

H₂ Separation from Gas Mixtures through Palladium Membranes on Metallic Porous Supports

Matteo Bientinesi^{*1}, Luigi Petarca²

¹ Consorzio Polo Tecnologico Magona

via Magona, 57023, Cecina (LI), Italy, matteo.bientinesi@polomagona.it

² Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università di Pisa
via Diotisalvi 2, 56126, Pisa, Italy

Thin-film palladium membranes are one of the most promising technologies for hydrogen separation from gas mixtures, involving advantages, such as a separation efficiency approaching 100%, high permeability, and operating conditions compatible with upstream fuel conversion processes. In this work, palladium films, with thickness between 10 μm and 40 μm , were deposited above stainless steel porous tubular supports using a modified electroless plating technique. The application of vacuum during palladium deposition, together with support abrasion and oxidation above 700°C, were demonstrated to be effective in limiting the presence of film defects.

The prepared membranes were then tested in an experimental set-up using a wide range of operating conditions (transmembranal pressure 2-20 bar, temperature 300-550°C) in order to evaluate their performances. A hydrogen permeation flow rate of 0.25 mol/m²s, with a selectivity with respect to CO₂ as high as 5000, was obtained at 450°C and 10 bar of partial transmembranal pressure.

A mathematical model was set in order to interpolate the experimental data and simulate the permeation of hydrogen through palladium. A good agreement between experimental and simulation results was obtained.

1. Introduction

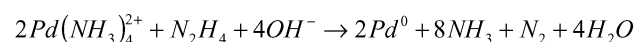
The industrial application of palladium membranes can lead to important improvements in the separation of H₂ from hydrogen-rich gas mixtures streams and to the development of innovative applications such as membrane reactors for methane steam reforming and water gas shift reaction (Paglieri and Way, 2002). Palladium membranes have a really high selectivity coupled with thermal and mechanical resistance. The disadvantages that have limited their large scale application are the low permeability and the high cost. Both these problems can be reduced by lowering the selective layer thickness, still preserving the mechanical strength. For this reason attention is focusing on the development of thin (0.1-20 μm) Pd film deposited on porous supports. Among the possible different porous support used (ceramic, glass, metallic), stainless steel sintered porous supports are particularly suitable for the integration of palladium membranes in large area industrial configurations such as shell-and-tube modules, since they can be easily welded to dense metallic materials, thus avoiding sealing problems typical of

ceramic supports, which are widely used in small-scale laboratory experimentations. Other advantages of stainless steel supports are the high mechanical strength, a coefficient of linear thermal expansion close to that of palladium, and the relatively low price. One drawback in the use of metallic supports is the difficulty to form very thin (<10 μm) dense palladium films above them, due to the relatively high surface roughness and pores dimension. This problem can be limited to some extent by a mechanical treatment of surface abrasion (Li et al., 2007) before palladium deposition. The intermetallic diffusion of Pd and Fe into each other at temperature above 400°C can be avoided by forming, through different methods, a thin anti-diffusive ceramic layer above the support surface, which block the migration of metallic atoms at high temperature (Yepes et al., 2006). Among the possible methods of deposition of metallic films on porous supports, Electroless Plating (ELP) is largely the most popular technique, since it requires low cost equipment, can be performed on every type of support, and allows the deposition of Pd alloy as well as of pure palladium. In this article, we describe the optimization of the procedure of preparation of palladium thin-film membranes above stainless steel porous support, the successive testing for permeability and selectivity determination and the modeling of the membrane, in order to interpolate test data and extrapolate the results for large-scale applications.

2. Experimental and Methods

2.1 Membrane preparation

A procedure for membrane preparation was developed through several tests, by optimizing the experimental conditions. The deposition technique involves the following steps: porous support pre-treatments, surface sensitization/activation with SnCl_2 and PdCl_2 solutions, electroless plating (ELP), annealing. Pd was deposited on the outer surface of porous AISI 316 L stainless steel tubes (L = 100 mm, O.D. 6.4 mm, I.D. 3.2 mm) supplied by Mott™. Supports were first abraded in several steps with increasingly finer sandpaper (P220, P400, P1000), then they were cleaned in a ultrasonic bath with alkaline and acidic solutions and with acetone. Cleaned supports were oxidized (500-800°C for 12 h) to form a metal oxide layer blocking intermetallic diffusion at high temperature. Pd ELP in alkaline solution with hydrazine as the reducing agent takes place via the following redox reaction (Cheng and Yeung, 2001):



The composition of the Pd plating bath is reported in Table 1. ELP was conducted at 60°C, and 70 ml of bath were used. Hydrazine (in 1 M solution) was added at the beginning of the reaction or in several small doses. The whole procedure was repeated from 2 to 6 times. In order to furnish an additional driving force for the deposition, moderate vacuum (0.7 to 0.9 bar) was applied in some experiments on the internal side of tubular supports. The final treatment of thermal annealing was conducted by maintaining the membrane at 500°C for 12 h in H_2 flow.

