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N₂, He and CO₂ diffusion mechanism through nanoporous YSZ/ γ -Al₂O₃ layers and their use in a pore-filled membrane for hydrogen membrane reactors

Alba Arratibel ^{a,b}, Uxue Astobieta ^{a,c}, David Alfredo Pacheco Tanaka ^a,
Martin van Sint Annaland ^b, Fausto Gallucci ^{b,*}

^a TECNALIA, Energy and Environment Division, Mikeletegi Pasealekua 2, 20009, San Sebastian-Donostia, Spain

^b Chemical Process Intensification, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology (TU/e), Den Dolech 2, 5612AD, Eindhoven, The Netherlands

^c Chemical Engineering Department, University of the Basque Country (UPV-EHU), PO Box 644, 48080, Bilbao, Spain

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ABSTRACT

Nanoporous ceramic supports for pore filled membranes were prepared on ceramic supports (α -Al₂O₃) with pore size of 100 nm by adding additional layers with different proportions of YSZ/ γ -Al₂O₃ (ranging from 50% to 90% of YSZ) by dip-coating and the effect of different parameters in the preparation method have been investigated. The diffusion mechanisms of N₂, He and CO₂ through the supported nanoporous layers have been studied in detail with permeation measurements at a temperature range of 50–400 °C and pressure difference of 30–100 kPa. It was observed that as the amount of γ -Al₂O₃ in the nanoporous layers increases, the adsorption of CO₂ is favored at low temperatures and pressures. Finally, a pore-filled Pd/YSZ/ γ -Al₂O₃ (60 wt%YSZ-40 wt. γ -Al₂O₃) membrane was successfully prepared and its permeation performance was tested over 900 h at 500 and 550 °C, showing relatively low ideal H₂/N₂ perm-selectivity of about 50 due to low hydrogen flux.

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Introduction

Hydrogen production is attracting increasing attention, not only for large-scale applications such as refineries, but also for small-scale applications like heat and power (micro) co-generation systems [1]. More and more research projects focus on the production and separation of hydrogen using various carbon feedstocks (methane, methanol and ethanol) by steam reforming or autothermal reforming [2–5]. To further increase the efficiency of reforming systems and decrease the

required volumes of reactors/separators, research efforts are being invested in developing novel membrane reactors, where reaction and hydrogen separation and purification (often through Pd-based membranes) are integrated in a single process unit. Shifting of the reaction conversion via the Le Chatelier principle also enables operation of the reactors at milder conditions, thus improving the overall process efficiency.

Membrane reactors for hydrogen production are being studied in different configurations, ranging from packed-bed

* Corresponding author.

E-mail address: F.Gallucci@tue.nl (F. Gallucci).

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reactors and micro-channel reactors to fluidized-bed reactors [6]. While packed-bed reactors suffer from significant heat and mass transfer limitations, micro-reactors can overcome these problems [7,8], however, in micro-membrane reactors it is very difficult to match the membrane permeation rates and the required catalyst volume/activity [9]. On the other hand, fluidized-bed reactors can offer very good mass and heat transfer characteristics, while also allowing sufficient freedom to tune the installed membrane area and required catalyst volume [10]. One important concern possibly affecting fluidized bed membrane reactors is possible erosion or damage of the membrane surface by the scouring action of the moving and colliding fluidized particles. Indeed, the selective layer should be on the reaction side where the pressure is much higher, otherwise the membrane layer could be peeled-off due to the pressure difference. To solve this problem one should either use very thick membrane layers (which is not economically feasible due to low flux and high costs) or somehow protect the membrane layer with an additional porous layer where the pores have a smaller size compared to the fluidized catalyst particles (to avoid clogging of the porous structure).

