Synthesis of Pd-Ag alloy membranes and their application in membrane reactors for hydrogen production and purification

Patricia Pérez[1], Miguel A. Soria[1], Ana I. Pereira[2], Carlos J. Tavares[2], Silvano Tosti[3], Adélio Mendes[1] and Luis M. Madeira[1]

[1] LEPAE, Chemical Engineering Department – Faculty of Engineering - University of Porto, Portugal.
Email: deq10022@fe.up.pt, masoria@fe.up.pt, mendes@fe.up.pt, mmadeira@fe.up.pt → URL: http://paginas.fe.up.pt/lepae/
[2] CFUM, Department of Physics - University of Minho, Portugal.
Email: a55650@alunos.uminho.pt, ctavares@fisica.uminho.pt → URL: http://www.fisica.uminho.pt/
[3] ENEA, Unità Tecnica Fusione - C.R. ENEA Frascati, Italy.
Email: silvano.tosti@enea.it → URL: http://www.fusione.enea.it/

Abstract

Pd-Ag based membranes, self-supported and supported on porous α-Al₂O₃, have been studied for hydrogen selective separation. In the case of the self-supported membranes the Pd-Ag permeator tube was prepared by cold-rolling and diffusion welding technique; magnetron sputtering technique was employed for the synthesis of the membrane supported on porous α-Al₂O₃. The results have shown that the self supported Pd-Ag membranes are infinitively H₂-selective and the H₂-permeation rate through this membrane is in accordance with Sieverts´ law for detect-free meal membranes; hence, an ultra-pure hydrogen stream can be obtained. The Pd-Ag membrane supported on porous α-Al₂O₃ is not completely selective towards H₂, but requires much less metal since it is much thinner (ca. ~50 vs. 1 μm).

In this work, it was studied the water-gas shift on Pd-Ag membrane reactor, but it was also illustrated another application of palladium membranes, in the ethanol steam reforming. The use of the self-supported Pd-Ag membrane leads to enhance the H₂ yield in both reactions, providing much better performances than conventional reactors.

Keywords: Hydrogen production, Water-Gas Shift reaction, Pd-Ag membrane, Membrane reactor

1   Introduction

Energy consumption has been growing every year. Besides this, the global warming and the depletion of fossil resources lead to an urgency in the need to generate clean energy.
Considering these aspects, it is essential to look for alternative sources to gradually start replacing fossil fuels dependence [1]. Among alternative fuels, hydrogen is the most attractive option as a future energy carrier.
Pure hydrogen does not exist naturally on Earth, but, there are several methods to obtain it, like steam reforming, among others [2].
The use of Membrane Reactors (MRs) combining H₂ production by catalytic reaction and a H₂-selective membrane has gained substantial importance. In thermodynamic limited reversible reactions, MRs can be used to overcome the equilibrium conversion based on feed conditions.

H₂-selective Pd-Ag alloy membranes are suitable for such purposes and also for integration with different catalytic processes as described below.

The aim of this work is to prepare H₂-selective Pd-Ag membranes by different methods. Cold-rolling combined with diffusion welding and magnetron sputtering methods have been employed and are herein described.

1.1 Pd-Ag alloys membrane applications

1.1.1   Water Gas Shift Reaction (WGSR)

WGSR (eq. 1) is often used as a step following to hydrocarbons steam reforming, in order to produce highly-pure hydrogen [3]. It is particularly important for reducing the carbon monoxide content in fuel cell applications.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{1}$$

1.1.2 Ethanol Steam Reforming (ESR)

Alcohol from biomass can be used to produce hydrogen via ESR – eq. 2 [4].

$$C_2H_5OH + H_2O \leftrightarrow 2CO_2 + 4H_2 \qquad (2)$$
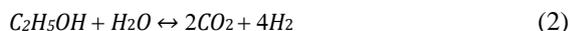
2 Experimental

2.1 Pd-Ag membrane supported on α-Al₂O₃

Palladium and silver were deposited on a porous support of alumina by the Magnetron Sputtering (MS) technique. MS is a type of Physical Vapor Deposition (PVD) technique, using high vacuum and metal targets-loaded magnetrons. This method consists in bombarding both Pd and Ag targets with energetic argon ions and subsequent ejection of the neutral metal atoms species, which will them condense as a growing thin film on the porous α-Al₂O₃ surface. In Figure 1 is a sketch that illustrates the sputtering process from 2 magnetrons in the customized PVD setup at CFUM. The process parameters were: Base pressure $\approx 10^{-4}$ Pa, working pressure = 0.37 to 3.00 Pa, magnetron current density (Pd) = 7.6 x10^{-3} to 1.0 x10^{-2} A.cm^{-2}, magnetron current density (Ag) = 1.6 x10^{-3} A.cm^{-2}, bias voltage = -60 V, flux (Ar) = 35 to 50 sccm; heating power = 100 W; pre-etching = 5 to 15 min.
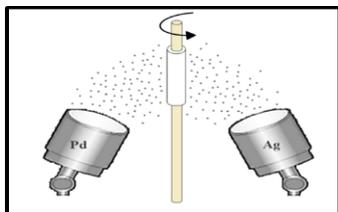

Figure 1. Magnetron Sputtering chamber.

