

## Long-term tests of Pd–Ag thin wall permeator tube

S. Tosti<sup>a,\*</sup>, A. Basile<sup>b,1</sup>, L. Bettinali<sup>a</sup>, F. Borgognoni<sup>c,2</sup>,  
F. Chiaravalloti<sup>b,1</sup>, F. Gallucci<sup>b,1</sup>

<sup>a</sup> ENEA, Unità Tecnico Scientifica Fusione, C.R. ENEA Frascati, Via E. Fermi 45, Frascati, Roma I-00044, Italy

<sup>b</sup> Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, Via P. Bucci, Cubo 17/C, I-87030 Rende (CS), Italy

<sup>c</sup> Tesi Sas, Via Bolzano 28, Roma, Italy

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### Abstract

Thin wall permeator tubes have been produced by diffusion welding of Pd–Ag foils. These dense metal membranes are proposed for separating and producing ultra-pure hydrogen as a result of their complete hydrogen selectivity. Furthermore, they present high hydrogen permeation fluxes as well as reduced costs on account of their reduced metal thickness.

The reliability of these membrane tubes has been continuously tested during over 12 months of experimental campaign in presence of thermal and hydrogenation cycles. The permeability tests have been carried out measuring the hydrogen fluxes under controlled conditions of temperature and trans-membrane differential pressure. In particular, the behaviour of the membrane tube has been investigated in a wide range of temperatures (150–400 °C) and pressures (100–200 kPa) in order to simulate the use within permeators and membrane reactors where processes for producing hydrogen from hydrocarbons takes place.

At temperature of 350–400 °C hydrogen permeability values around  $1.0 \times 10^{-8} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$  have been measured and they are comparable with the literature data. A new mechanical design (finger-like configuration) of the membrane module has ensured the long life of the Pd–Ag permeator. The complete hydrogen selectivity of the membrane has been demonstrated by the tests.

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### 1. Introduction

Pd and Pd alloys membranes present growing interest for their capability to separate ultra-pure hydrogen from gaseous mixture.

The first commercial application of a metal membrane concerning the hydrogen purification used a 23 wt.% palladium–silver membrane by Johnson Matthey in 1964 [1]. This process was used in small to medium scale plants, with individual units for the production of up to  $56 \text{ Nm}^3 \text{ h}^{-1}$  of high purity hydrogen containing less than 0.1 ppm total impurities [2,3].

Actual potential applications concern the hydrogen production from hydrocarbons in membrane reactors. The first pilot-

scale membrane reformer for producing hydrogen has been built by Tokyo Gas Co., the largest gas company in Tokyo (Japan). This reformer was indicated as World's first membranes type hydrogen producer [4,5]. The reaction of interest was the steam reforming of methane bound to the water gas shift reaction. The purity of hydrogen produced is greater than 99.999% with a flow rate of  $4 \text{ Nm}^3 \text{ h}^{-1}$  obtained in the range between 500 and 550 °C, lower than 800–850 °C required in the traditional reactor.

Another typical example is given by palladium membrane alcohol reformers producing pure hydrogen used for feeding polymeric fuel cells for both vehicular and small size stationary applications [6–9]. The palladium membrane gives both CO-free hydrogen production and higher conversions than the traditional system, when methanol is reformed by steam [9,10].

However, a limit for the wide use of these devices is given by the cost of the palladium. On the other hand, the application of thin palladium films in composite membranes (i.e. palladium on ceramic, palladium on porous steel or nickel) is characterized by loss of selectivity as well as reduced life-

\* Corresponding author. Tel.: +39 06 94005160; fax: +39 06 94005374.

E-mail address: [tosti@frascati.enea.it](mailto:tosti@frascati.enea.it) (S. Tosti).

<sup>1</sup> Tel.: +39 0984 492013; fax: +39 0984 402103.