This protection can be achieved with an interesting membrane concept previously reported by Pacheco Tanaka [11,12], the so-called pore-filled membrane concept. In these membranes the palladium selective layer is located in the pores of a mesoporous γ - Al_2O_3 or YSZ/ γ - Al_2O_3 layer and protected by a top ceramic nano-porous layer. In this type of membranes, the palladium is filled into the pores of the support by vacuum assisted electroless plating. Embrittlement of convectional supported membranes in the presence of hydrogen ($\alpha \rightarrow \beta$ phase transition) is suppressed in pore-filled membranes due to the particle size of the palladium [13]. However, these types of membrane have not yet been tested for fluidized-bed membrane reactor (FBMR) concepts. Moreover, the observed thermal instability of the Pd/ γ - Al_2O_3 system in long-term tests at 400 °C can be attributed to the mismatch of the thermal expansion coefficients of alumina and palladium. This can be circumvented by using a composite based on mixed sol of γ - Al_2O_3 and yttria stabilized zirconia (YSZ) that presents a similar thermal expansion as palladium. The presence of alumina into the matrix gives resistance to the fatigue and higher hardness values than YSZ alone [14]. Although the pore-filled membrane may promise to be an interesting concept [12,15,16], a more systematic study on the characteristic of the support modification and porous structure is required to be able to produce stable pore-filled membranes with reproducible results.

At high temperatures (more than 600 °C) under hydrogen, alumina can react with Pd membranes reducing the hydrogen permeation [17–19]. The focus of this paper is the study of the deposition of YSZ/ γ - Al_2O_3 nanoporous layers with more than 50 wt. % of YSZ, where the Pd layer should be located in pore-filled membranes. The aim is clearly to find suitable compositions that make possible to produce pore-filled membranes while also allowing working at higher temperatures. Additionally, the transport mechanism through this porous support will be evaluated from gas permeation experiments for different gas components, viz. nitrogen, helium and carbon dioxide, at different temperatures and pressures. The surface

area and pore size distribution of the composite layers have been measured and are discussed. Finally, the performance of a pore-filled membrane created in the most promising structure was assessed with long-term experiments (900 h) at 500 and 550 °C.

Experimental

Membrane preparation

Synthesis of yttria-stabilized zirconia (YSZ) sol

The YSZ nanoparticles were prepared by the hydrothermal synthesis method (8 mol% of Y_2O_3) [12]. An aqueous solution containing 0.92 M of $\text{ZrO}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and 0.16 M of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was stirred for 4 h and heated in an autoclave at 110 °C for 13 h. Purification of YSZ was done after thermal treatment adding ammonia to adjust the solution at pH 9. The precipitate was filtered and washed with distilled water until pH 6. The dispersed sol obtained was acidified with nitric acid and peptized at 95 °C overnight. The final pH was around 1. The particle size of YSZ was measured by DLS. The distribution size of hydrodynamic particles was 7–15 nm. The final concentration of the ceramics in the sol was obtained by ICP measurement.

Preparation of YSZ/ γ - Al_2O_3 mixed sol

Sol mixtures of various YSZ/ γ - Al_2O_3 proportions were prepared from, commercial boehmite (γ - $\text{AlO}(\text{OH})$), Kawaken Fine Chemical Co. with a particle size range of 8–20 nm, the synthesized YSZ and PVA-PEG as drying controlling agents [12]. For the study of the dipping parameters on the thickness of the layer, the total concentration of ceramics was fixed at 1.6 wt% with a mass ratio of 50 wt% YSZ and 50 wt% boehmite; and the total amount of PVA was modified from 0.4 to 2.0 wt%. On the other hand, for the diffusion mechanism study, the PVA was fixed at 1.2 wt%, while the total concentration of ceramics was decreased from 1.6 to 1.2 and the YSZ content was increased from 50% to 90%. In all cases a PEG concentration of 0.3 wt% was used.

Preparation of modified tubular substrates with YSZ/ γ - Al_2O_3

α - Al_2O_3 tube with an asymmetrical multilayer (pore size of the top layer of 100.) outer diameter of 10.0–10.3 mm with wall thickness of 1–1.5 mm were provided by Rauschert Kloster Veilsdorf were used as porous substrate. For proper handling of the membrane during the preparation, the porous tubes were joined to dense alumina tubes (provided by OMEGA with 6 mm OD and a wall thickness of 1 mm). The applied glass (ASF1761, Asashi Glass Co., Ltd) in the junction between porous and dense tube is cured at 1050 °C for 40 min in air. The heating ramps from room temperature to 200 °C was 3 °C min⁻¹ and then to 1050 °C with 12 °C min⁻¹ [20].