2.2 Self-supported Pd-Ag membranes

A self-supported Pd-Ag membrane was produced via a new technique based on cold-rolling and diffusion welding. The membranes were obtained from a commercial flat sheet of Pd–Ag (23–25% wt. of silver) in a "finger-like" configuration.

The production of Pd-Ag thin wall tubes consists of two main processes: the reduction of the metal foils thickness and their joining in order to form the tube [5]. The production requires a thermo-mechanical press that is used for joining via diffusion welding the Pd–Ag cold rolled sheet, resulting in a membrane tube with about 50μm of wall thickness. More details to this process are described elsewhere [6].

2.3 Characterization of the membranes

The scanning electron microscopy (SEM) technique was used to observe the surface and cross section of the PVD-deposited Pd-Ag thin film membranes supported on α-Al₂O₃ (for which pore dimensions were reduced with yttria-stabilized-zirconia before MS) in order to evaluate the chemical composition (by coupling with EDX - Energy-dispersive X-ray Spectroscopy technique), thickness and surface morphology. The equipment used was a Nano SEM-FEI Nova 200 (FEG / SEM), EDAX Pegasus-X4M (EDX).

2.4 Membrane Reactor (MR)

According with Figure 2, the MR used consists of a tubular stainless steel module, length 180 mm, i.d.30 mm, containing the Pd-Ag membrane with 50 μm of wall thickness, o.d.10 mm and length 50 mm - self supported Pd-Ag membrane tube was employed. Operating conditions, catalyst used, etc., are described elsewhere [7]. The same module was used for permeation experiments, without catalyst.
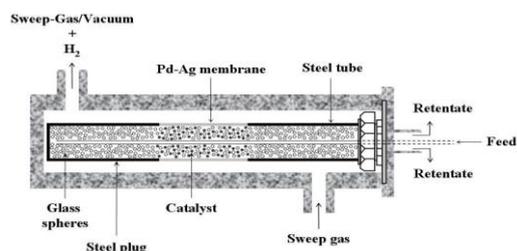

Figure 2. Pd-Ag supported membranes on MR assembly.

3 Results and discussion

3.1 Preparation of the Pd-Ag membrane supported on porous α-Al₂O₃

3.1.1 Influence of working pressure

Pd and Ag were deposited on the α-Al₂O₃ support at different sputtering pressures, while keeping constant the deposition time (See Table 1) and other conditions.

Table 1. Deposition parameters and wt. % of Ag in the films, along with their thickness.

Membrane	Pressure [Pa]	Time [min]	%wt. (Ag)	Thickness [μm]
M57	3.00	20	18.9	1.41
M56	1.00	20	17.5	0.97
M58	0.43	20	14.8	0.73
M60	0.37	20	12.6	0.82

Figure 3 shows the morphology of the thin film surface obtained for each of the membranes listed in Table 1.

At higher sputtering working pressures, it is possible to observe a columnar structure, with voids between columns (membrane M57). The voids enable the permeation of H₂ as well as of air through the membrane structure by a Knudsen diffusion mechanism. Conversely, if the working

pressure is decreased, the columnar structure becomes tighter with less inter columnar space, allowing, in principle, to obtain a more selective membrane (Thornton Model) [8].
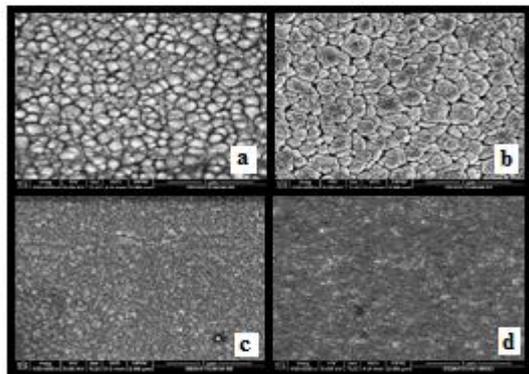

Figure. 3. SEM Micrographs of the membrane surface: M56 (a), M57 (b), M58 (c) and M60 (d).