Table 1: Composition of palladium electroless plating solution.

Reagent	ELP sol. [mol/L]
PdCl ₂	0.02
Na ₂ EDTA	0.18
NH ₄ OH	10.4
N ₂ H ₄	0.01

2.2 Membrane characterization and testing

During membrane preparation, membrane weight was monitored, mainly in order to control the amount of metal deposited on the support. Before weighting on a precision balance, supports or membranes were dried at 120°C for 1 h. After each ELP cycle, the amount of deposited palladium (W_{Pd}) was estimated by weight gain, and the average film thickness (t_{mem}) was calculated by the following equation:

$$t_{mem} = \frac{W_{Pd}}{\rho_{Pd} A} \quad (1)$$

where ρ_{Pd} is the metallic palladium density (12023 kg/m³) and A is the geometric surface area of the support outer side (1995 mm²). Deposited Pd films were analyzed with SEM both on the surface and on the cross-section, mainly in order to observe the mechanism of film formation and to confirm the film thickness estimated by weight measurements. Moreover, nitrogen was fluxed through the membrane at limited pressure and at room temperature to evaluate the possible presence of defects. Finally, membranes were tested for hydrogen, carbon dioxide and nitrogen permeability in a specially designed set-up (Bientinesi, 2010) with operating temperature variable between room temperature and 650°C, feed pressure in the range 1-30 bar and feed gas flow in the range 0.005-0.14 mol/min. Each test is conducted at constant temperature by feeding a constant flow-rate of a single gas (H₂, CO₂ or N₂) to the outside of the tubular membrane and by measuring the permeate flow rate. The pressure inside the tubular membrane is held constant (1.2 bar) while the feed pressure can be varied, so exploring the variation of the gas permeability with changing transmembranal pressure.

2.3 Model development

We assumed a uniform thickness of the Pd film throughout the membrane length, and considered the film as a porous material, since it was experimentally found that all prepared membranes contains a small number of defects in the film. An uniform distribution of defect pore radius was assumed. The energy balance and pressure drops in the gas phase and through the porous support were neglected.

Data from H₂ permeation tests were fitted by means of Eq. 2 (Bientinesi, 2010):

$$N_{H_2}(x) = \frac{1}{r_{o,d} \ln\left(\frac{r_{o,d} + t_{mem}}{r_{o,d}}\right)} \left\{ \Pi_0 \exp\left(-\frac{E_a}{RT}\right) (P_{H_2,ret}^n - P_{H_2,per}^n) + \frac{\varepsilon_{mem} r_{p,mem}}{\tau_{mem}} \left[\frac{2}{3} \left(\frac{8}{\pi}\right)^{0.5} \frac{1}{(RTM_{H_2})^{0.5}} (P_{H_2,ret} - P_{H_2,per}) + \frac{1}{16} \frac{r_{p,mem}}{\mu_{H_2} RT} (P_{H_2,ret}^2 - P_{H_2,per}^2) \right] \right\} \quad (2)$$

where N_{H_2} [mol/s·m²] is the molar H₂ flux through Pd film for unit membrane area, Π_0 [mol/m³·s·Pa] and E_a [J/mol] are the pre-exponential factor and the activation energy of Arrhenius law for the calculation of membrane permeability, n the exponential factor of Sievert law, ε_{mem} and τ_{mem} are the membrane porosity and tortuosity due to film defects, $r_{p,mem}$ [m] is the average film defect radius, $r_{o,t}$ [m] is the outer radius of the porous support, t_{mem} [m] is the membrane thickness (calculated by Eq.1), T [K] is the temperature, M_{H_2} [kg/mol] the molar mass of hydrogen, μ_{H_2} [kg/m·s] the gas viscosity, and finally $P_{H_2,per}$ and $P_{H_2,ret}$ [Pa] are the hydrogen partial pressure in the permeate and in the retentate sides. The total permeation flow is the sum of 3 different contribution: the atomic flow through palladium and the flow through membrane defects via Knudsen diffusion and viscous flow. For CO₂ and N₂ the expression is analogue, except for the contribution of atomic diffusion through Pd that is not present.