The nanoporous layers were prepared by the dip-coating, drying and calcination process. The composite solution was warmed up at 25 °C before the dipping under stirring. The dipping solutions prepared for the diffusion mechanism study are presented at Table 1. The parameters used for the study the effect of the coating parameters on the thickness of the layer, viz. the dipping time, the amount of PVA and whether

vacuum is applied or not during the dipping, are presented in Table 2. Subsequently, the tubes were slowly lifted and dried in a climatic chamber (40 °C and 60% RH) for 5 h. The samples were turning during the drying process in order to obtain a homogeneous layer over the entire surface. Finally, the calcination of the coated layer was performed at 550 °C with a heating rate of 1 °C min⁻¹ and 3 h dwelling in air.

The prepared mixed sols were dropped on a Teflon petri dish and dried at the same condition as the coated supports for 24–48 h and the films obtained were also calcined in air at 550 °C for 3 h. The obtained powders were characterized by XRD and BET.

Preparation of the PF membrane

After modification with the mesoporous composite of YSZ/ γ -Al₂O₃ (see step 1 at Fig. 1), the tubular support was activated with nano-palladium nuclei by dipping it into a chloroform solution of palladium acetate (0.4 wt %) and applying vacuum from the inner part of the tube in order to fill the pores with the solution containing Pd²⁺. The impregnated support was dried at 105 °C and subsequently reduced with hydrazine solution (2 M) at room temperature for 1–2 min (step 2 at Fig. 1). The sample was afterwards cleaned with distilled water and dried for 1 h at 105 °C. This cycle was repeated till the surface of the modified support became black. Depending on the mass ratio of YSZ/ γ -Al₂O₃ the number of cycles was varied between 6 and 8 times. This is clearly a procedure to be further optimized in a second stage of the work.

Once the activation was completed, the support was again coated with the composite as a protecting layer (third step at Fig. 1), calcined and cooled down under 10 vol% H₂/N₂ atmosphere. Afterward, the activated support was treated with electroless plating at 40–44 °C while applying vacuum (last step at Fig. 1). The required plating time ranged from 12 to 60 min. The composition of the electroless-plating bath is reported in Table 3.

Gas permeation measurements

A classical steady state permeation experiment was used for the determination of the composite parameters. The set up used for a single gas measurement is illustrated in Fig. 2. The driving force between the retentate and permeate zone (pressure difference) is regulated by a back pressure controller (Horiba Tec, UR-7340 model). The permeate is maintained at

Table 1 – Parameters used for the dip-coating of samples used in the diffusion mechanism study^a.

Dip-coating parameters			
Amount of ceramic (wt. %)	Mass ratio YSZ/ γ -Al ₂ O ₃	PVA (wt. %)	Dipping time (s)
1.6	50/50	1.2	12
1.5	60/40	1.2	12
1.4	70/30	1.2	12
1.3	80/20	1.2	12
1.2	90/10	1.2	12

^a In all cases: concentration of PVA 1.2 wt%, dipping time 12s, dipping using vacuum.

Table 2 – Samples for the study of the dipping parameters on the membrane thickness (^a).

Sample	Parameters		
	PVA (wt%)	Dipping time (s)	Vacuum
PF-A72	1.2	48	Yes
PF-A73	1.2	48	No
PF-A74	1.2	12	Yes
PF-A75	1.2	12	No
PF-A76	1.2	3	Yes
PF-A77	1.2	3	No
PF-A78	0.6	12	Yes
PF-A79	0.6	12	No
PF-A80	1.0	12	Yes
PF-A81	1.0	12	No
PF-A82	1.4	12	Yes
PF-A83	1.4	12	No
PF-A84	2.0	12	Yes
PF-A85	2.0	12	No

^a In all cases the prepared sol was 1.6 wt% of ceramic with the same mass ratio YSZ/ γ -Al₂O₃ (50/50).

Fig. 1 – Schematic description of the preparation of Pd pore-filled membranes.

Table 3 – Composition of the electroless plating bath for pore-filled membranes.

Chemical	Concentration (M)
Palladium acetate	0.02
Ammonia	2
Phosphinic acid	0.004
Formic acid	0.1

atmospheric pressure. The permeated flux is measured by Horiba flow meters (STEC PV-2 and STEC PV-3).

