EFFECT OF SUBSTRATE RESISTANCE ON HYDROGEN PERMEANCE THROUGH Pd/Al_2O_3 COMPOSITE HOLLOW FIBRE MEMBRANES

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ABSTRACT – Application of composite Pd based membranes represents a promising alternative for hydrogen purification. Here we propose the application of asymmetric alumina hollow fibres as a support for Pd deposition. Hollow fibres were sintered at different temperatures (1300 and 1400 ^oC). Characterisations of the substrate showed that it presents the desired morphological structure, with finger-voids extending to almost 90% of the fibre, high porosity and suitable mechanical strength. Hydrogen permeations through the composite membrane formed by the deposition of one palladium (Pd) layer on the alumina hollow fibre sintered at 1300^oC was on average 100% greater than using the hollow fibre sintered at 1400^oC. For 2 Pd layers, this difference decreased to 22%, showing that the substrate influence is more evident in thinner Pd membranes. The obtained H_2 flux was equal to 0.80 µmol m^{-2} s^{-1} (at 450^oC and 180 kPa) and it is one of highest flux reported in the literature.

1. INTRODUCTION

Among the numerous hydrogen separation techniques, palladium (Pd) and palladium alloy membranes have been extensively investigated for this separation due to its theoretically infinite selective and high permeability (Yun and Oyama, 2011). Initially, Pd membranes were self-supported in the form of finite sized tubes or flat discs, which usually presented lower hydrogen (H_2) permeability and high cost. Currently, research is focused on the development of high permselective composite Pd membranes with suitable mechanical strength.

Due to its wide availability, thermal stability and good mechanical strength, alumina (Al_2O_3), in the form of tubes or plane sheets, is the ceramic material commonly used as substrate for Pd deposition (Yun and Oyama, 2011). Application of ceramic hollow fibres, instead of single ceramic tubes, enables higher ratio between the surface area of the membrane and the volume of the system.

The phase inversion process used to fabricate ceramic hollow fibre membranes allows the single-step formation of a unique asymmetric structure consisted of two different regions: a thin sponge-like layer with smaller porosity and a finger-like layer with many micro-channels of larger porosity (Kingsbury and Li, 2009). The existence of these micro-channels reduces the substrate mass

transfer resistance. The asymmetric structure, presenting regions of different pore sizes, must be carefully prepared in order to achieve the desired morphology. For hydrogen permeations, it is desired to have fibres with long inner micro-voids, which contribute to reduce mass transfer resistance. The sponge like layer should present smaller pore sizes and a smooth surface in order to increase the substrate mechanical strength and to allow the deposition of a thin defect-free Pd membrane, respectively. Sun et al. (2006) investigated the influence of the concentration and composition of internal and external coagulant solutions, as well as of the sintering temperature, on the morphology of the prepared hollow fibres. Sun et al. (2006) observed that an increase in the sintering temperature increased the mechanical strength of the fibre, but with a greater densification of the sponge-like region of the fibre, as also reported by Kingsbury and Li (2009). This densification is not always desired since it will increase the mass transfer resistance of the substrate. Irfan Hatim et al. (2011) prepared asymmetric hollow fibres by applying different air gap lengths and concluded that the hollow fibres produced with the smallest air gap (3 cm) presented the smallest mass transfer resistance and, consequently, the highest H_2 permeance.

The main objective of this research is to evaluate the hydrogen fluxes in asymmetric Pd/Al_2O_3 composite hollow fibre membranes. Hollow fibres were sintered at different temperatures (1300 and 1400^{o}C) and Pd was deposited on the outer surface these substrates using one or two plating cycles, resulting in membranes with different thicknesses.

2. MATERIAL AND METHODS

2.1. Fabrication and characterisation of asymmetric Al_2O_3 hollow fibre substrates

The asymmetric Al_2O_3 hollow fibres were fabricated using the phase inversion/sintering method (Kingsbury and Li, 2009). Alumina (1.0 μm, alpha, 99.9% metal basis, surface area 6-8 m^2 g^{-1}, Alfa Aesar) was mixed with solvent (DMSO, VWR), polymer blinder (Polyethersulfone-PESf, Radel A-300, Ameco Performance, USA) and additive (Arlacel P135, Uniqema, UK) to prepare the spinning suspension. After mixing for 7 days and degassing, the spinning suspension was extruded through a tube-in-orifice spinneret (outer diameter 3 mm, inner diameter 1.2 mm) into the external coagulation bath with no air gap between the fibre precursor and the external coagulant. Tap water was used as external coagulant. The produced fibre precursors were kept in water for 12 h in order to remove the excess of solvent. After drying for 48 h under atmospheric conditions during, fibre precursors were sintered in a tubular furnace (Elite, Model TSH 17/75/450). The temperature was increased from room temperature to 600°C at a rate of 2°C min^{-1} followed by a dwell of 2 h. In a second stage, the temperature was increased to 1300 or 1400^{o}C (target temperature) at a rate of 5°C min^{-1} followed by a dwell of 4 h. After the sintering was completed, the hollow fibres were cooled to room temperature at a rate of 3°C min^{-1}.