On the other hand, decreasing the working pressure should be limited since it contributes to the reduction of sputtering rate, which results in a lower deposition of silver and palladium and hence film thickness decreases (at least down to pressures around 0.4 Pa – Table 1).

3.1.2 Selectivity studies

According to the previous section, particular conditions were chosen to obtain a high H_2-selectivity membrane (deposition pressure = 0.37-0.43 Pa and deposition time = 20 min.).

For a new set membranes prepared under such conditions (data not shown), membrane M61 presents the lowest permeate flow rate of N_2 and, for this reason, it was tested for H_2 selectivity assessment.

Figure 4 shows the selectivity test results. The permeation values obtained for hydrogen are high. The membrane ideal selectivity ratio ($\alpha_{H2/N2}$) is 10 for P_{feed} = 300 kPa, so this value still needs to be improved in order to increase the membrane H_2-selectivity. Nevertheless, as a preliminary result, it is still worth mentioning.
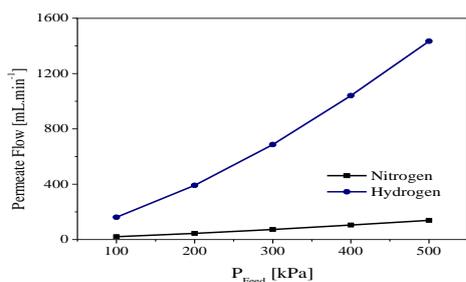

Figure 4. Permeate flow for nitrogen and hydrogen as a function of feed pressure for membrane M61 (Pfeed = 100 to 500 kPa at RT).

3.2 Pd-Ag self-supported membrane: permeation tests

Figure 5 shows that the self-supported Pd-Ag membrane is infinitely H_2-selective and revealed that the H_2 permeation rate is directly proportional to the difference of the square root of the H_2 partial pressure in the retentate and permeate sides at all temperatures, accordingly with the Sievert's law for defect-free metal membranes.
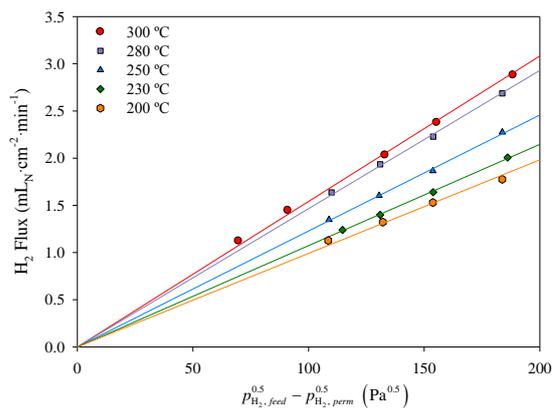

Figure 5. H_2 flux at different temperatures for the Pd-Ag membrane (50 µm) as a function of the difference of the square root of the H_2 partial pressure in the retentate and permeate sides.

3.3. Pd-Ag alloy membranes applications

3.3.1. Effect of the Pd-Ag membrane in WGS reaction

Figure 6 illustrates the CO conversion in the WGS reaction (eq. 1) and the H_2 recovery obtained in a self-supported Pd-Ag MR as a function of the temperature. Operating with the Pd-Ag MR, the CO conversion is enhanced in the entire range of temperatures used as compared with a conventional packed bed reactor (PBR), exceeding inclusively the thermodynamic value (TEC; dotted curve). So, a much better performance is obtained while simultaneously producing an ultra-pure H_2 stream.
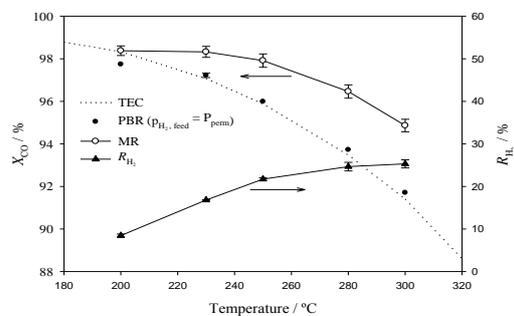

Figure 6 – Influence of the reaction temperature on the CO conversion and H_2 recovery for the WGS MR. P_{perm} ~ 30 mbar, P_{feed} = 1.1 bar and a GHSV (gas hourly space velocity) = 3200 $L_N \cdot kg_{cat}^{-1} \cdot h^{-1}$. 1.5 g of CuO/ZnO/$Al_2O_3$ catalyst.