Hydrogen was used for the single gas test of Pd permselective membranes, for safety reasons such a test with hydrogen was not carried out with the mesoporous layers due to the very high hydrogen permeation (several liters per minute). The steady state permeation experiments were performed at temperatures between 50 and 400 °C and in the pressure difference range of 30–100 kPa using single gases

Fig. 2 – Set-up for the permeation measurements.

helium, nitrogen and carbon dioxide. The same set-up was used for the case of pore-filled membranes: in this case single gas-tests (hydrogen and nitrogen) were performed at 500 °C and 550 °C for up to 900 h.

Characterization

A Zetasizer Nano SZ ZEN3600 (Malvern Instruments) was used for the determination of the particle size of the sols (YSZ and boehmite). Thickness measurements of the nanoporous layers were carried out using cross-sectional images with a SEM (FEI Quanta 250 FEG). A cross-section EDX study of pore-filled membrane was performed using a JEOL JSM-5910LV. The pore size and surface area of the unsupported and supported membranes were obtained from the BET nitrogen adsorption isotherm obtained with a Thermo Scientific Surfer. The crystal structure of the nanoporous powders was obtained by powder X-ray diffraction (Rigaku MiniFlex 600) in the 2θ range of 20–90° with a step size of 0.02° 2θ , operating at 40 kV and 15 mA with CuK α radiation.

Results and discussion

Preparation of YSZ/ γ -Al₂O₃ mesoporous membranes

The particle size distributions of the YSZ sol (7–15 nm) and boehmite (8–20 nm) measured by dynamic light scattering methods were practically the same with a mean diameter of 10 nm (hydrodynamic diameter). Measured particle size of YSZ and boehmite particle size are represented in

Supplementary Figs. 1 and 2 respectively in Supplementary material. Supported YSZ/ γ -Al₂O₃ mixed membranes were prepared by dip-coating deposition and after drying in a climatic chamber calcining in air. Addition of boehmite sol to the YSZ, improves the adhesion with the surface of α -which decreases the thermal expansion of the mixture and improves the resistance to fatigue of YSZ [14].

Thickness measurement of nanoporous YSZ/ γ -Al₂O₃ layers

The effect of the following parameters in the preparation procedure of the nanoporous YSZ/ γ -Al₂O₃ layers on the thickness of the obtained layers have been investigated:

- Ceramic concentration in the solution.
- Deposition time.
- Polymer content.
- Applying vacuum during deposition.

The thickness of the deposited layers using different concentrations of ceramics was measured with SEM (cross section) and the results are shown in Fig. 3. The temperature of the solution was fixed at 25 °C, the deposition time to 12 s and vacuum was applied during the coating. Different mass ratios of YSZ and boehmite were used. As the amount of YSZ increase, thinner membranes without cracks should be prepared; the concentration and YSZ composition selected produced membranes without cracks. The coated porous support is made by α -Al₂O₃, which has a lower expansion coefficient than the deposited mixed YSZ/ γ -Al₂O₃. In order to

avoid cracks formation at the surface due to this difference in expansion coefficients, the amount of YSZ was increased while the total content in ceramics was decreased. The average measured thickness and the errors (from at least 4 measurements) as a function of the concentration of the solutions is presented in Fig. 3. The thickness increases linearly with the concentration of the solution ($R^2 = 0.985$), which means that the thickness can be controlled by the concentration of the solution when the coating time is fixed to 12 s and vacuum is applied.

The second study was performed by fixing the concentration of ceramics of the solution to 1.6 wt% with the same YSZ/ γ - Al_2O_3 ratio (50/50) (Table 2). As it can be observed in Fig. 4 (left), when the coating time is increased, the thickness also increases. Better correlation is obtained when the vacuum is applied. Samples deposited during 48 s show cracks at the surface. On the other hand, as the amount of polymer is increased in the solution, the thickness of the layer increases. However, a direct correlation for both samples (deposited with and without vacuum) was not obtained (Fig. 4 right).

Fig. 5 shows the cross-section of a nanoporous layer with 60 wt% YSZ (left) and 70 wt% YSZ (right) deposited on top of α -alumina asymmetric supports (with a mean pore size of 100 nm). The concentration of the ceramics in the solution was 1.4 wt%. The coating was performed applying vacuum from the inner part for 12 s and the amount of PVA was 1.2 wt%. A relatively uniform and denser layer is created on the support structure.