2.2. Palladium depositions on the substrate surface

Palladium layers were deposited on the outer surface of the asymmetric Al_2O_3 hollow fibre substrates using the electroless plating procedure, as described by Paglieri and Way (2002) and

Mardilovich et al. (1999). Tin(II) chloride dehydrate ($SnCl_2$, puriss. p.a., Sigma-Aldrich) and palladium(II) chloride ($PdCl_2$, 99.999%,Sigma-Aldrich) were mixed with hydrochloric acid (37%, AnalaR NORMAPUR) to prepare sensitisation and activation solutions, respectively. The plating solution was prepared using Tetraamminepalladium(II) chloride monohydrate ($Pd(NH_3)4Cl_2$-H_2O, 99.99% metals basis, Sigma-Aldrich), EDTA (IDRANAL®III, Riedel-deHaen), ammonium hydroxide (28%, Sigma-Aldrich) and hydrazine hydrate (Sigma-Aldrich).

Prior to the electroless plating, the substrates were activated applying the sensitisation/activation process. This process was carried out by immersing the fibres in five sequential chemical baths with bubbling air for agitation, as shown in Figure 1. The composition of each bath is presented in Table 1. The sensitisation/activation process was repeated 8 times.

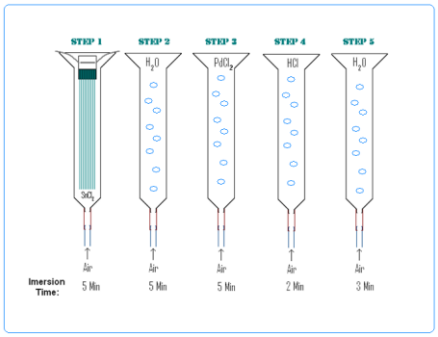


Figure 1 – Scheme of the sensitisation/activation process.

Table 1 - Sensitisation, activation and plating bath compositions.

Step	Compound	Concentration
Sensitisation	$SnCl_2$	1 g L^{-1}
	HCl (37%)	1 mL L^{-1}
Activation	$PdCl_2$	0.1 g L^{-1}
	HCl (37%)	1 mL L^{-1}
Plating	$Pd(NH_3)4Cl_2$-H2O	4 g L^{-1}
	Na_2EDTA-$2H_2O$	40.1 g L^{-1}
	NH_3-H_2O (28%)	198 mL L^{-1}
	N_2H_4 (1M)	5.6 mL L^{-1}

After the sensitisation/activation process, the substrates were immersed in the $Pd(NH_3)4Cl_2$-H_2O solution at 60°C to deposit metallic Pd on the activated substrate surface. The amount of $Pd(NH_3)4Cl_2$-H_2O solution was fixed at 3.5 mL per cm^2 of fibre (surface area), as suggested by Mardilovich et al. (1998). The amount of injected hydrazine was calculated such that its concentration in the plating bath was equal to 5.6 mL L^{-1}. The substrates were kept in the plating bath for 60 min. The plating procedure was performed either once or twice.

The asymmetric Pd/Al_2O_3 composite hollow fibre membranes were characterised using a high resolution scanning electron microscope (JEOL JSM-5610LV)) equipped with EDX for elemental composition analysis (JEOL 2000FX TEM).

2.3. Gas permeation measurements through asymmetric Pd/Al_2O_3 composite hollow fibre membranes

The asymmetric Pd/Al_2O_3 composite hollow fibre membranes with one-end sealed were glued with epoxy-resin (Araldite®) on a stainless steel holder that was assembled in a stainless steel tube. This tube was placed in a tubular furnace (CARBOLITE, MTF 10/25/130) and was connected to the gas lines. The gas (N_2 or H_2) was fed to the fibre shell side and collected from the fibre lumen side. A bubble flow metre was used to measure the permeate flux. The feed pressure was adjusted using a

pressure regulator (OMEGA, PRG101-120) and monitored using a pressure gauge with a resolution of 0.1 psi (OMEGA, DPG1000B-10G). The schematic representation of the apparatus used is presented in Figure 2.

