force for the permeation for all experiments is the same. The results show that the hydrogen flux decreases when the partial pressure of hydrogen decreases in the feed gas stream (at the same driving force over the membrane). This behavior confirms that external mass transfer limitations (concentration polarization) are prevailing when using gas mixtures, as was also found for other highly permeable membranes [20]. On the other hand, it is well known that CO can block the active sites of the membrane (CO inhibition effect) and decrease

Fig. 9. Effect of CO inhibition on hydrogen flux of the membrane at different $H_2:N_2:CO$ feed compositions (400 °C) and total gas flow rate up to 3000 ml/min.

the performance of the membranes [26]; this effect can be more pronounced for highly permeable membranes. In order to validate this assumption, the CO inhibition was measured in a gas mixture containing 80% of hydrogen and increasing the amount of CO from 0 to 15% in steps of 5% (balanced with N_2). The results obtained in Fig. 9 confirmed the decrease in H_2 permeance when the CO content is increased in the feed mixture. The permeance decreased about 25% for 15% of CO in the feed gas stream, and this decrease is much larger in comparison to the 3.2 μm thick Pd–Ag supported membranes at the same conditions (7% reduction for 15% CO) [20]. In this case, the adsorption of H_2 may be the rate-limiting step for H_2 transport through the membrane because the adsorption sites are occupied by CO [27].

4. Conclusions

Ultra-thin composite Pd-based membrane layers have been prepared by a combination of PVD–MS and ELP techniques, showing a very high H_2 permeance ($8 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 400 °C and 100 kPa); the highest reported for supported membranes and around half of the highest reported self-supported membrane. According to the SEM images the composite layer is $\sim 1 \mu m$ thick, but the hydrogen permeation results indicate that the effective membrane thickness corresponds to 0.7–0.8 μm . The H_2/N_2 perm-selectivity obtained is around 500 at 400 °C, and the Pd ELP layer contributed to have this good selectivity since the Pd₇₇–Ag₂₃ PVD layer deposited on ZrO₂ 3 nm pore size support is porous with very low selectivity. The PVD layer copies the surface profile of the ZrO₂ support; the second Pd ELP layer, close the pores increasing the permselectivity considerably. The hydrogen permeation values at 450 °C and 500 °C are very similar which may be caused by gas resistance of the support. Due to the high permeance of these membranes, external mass transfer limitations start to become a limiting factor for the hydrogen permeation. The CO inhibition is more pronounced for these membranes compared to thicker membranes of 3–4 μm , where the adsorption of H_2 becomes the rate-limiting step for H_2 transport through the ultra-thin membranes.

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