Surface area and pore size distribution

Fig. 6 shows the nitrogen adsorption/desorption isotherm of the YSZ/ Al_2O_3 (mass ratio 50:50) calcined at 550 °C. The isotherm profiles present a typical IV characteristic with a recognizable hysteresis loop typical of mesoporous materials [18]. The curve at low p/p_0 indicates that multilayer adsorption prevails, since the first monolayer was completed on the

Fig. 3 – Measured thickness of the ceramic layers in cross section with SEM for solutions with different ceramics concentrations in the solution.

mesoporous walls. The calculated BET surface area was 309 $\text{m}^2 \text{g}^{-1}$. In Fig. 7 (left) the surface area for all the mixtures of YSZ/ γ - Al_2O_3 calcined at 550 °C is reported as a function of the YSZ concentration (pure YSZ was included in the graph for comparison). It can be observed that as the amount of YSZ increases from 50 wt% to 100 wt%, the surface area decreases from 300 $\text{m}^2 \text{g}^{-1}$ to 50 $\text{m}^2 \text{g}^{-1}$. This is related to the increased sintering behavior of YSZ particles comparing with γ - Al_2O_3 . The pore size distribution of these mixtures increases when the amount of YSZ is increased. As shown in Fig. 7 (right), the pore diameter of the mixtures containing 50 wt% of YSZ varies roughly from 1 to 4 nm, while for pure YSZ the distribution is much broader ranging from 2 nm to 5 nm.

Crystallite and particle size

According to the XRD patterns for the samples calcined at 550 °C shown in Fig. 8 (left), the YSZ is related to the cubic phase. The peak broadening could be due to the presence of a tetragonal phase [19]. It is observed that as the amount of γ - Al_2O_3 increases, the intensity of the peaks related to the cubic YSZ crystals decreases and they become broader. This relates to the presence of amorphous γ - Al_2O_3 , which remains as such in the temperature range of 350–1000 °C [20,21].

The crystallite size can be calculated from the XRD patterns using the Scherrer equation by measuring the FWHM (full width at half maximum) of the diffraction peaks. The relation between crystallite size and the FWHM reads as follows [22]:

$$L_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (1)$$

where L_{hkl} is the mean crystallite size, λ is the X-ray wavelength of $\text{CuK}\alpha$ (1.5418 Å), β_{hkl} is the FWHM (in radians), K is the shape factor and θ is the Bragg angle. The value of K varies from 0.89 for spherical to 0.94 for cubic particles. Usually 0.9 is used assuming that crystallites are spherical [19]. This relation is valid for crystallites smaller than 100 nm [23]. The crystallite size of the YSZ phase was determined for the peak (101) centered at $\sim 30^\circ$ and is shown in Fig. 8 (right), showing the trend that the crystal size decreases for increased γ - Al_2O_3 content. The calculated crystal size for the samples with 70 and 80 wt% YSZ are somewhat smaller than expected (Fig. 8 left), similar anomalous behavior are observed in the pore size distribution (Fig. 7), this will be studied in the future. As was explained before, the crystal growth of YSZ is hindered due to the presence of γ - Al_2O_3 . According to Vegard's law, the solubility of Al_2O_3 in YSZ is only around 0.3 wt% because of the differences in their crystal structures. This means that they cannot form a solid solution and most of the Al_2O_3 is going to segregate at the grain boundary of YSZ, inhibiting the sintering process thereof.

Before calcination at 550 °C, the hydrodynamic particle size of boehmite and YSZ was measured by DLS. Both solutions showed a peak centered at 10 nm. After calcination, the particle size was obtained by TEM images. As shown in Fig. 9, the particle size of pure YSZ calcined at 550 °C is higher (10–20 nm) than the particle size obtained for the mixture with 50 wt% of γ - Al_2O_3 (<7 nm). Thus, the particle size of YSZ/ γ - Al_2O_3 mixtures decreases, as the amount of gamma-

Fig. 4 – Measured thickness over the cross section as a function of the dipping time (left) and PVA content in the solution (right). (● Applying vacuum; ■ without applying vacuum).

Fig. 5 – SEM cross section of nanoporous layer with 60 wt% YSZ (left) and 70 wt% YSZ (right) on top α -alumina asymmetric support.

alumina increases. This effect can be explained with the same reasoning as for the crystal size: sintering of YSZ is blocked due to the presence of amorphous γ - Al_2O_3 [19].