There are 5 unknown parameters in Eq. 2: $\varepsilon_{mem}/\tau_{mem}$ and $r_{p,mem}$ are calculated by a data fitting algorithm using CO₂ and N₂ permeation data, Π_0 , E_a , and n are found using H₂ permeation data through the same algorithm. If no CO₂ and N₂ flow is measurable during membrane test, H₂ data were used to calculate all the parameters.

Calculated parameters were then used to set a model of an industrial membrane, by integrating on the membrane length the mass balance for H₂ and CO₂, with the flow from the retentate side to the permeate side described by Eq. 2. Some simulations were performed in order to evaluate the industrial performances of the membrane.

Data fitting and model simulation were implemented in Matlab environment.

3. Results and discussion

The procedure of Pd deposition on porous stainless steel support was optimized in order to maximize the deposition yield and minimize the flow of N₂ at room temperature through the Pd film, which indicates the presence of defects. The abrasion of the support and its oxidation at temperatures above 700°C, as well as the application of vacuum during ELP, were effective in reducing the amount of defects formed in the film, even for film thickness of only 10 μm (Table 2). The progressive dosage of hydrazine turned out to be fundamental to enhance the Pd deposition yield over 80%.

SEM pictures (see Figure 1) showed that the Pd film forms via the successive deposition of Pd grains with dimension between 1 and 15 μm, partially penetrating in the pores of the support, so assuring an optimal adhesion of the film. The observed thickness is comparable to the value calculated from weight gain data.

All produced membranes turned out to be not completely tight to nitrogen and carbon dioxide, revealing the presence of a limited number of defects. The model developed was really good in fitting experimental permeation data, as depicted in Figure 2 for membrane T8. For this membrane, carbon dioxide permeation flow-rate was under the detection limit (0.01 mol/m²·s) but was anyway observed. We calculated from H₂ permeation data the following parameters: $\varepsilon_{mem}/\tau_{mem} = 1.7 \cdot 10^{-8}$, $r_{p,mem} = 0.21 \mu\text{m}$, $\Pi'_0 = 4.0 \cdot 10^{-5} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}^n$, $E_a = 17100 \text{ J/mol}$, $n = 0.84$. A really limited number of defects is present in the Pd film, and the calculated H₂/CO₂ selectivity for T8 is higher than 2000 both at 400°C and 450°C, for pressures well above 15 bar (Figure 2).

Table 2: Results for Pd deposition on tube supports (area 19.9 cm²).

ID membrane	T1	T2	T3	T4	T5	T6	T7	T8
Abrasion	No	No	Yes	No	Yes	Yes	Yes	Yes
Thermal oxidation	No	500°C	500°C	500°C	500°C	500°C	800°C	700°C
ELP cycles	4	4	4	6	6	6	6	2
Vacuum [barg]	No	No	No	No	0.1	0.1	0.1	0.3
Film thickness ¹ [μm]	9.5	11	11.6	15.5	16.7	29.5	24.3	10.2
$\Pi_{N_2,25^\circ C}$ ² [mol/m ² ·s·bar]	0.77	0.25	0.10	0.040	0.0056	n.d. ¹	n.d. ¹	n.d. ¹

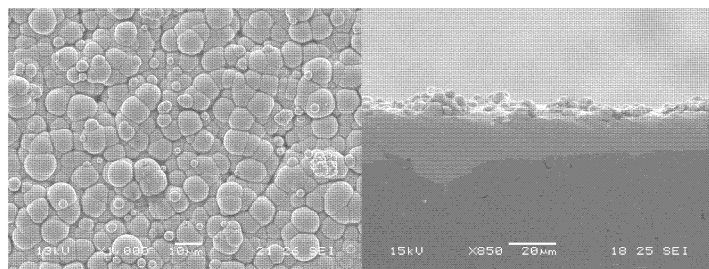


Figure 1: SEM pictures of the surface (left) and the cross-section (right) of a palladium membrane (T7) before thermal annealing.