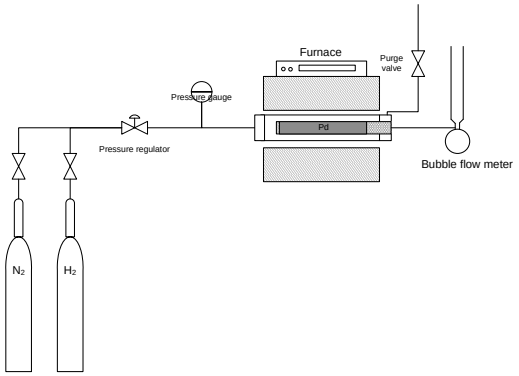


Figure 2 - Schematic representation of the apparatus used for gas permeation tests through the asymmetric Pd/Al_2O_3 composite hollow fibre membranes.

Prior to the H_2 permeation tests, the gas tightness of the Pd/Al_2O_3 composite hollow fibre membranes was accessed under N_2 atmosphere at 276 kPa and at room temperature. The H_2 permeation tests were conducted exclusively in membranes which were gas-tight to N_2, i.e., if no bubble was detected in the bubble flow metre.

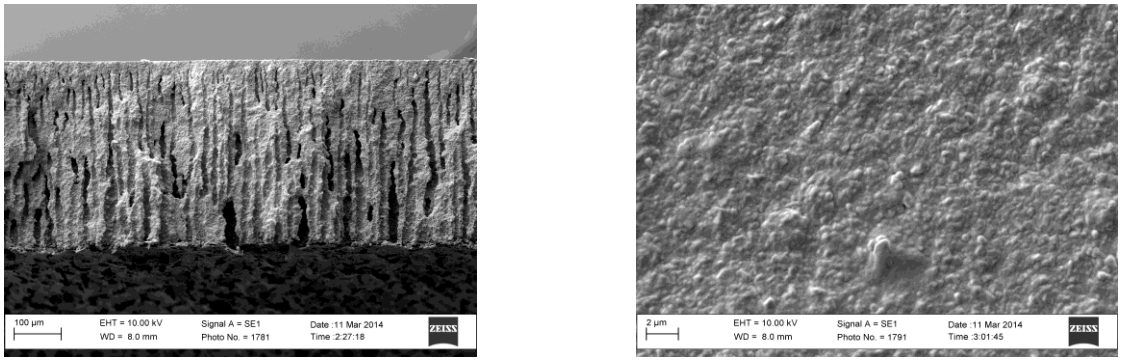
Hydrogen fluxes were measured through different asymmetric Pd/Al_2O_3 composite hollow fibre membranes, prepared with 1 or 2 plating cycles and, consequently, having different Pd thicknesses, and using the substrate sintered at different temperatures, 1300 and 1400^{o}C. Firstly, the membrane was annealed at 450^{o}C for 2 h under hydrogen flow. Hydrogen permeation fluxes were measured at temperatures of 450, 400, 350 and 300^{o}C and at pressures from 40 to 160 kPa for each temperature. The heating/cooling rate was 3^{o}C min^{-1}.

3. RESULTS AND DISCUSSION

The different applied sintering temperatures did not influence the morphological aspect of the obtained hollow fibres, as could be visualized in the SEM pictures. Figure 3(a) presents the SEM image of the substrate, which presents the desired asymmetric structure with an outer denser layer and inner micro-channels. Figure 3(b) presents the top view of the plated hollow fibre and shows that the top surface of the Pd membranes exhibits rounded clusters. The elemental analysis of the top surface of both membranes presented a composition of 100% Pd.