Permeation measurements

The quality of the top layer was evaluated by N_2 , He and CO_2 gas permeation experiments at different temperatures (from 50 °C to 400 °C) with a pressure difference range of 30–100 kPa for the mesoporous YSZ/ γ - Al_2O_3 membranes with different mass ratios (ranging from 50% to 90% of YSZ). All the results obtained for all the porous membranes are included in the section Supplementary material.

The gas permeance (J_0) is related to the mean pressure (P_m) by Eq. (1), where C_1 and C_2 denotes the Knudsen and viscous (Poiseuille) flow respectively [12,27].

$$J_0 = C_1 + C_2 P_{ave} \quad (2)$$

When the permeance (J_0) is independent of the average pressure (P_{ave}), Knudsen diffusion occurs as the transport mechanism. This means that the membrane is defect free. On the contrary, large slope in Eq. (2) indicates the presence of large pores or defects.

The permeances of three gases for a mesoporous layer with 60 wt% YSZ at 400 °C are reported in Fig. 10(left), showing that

Fig. 6 – Nitrogen adsorption/desorption isotherm of YSZ- γ - Al_2O_3 (50:50) calcined at 550 °C.

the permeance is almost constant or only slightly increases as a function of the pressure difference for the three different gases. In particular, for helium, the permeance slightly increases as the pressure difference increases. This effect is related to a slightly larger contribution of viscous flow at higher pressures, while Knudsen flow is independent of pressure. Since the kinetic diameter of nitrogen and carbon dioxide are larger than the kinetic diameter of helium, the viscous flow contribution is much less important. The ideal perm-selectivities of binary gases used in this work are summarized in Tables 4 and 5. Moreover, the slope and intercept obtained by plotting permeance versus average pressure of three gases. For three gases, the slope is in the order of $10^{-12} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-2}$, which means that Knudsen contribution is much larger than the viscous flow. Graphs from were calculated the slopes and intercepts for all the membranes are in “Supplementary material”.

Composition dependence

Diffusion of gases through porous media depends on the internal configuration such as the porosity, tortuosity, mean pore size and the thickness of the layer. Addition of $\gamma\text{-Al}_2\text{O}_3$ influences the transport properties of the membrane. In Fig. 11 permeance of N_2 , He and CO_2 obtained at 400 °C and 100 kPa of pressure difference for various YSZ/ $\gamma\text{-Al}_2\text{O}_3$ is reported. It is clear that a larger presence of YSZ increases the total flux of the diffusive species; since YSZ is more easily sintered than $\gamma\text{-Al}_2\text{O}_3$, and the total surface of the membrane is the same, the growth of YSZ leaves larger spaces (bigger porous) between the alumina grains increasing the passage of gases. At the same time the ideal Knudsen perm-selectivities (Fig. 11, right) are closer to ideal values when the amount of alumina in the mesoporous layer is increased.

However, as will be explained in more detail below, the thickness of the mesoporous layer is larger for composites with a smaller amount of YSZ, since the prepared solutions for the coating contains a smaller total amount of ceramics when the composition of YSZ is higher.

In order to compare the effect of the composition of the permeation properties with the surface area, the permeability (thickness standardized) values were compared and can be observed in Fig. 12, showing that lower content of YSZ result in larger permeabilities for the case of a nanoporous layer based on 50 wt% $\gamma\text{-Al}_2\text{O}_3$, which represents the best alternative for their application as matrix phase in palladium based pore-filled membranes.

Temperature dependence

In order to analyze the temperature influence on the diffusion mechanism through the nanoporous layers, experiments were performed at different temperatures (from 50 °C to 400 °C). As an example, for a nanoporous layer with 50 wt% YSZ and 100 kPa pressure difference, when the temperature is increased, the permeance of the three gases strongly decreases (see Fig. 13). The decrease in the permeance for different gases follows the expected trend (Fig. 13 left), since at lower temperatures the viscous contribution is more significant than Knudsen flow. The viscosity of the permeated gases is higher when the operating temperature is increased, which entails an increase in the frictional resistance thereof, rendering the relative contribution of the Knudsen mechanism more important for non-adsorbable gases (helium and nitrogen). However, for CO_2 (adsorbable gas) at lower temperatures, the permeance is higher due to the contribution of surface diffusion.