The found parameters were used for a simulation implemented with the realized model in order to evaluate the performances of membrane T8 in an industrial configuration: considering a feed made of 50% H₂ and 50% CO₂ by volume and a total flow-rate of 0.016 mol/s, with a membrane length of 3 m, the hydrogen recovery is higher than 90% with a product purity over 99.88% (Figure 3).

The developed model can be useful in optimizing the operating conditions for a separation process, once the parameters of the membrane are extensively known.

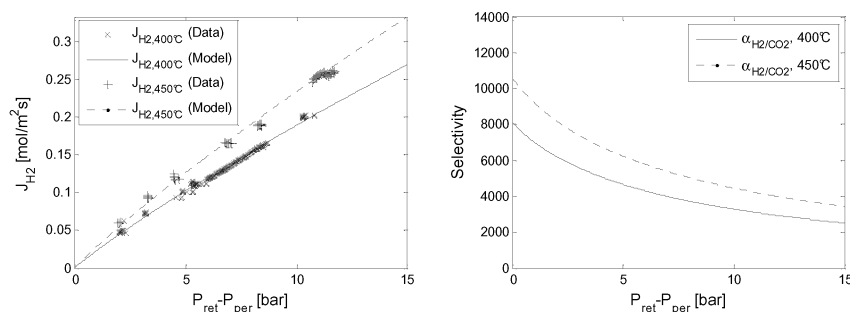


Figure 2: Hydrogen permeate flow data fitting (left) and H₂/CO₂ calculated selectivity for membrane T8.

¹ Estimated by weight measurements through Eq.1.

² Nitrogen permeability at room temperature; n.d.: not detected flow-rate ($< 2 \cdot 10^{-3}$ mol/m²·s·bar).

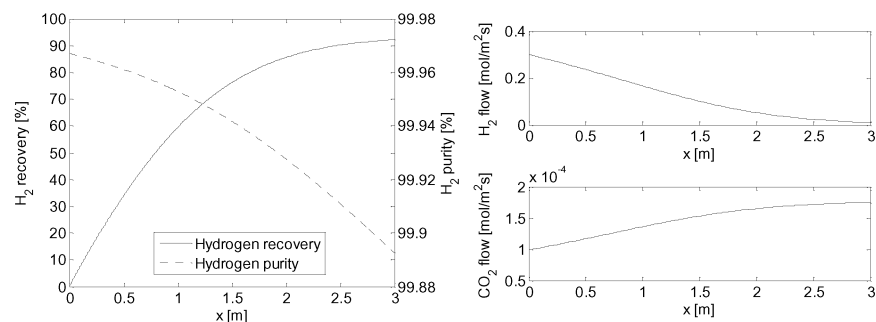


Figure 3: Model calculation of hydrogen recovery and purity (left) and H_2 and CO_2 permeation flow-rate (right).

4. Conclusion

The procedure of palladium deposition above porous stainless steel supports via ELP was optimized in order to form thin dense films with a minimum number of defects. The produced thin-film Pd membranes were tested at high temperature showing hydrogen permeation rates as high as $0.25 mol/m^2s$ at 10 bar of transmembranal pressure and selectivities with respect to CO_2 well over 2000. No changes in performance was detected after over 500 h of high temperature testing.

The developed model was able to interpolate experimental data and was useful in order to evaluate the performance of Pd membranes in industrial configurations.

Acknowledgements

This work was partially financed by the Italian Ministry of University and Research (MIUR) in the ambit of the project FISR 2006 "Integrated System for Hydrogen Production and Use in Distributed Generation".

References

- Bientinesi M., 2010, Hydrogen separation from synthesis gas through membranes, Ph.D. Thesis, Università di Pisa, 2010.
- Cheng Y.S. and Yeung K.L., 2001, Effects of electroless plating chemistry on the synthesis of palladium membranes, *Journal of Membrane Science*, 182, 195-203.
- Li A., Grace J.R. and Lim C.J., 2007, Preparation of thin Pd-based composite membrane on planar metallic substrate. Part I: Pre-treatment of porous stainless steel substrate, *Journal of Membrane Science*, 298, 175-181.
- Pagliari S.N. and Way J.D., 2002, Innovation in Palladium Membrane Research, *Separation and Purification Reviews*, 31, 1-169.
- Yepes D., Cornaglia L.M., Irusta S. and Lombardo E.A., 2006, Different oxides used as diffusion barriers in composite hydrogen permeable membranes, *Journal of Membrane Science*, 274, 92-101.