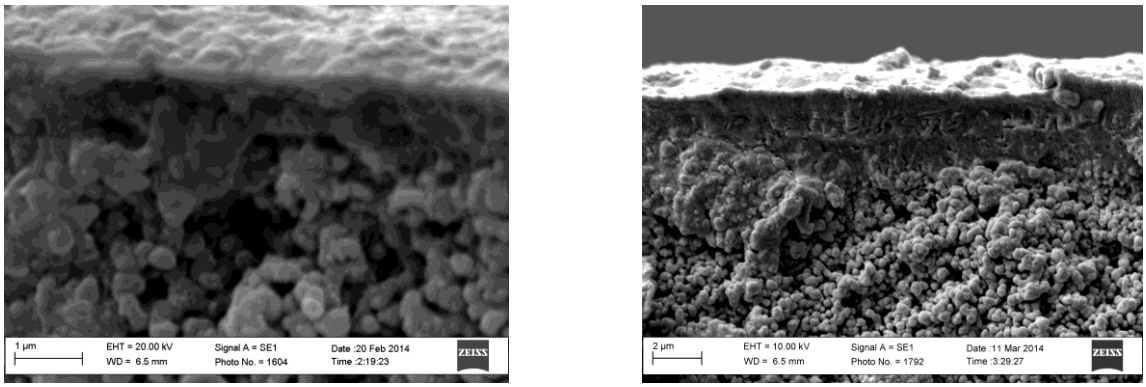
Cross-section images of the hollow fibres coated with 1 and 2 plating cycles are presented in Figures 4a and 4b, respectively. According to these figures, the thickness of the fibres plated with 1 and 2 cycles are equal to 0.85 and 2.78 µm, respectively. In Figure 4b it is possible to recognize two layers of approximately the same thickness, as consequence of the two plating cycles. As expected,

the thickness of the Pd membrane plated with 2 cycles was greater than with 1 cycle. Dittmeyer et al. (2001) suggested a minimum Pd thickness equals to 3 μm in order to have a defect free membrane on porous stainless steel supports. However, thinner selective Pd membranes are reported in the literature, especially using ceramic supports (Yun et al., 2011).



(a) (b)

Figure 3 – (a) Cross-section image of the asymmetric Al_2O_3 hollow fibre substrate. (b) Top surface SEM image of the asymmetric Pd/Al_2O_3 composite hollow fibre membrane.



(a) (b)

Figure 4 – Cross-section SEM images of the asymmetric Pd/Al_2O_3 composite hollow fibre membranes coated with (a) 1 plating cycle and (b) 2 plating cycles.

Single nitrogen permeation tests were conducted at room temperature to verify if the prepared Pd/Al_2O_3 composite membranes were gas tight to nitrogen. The obtained results showed that at pressure differences up to 275 kPa the N_2 flow through the fabricated asymmetric Pd/Al_2O_3 composite hollow fibre membranes (with one or two plating cycles) was negligible, i.e., not detectable in the bubble flow meter.

Figure 5 shows the hydrogen permeation through the asymmetric Pd/Al_2O_3 composite hollow fibre membranes formed by the coating of Pd with 1 or 2 plating cycles on the support sintered at 1300 or 1400°C. Hydrogen fluxes were measured at different temperatures (450, 400, 350 and 300°C) and transmembrane pressures (from 40 to 160 kPa). As expected, the permeation was higher at higher temperatures and transmembrane pressures. The obtained hydrogen flux presented a linear

relationship with the pressure.