Thus, one would expect that the Knudsen contribution increases for increasing temperatures, and the ideal selectivity to approach the ideal Knudsen perm-selectivity. As shown in Fig. 13 (right), this is not the case for all gases, probably because the separation factors are influenced by interactions between the gases and the walls of the pores. Inspecting the permselectivity for non-adsorbable pure gases (He/N_2) relative to the ideal selectivity, it shows a slight decrease when increasing the operating temperature, against all expectations. However, they are close to the ideal Knudsen selectivity (2.65), which implies that adsorption does not take

Fig. 7 – BET surface area (left) and pore diameter distribution (right) of different YSZ/ γ -Al₂O₃ powders calcined at 550 °C in air for 3 h.

Fig. 8 – XRD patterns (left) and crystallite size (right) of different YSZ- γ -Al₂O₃ powders calcined in air at 550° for 3 h. (♦): (ZrO₂)_{0.92}(Y₂O₃)_{0.08} (JCPDS 01-070-4431); (◻) Gamma-Al₂O₃ (JCPDS 00-002-1420).

place significantly and that permeation takes place predominantly by Knudsen diffusion. In contrast, the observed ideal perm-selectivity for He/CO₂ and N₂/CO₂, exhibit a much more pronounced dependence on temperature, explained by the exothermic nature of the surface adsorption of CO₂, increasing the perm-selectivity at higher temperatures.

An Arrhenius like relationship can describe the change of permeation with temperature:

$$J = J_0 \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where J is the permeability, J_0 is the pre-exponential permeability constant, E_a the apparent activation energy and T the

temperature (K). The activation energy, E_a , is the sum of two contributions: the heat of sorption of the molecules and the activation energy associated with the mobility of the molecules [25]. The activation energies evaluated (Eq. (3)) in this study are shown in Fig. 14. Negative values of activation energy are generally associated to an adsorption of the molecule on the surface of the pore as well as the contribution of viscous and Knudsen flow due to the inverse dependence with temperature. CO₂ adsorption occurs on the γ -Al₂O₃ layers since the gas molecules interact with the material at the pore wall. Thus, CO₂ is adsorbed at the surface of the pores and diffuse along the pores due to pressure difference, resulting in an additional flow [16].

Fig. 9 – TEM images of samples calcined at 550 °C during 3 h in air: 50 wt% YSZ/50wt%Al₂O₃ (left) and YSZ (right).

Fig. 10 – N₂, He and CO₂ permeance (left) and ideal selectivities (right) of (60 wt%) YSZ/(40 wt. %) γ-Al₂O₃ layer at 400 °C and different pressures.

Regarding the structural properties of the studied layers, the activation energy provides an indication of the probability of the molecules to cross the channels of the porous structure. As the pores constrictions increase, the activation energy involved in the diffusion process is increased, related to a larger number of interactions between the permeating molecule and the pore wall, reducing the

amount of permeated gas. At the same time, the transport resistance increases as the alumina content increases. However, the experimental results show for non-adsorbable gases (nitrogen and helium) a linear trend of E_a with the concentration of alumina, while for the adsorbable CO₂ the same tendency is found until 30 wt% of γ-Al₂O₃ in content. For higher concentrations of gamma-

Table 4 – Ideal Knudsen perm-selectivities for different binary mixtures of gases used in this work.

Diffusing gases	Knudsen selectivity
He/N ₂	2.65
He/CO ₂	3.32
N ₂ /CO ₂	1.25
H ₂ /N ₂	3.74

Table 5 – Slope and intercept calculated for a porous membrane with 60 wt. % YSZ at 400 °C.

Gas	Slope (mol m ⁻² s ⁻¹ Pa ⁻²)	Intercept (mol m ⁻² s ⁻¹ Pa ⁻¹)
He	9.03×10^{-12}	1.00×10^{-5}
N ₂	1.89×10^{-12}	4.91×10^{-6}
CO ₂	3.71×10^{-12}	4.23×10^{-6}

Fig. 11 – N₂, He and CO₂ permeance (left) and ideal perm-selectivities at 100 kPa of pressure difference (right) for different YSZ/γ-Al₂O₃ layers at 400 °C and 100 kPa pressure difference.