3.3.2. Effect of the Pd-Ag self-supported membrane in ESR reaction

To compare the Traditional Reactor (TR) with the MR, different operating parameters were considered by Gallucci et at. [9]. Figure 7 shows that the MR performs always better, whatever the temperature and the contact time (W/F).

Here there are some of the results of a model work (temperature effect and feed molar ratio). The rest of the results are available on the document corresponding reference number 9.
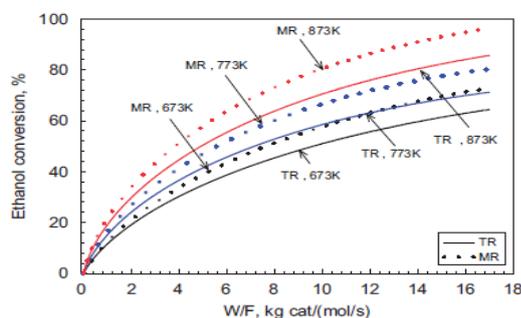

Figure 7 – Ethanol conversion vs W/F for MR and TR at different temperatures. Theoretical results P_{lumen} = 1 bar, P_{shell} = 1 bar.

4 Conclusions

For Pd-Ag thin film membranes on porous α-Al_2O_3 support the columnar structure of Pd-Ag films is very important for obtaining a good H_2-selectivity.The deposition at low working pressures/high temperatures by magnetron sputtering is ideal for achieving a high selectivity. It is therefore necessary to optimize these deposition parameters in order to obtain a thin and homogeneous film, as well to study the optimized Pd/Ag ratio. However, the preliminary results are quite encouraging.

The results of the permeation tests indicate that the mass transport in self-supported Pd-Ag membranes is controlled by the diffusion of atomic H_2 through the film – Sieverts' law.

For these membranes in MR applications, higher conversions can generally be achieved when integrated in a membrane reactor assembly, in particularly for the exothermal WGS reaction at lower temperatures where the equilibrium conversion is favored. On the other hand, it was found that some parameters have a great influence on the reactor performances. H_2 recovery can be improved increasing the operating temperature and/or applying a higher H_2 partial pressure difference between the retentate and permeate sides of the dense Pd-Ag membrane.

The results of the application of the membrane in the WGS and ESR reactions, demonstrate the ability of the membrane to increase the conversion when compared with traditional reactors, while simultaneously producing ultra-pure H2 stream (i.e. free of CO). This ultrapure H_2 can be directly fed to PEM fuel cells without further purification steps.

References

[1] D. Das and T. N. Veziroglu. Hydrogen production by biological processes: a survey of literature. *Int. J. Hydrogen Energy* 26 (2001) 13–28.

[2] J. Larminie and A. Dicks. Fuel cell systems explained. *Second Edition John Wiley & Sons Ltd*, (2003) Chichester, England.

[3] D. Mendes, A. Mendes, L.M. Madeira, A. Iulianelli, J.M. Sousa and A. Basile. The water-gas shift reaction: From conventional catalytic systems to Pd-based membrane reactors - *A review. Asia-Pac. J. Chem. Eng.* 5 (2010) 111-137.

[4] A. Santucci, F. Borgognoni, C. Cordiner, E. Traversa, S. Tosti. Low temperature ethanol steam reforming in a Pd-Ag membrane reformer. *211th ECS Meeting, Chicago, Illinois* **(2007).**

[5] S. Tosti and L. Bettinali. Membranes for Membrane Reactors: Preparation, Optimization and Selection – Cap.4. Metallic Membranes Prepared by Cold Rolling and Diffusion Welding. (2011) 155–167.

[6]. S. Tosti. Metallic Membranes Prepared by Cold Rolling and Diffusion Welding in Membranes for Membrane Reactors: Preparation, Optimization and Selection. *Ed. A. Basile and F. Gallucci, Wiley*, *Ch. 4*, ISBN 978-0-470-74652-3, (2011) 155-167.

[7] D. Mendes, H. García, V. B. Silva, A. Méndes, L. M. Madeira. Comparison of nanosized gold-based and copper-based catalysts for the low-temperature water-gas shift reaction. *Ind. Eng. Chem. Res.* 48 (2009) 430–439.

[8] D. M. Mattox. Handbook of physical vapor deposition (PVD) processing - Film formation, Adhesion, Surface preparation and Contamination Control. *s.l: Nyoes Publications*, (1998).

[9] F. Gallucci, M. De Falco, S. Tosti, L. Marrelli, A. Basile. Ethanol steam reforming in a dense Pd–Ag membrane reactor: A modelling work. Comparison with the traditional system. *Int. J. Hydrogen Energy* 33 (2008) 644-651.