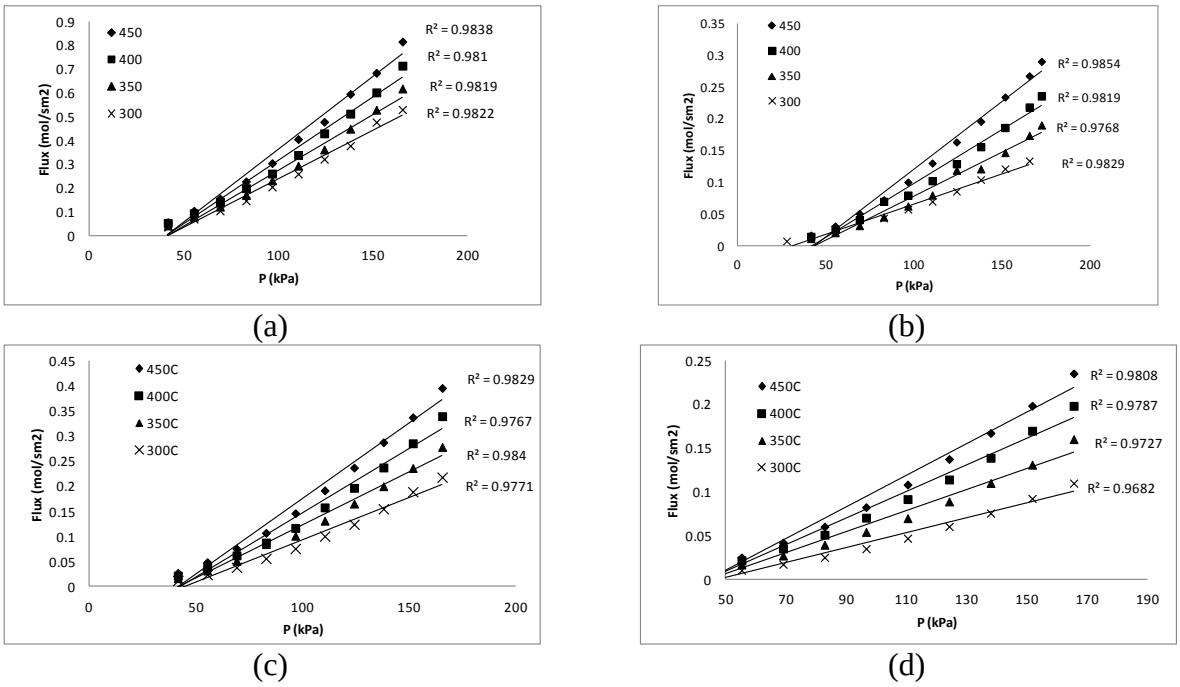


Figure 5. Hydrogen fluxes through the asymmetric Pd/Al_2O_3 composite hollow fibre membranes. (a) support sintered at 1300°C with 1 plating cycle, (b) support sintered at 1300°C with 2 plating cycles, (c) support sintered at 1400°C with 1 plating cycle, (d) support sintered at 1400°C with 2 plating cycles.

Figure 6 presents a comparison between the hydrogen fluxes measured at 450°C for all the evaluated composite membranes.

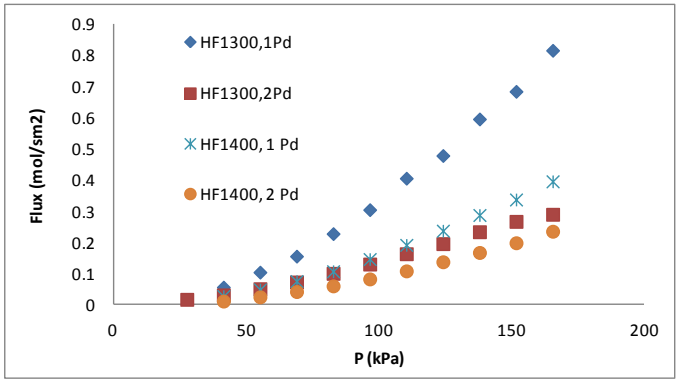


Figure 6. Comparison of hydrogen fluxes through the asymmetric Pd/Al_2O_3 composite hollow fibre membranes formed by the deposition of 1 or 2 palladium layers deposited on the support sintered at 1300 and 1400°C.

Highest hydrogen fluxes were obtained with the composite membrane formed by the deposition of 1 Pd layer deposited on the support sintered at 1300°C. Considering the membrane formed by 1 Pd layer, the decrease in the support sintering temperature increased the hydrogen flux in approximately 100%. For 2 Pd layers, this increase was less pronounced (22%), showing that the substrate influence is more evident in thinner Pd membranes. Considering the support sintered at 1300°C, the hydrogen flux through the membrane formed by 1 Pd layer was twice than through the membrane formed by 2 Pd layers. For the support sintered at 1400°C, this increase was reduced to 80%. These results prove the influence of the support on the obtained hydrogen fluxes.

The highest obtained flux was equal to 0.80 µmol m^{-2} s^{-1} (at 450°C and 180 kPa), greater than the values previously published by Irfan Hatim et al. (2011) and Sun et al. (2006) using similar substrates. This improvement is due to the lower mass transfer resistance of the support used in this work. Yun et al. (2011) obtained one of the highest hydrogen permeabilities (0.40 mol m^{-2} s^{-1} at 105 kPa and 460°C) using ultrathin Pd membranes (0.9 µm) supported on asymmetric Al_2O_3 tubes (od = 2.9 mm, id = 2.2 mm). This high hydrogen flux is attributed to the thinner Pd layer, which was achieved by a modified electroless plating method.

4. CONCLUSIONS

This research evaluated the influence of the substrate, as well as the Pd thickness, on the obtained hydrogen flux. The obtained results showed that the increase in the sintering temperature of the substrate, which leads to a greater densification of the sponge like layer and consequently an increase in the substrate mass transfer resistance, decreased the hydrogen flux through the substrate. The influence of the substrate was more pronounced in thinner membranes. Moreover, the increase in the Pd thickness increased the hydrogen flux. The highest obtained flux was equal to 0.80 µmol m^{-2} s^{-1} (at 450°C and 180 kPa) for a Pd membrane of 0.8 µm deposited on asymmetric alumina hollow fibre sintered at 1300°C. This is one of the highest hydrogen fluxes through Pd membranes due to the lower mass transfer resistance of the support used in this work.

5. ACKNOWLEDGMENTS

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6. REFERÊNCIAS

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