Fig. 12 – Permeabilities of N₂, He and CO₂ at 400 °C and 100 kPa pressure difference as a function of the amount of YSZ (wt.%) of the mesoporous composites.

alumina, the activation energy decreases dramatically, which indicates a change in the rate-limiting transport mechanism, i.e. the increased importance of surface diffusion, where CO₂ molecules are adsorbed on the pore surface of the membrane.

Pore-filled membrane

A Pd-membrane was deposited on an alumina support (100 nm pore size) modified with two mesoporous layers of 60 wt% YSZ deposited with a thickness of about 2 μm in total. The palladium is located in between the mesoporous layers. However, most of the palladium is at the first micrometer of the mesoporous layer as can be observed in Fig. 15, indicated

with the purple (in the web version) line. The blue (in the web version) line refers to zirconium and it can be seen that the presence of this element decreases as the amount of palladium is larger. At the mesoporous layer, the presence of alumina is increasing, as the analysis line goes to the support (α-Al₂O₃).

The hydrogen and nitrogen permeation were monitored at 500 °C and 550 °C under 50 kPa of trans-membrane pressure difference (Fig. 16). For a period of 340 h, single gas tests were performed at 500 °C. During this period, both hydrogen and nitrogen permeation rates were increasing while the selectivity decreased. Then, the operating temperature was increased to 550 °C. Since that moment the performance of the membrane was the same as before at 500 °C; The hydrogen and nitrogen permeance increased while the perm-selectivity decreased until about 20. However, after 600 h a sudden increase in the H₂ permeation rate was observed (due to higher purity in the hydrogen used for the test). After that, the hydrogen flux continued increasing while the nitrogen permeance decreased. At the end of the experiment the hydrogen and nitrogen permeance at 550 °C and 50 kPa of pressure difference were 1.76×10^{-7} and 3.5×10^{-9} mol m⁻² s⁻¹ Pa⁻¹, respectively, corresponding to an increase in the ideal perm-selectivity to approximately 50. It has been shown in this work that a Pd membrane can be deposited in between two nanoporous layers. Obviously this is a first step for the deposition of more selective membranes by further improving the conditions for the deposition of the nano/mesoporous layers, which will be the topic of future works. The ideal selectivity should be improved by increasing the hydrogen permeance and decreasing the nitrogen permeance through the membrane. To achieve this the thickness of the nanoporous layer and its calcination temperature will be modified by using higher calcination temperatures than the actual one (550 °C), which increases the pore size distribution of ceramic layer where the palladium is going to be located. The effect of those pore-sizes (and later of Pd particle size) is going to be studied in a next work.

Fig. 13 – N₂, He and CO₂ permeance (left) and ideal Knudsen selectivities (right) for a nanoporous layer with 50 wt% YSZ as a function of temperature (pressure difference was 100 kPa).

Fig. 14 – Calculated (lumped) activation energies for the permeation of different gases through the nanoporous layers as a function of the composition of the nanoporous layers.

Conclusions

A pore-filled Pd/YSZ/γ-Al₂O₃ membrane was successfully prepared and the parameters in the preparation of and the diffusion mechanisms of He, N₂ and CO₂ in the nano/mesoporous layers have been investigated in detail. The pore size of nanoporous layers decreases when the amount of γ-Al₂O₃ increases, and consequently the viscous flow contribution decreases: at 400 °C the ideal perm-selectivity

Fig. 15 – Cross-sectional SEM images of the pore-filled Pd/YSZ/γ-Al₂O₃ (60 wt. % YSZ) membrane with EDX line profiles of different elements present in the membrane (post-mortem).

increases from ~2.2 with (10 wt% γ-Al₂O₃) to ~2.7 (50 wt% γ-Al₂O₃), whereas the ideal Knudsen perm-selectivity for He/CO₂ is 3.32. The He/CO₂ separation factor decreases for higher operating temperatures, which could be related to the increased contribution of surface diffusion of CO₂. Long-term test of the prepared pore-filled membrane was performed for 900 h at 500 °C and 550 °C, showing that the performance of membrane was improving during the long-term test. The hydrogen permeance at the end of the experiments was $1.76 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with a H₂/N₂ permselectivity of 50.

Fig. 16 – Long-term permeation test of the pore-filled Pd/YSZ/ γ -Al₂O₃ (60 wt. % YSZ) type membrane performed during 900 h at 500 °C and 550 °C in pure hydrogen and nitrogen.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2015.11.152>.

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