<sup>2</sup> Tel.: +39 06 97273277; fax: +39 06 97273277.

time [11]. In fact, besides to the thermal cycling, the hydrogen absorption/desorption cycles involve a more significant elongation/contraction of the Pd alloy layers as compared to the support material. Tosti et al. have reported in a both theoretical and experimental paper [12] the study of the strains and stresses of the Pd–Ag layers deposited over the ceramic support of composite membranes.

Usually, a Pd–Ag dense membrane shows a very high permselectivity  $H_2$ /(other gas) and a moderate permeability. Different papers in literature are dealing with dense Pd-based membrane with an infinite hydrogen selectivity. In these cases, the relationship between the hydrogen permeability and the temperature is expected to be described by an Arrhenius law and the hydrogen permeation flow rate is proportional to the difference of the square root of the hydrogen partial pressure on both sides of the membrane and to the inverse of the membrane thickness (Sievert's law). Different authors report the values of the parameters present in the above equations for palladium alloy dense membranes [10,13–17].

Generally, the works present in the literature deal with short time experimental studies. The present work has the purpose of covering the lack of experimental data for long-term tests carried out on a Pd–Ag thin wall permeator under thermal and hydrogenation cycling.

In particular, permeator tubes with wall of thickness 50–60  $\mu\text{m}$  produced by diffusion welding of thin Pd–Ag foils [18] are proposed for their characteristics of an infinite hydrogen selectivity, a long duration and an acceptable cost as compared to the cost of other apparatus of energetic systems producing hydrogen. An economic analysis of an integrated system consisting of a membrane reformer producing hydrogen from ethanol reforming and a PEM fuel cell has been previously carried out [19]. The costs of membrane reactor made of Pd–Ag thin wall tubes resulted significantly lower than the cost of the fuel cell.

The chemical-physical stability of Pd–Ag thin wall tubes has been studied in a previous paper [20]. An increase of the hydrogen permeability through a Pd–Ag tube by a factor 2 has been observed during a 10-week test campaign.

Furthermore, the reduced thickness of the tube wall gives high hydrogen permeation fluxes according to the Sievert's law. The results of long-term permeability tests aimed at demonstrating the stability of the membrane selectivity are presented and discussed.

## 2. Experimental

### 2.1. Pd–Ag permeator tube

The thin wall permeator tube has been prepared starting from a Pd–Ag (with Ag 23 wt.%) foil of thickness 125  $\mu\text{m}$  furnished by Goodfellow. This metal foil has been cold-rolled in order to reduce its thickness down to 61  $\mu\text{m}$ ; then the foil has been annealed at 800  $^\circ\text{C}$  for 1 h under a reducing atmosphere (Ar with 5% of  $H_2$ ). The permeator tube has been obtained by joining the limbs of the metal foil via diffusion welding according to a previously described procedure [22]. Finally, the Pd–Ag tube of net length 148 mm has been joined to a steel tube and a steel plug

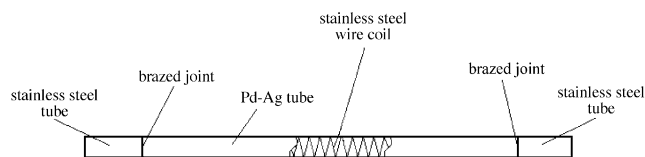


Fig. 1. Scheme of the permeator tube.

by brazing. In this way the permeator has the stiffness needed to assure a tight assembly into the membrane module. Fig. 1 shows a scheme of a thin wall permeator tube. It has been inserted into a Pyrex glass module, shown in Fig. 2, by using a finger-like configuration. An end of the membrane tube is closed by the brazed steel plug and the retentate stream is withdrawn via a small steel tube placed inside the membrane. Accordingly, the thin wall Pd–Ag tube is free in its expansion and contraction following the hydrogenation and thermal cycles. The absence of constrains between the membrane tube and the module avoids the presence of any mechanical (cyclic) stresses and assures a long lifetime. In fact, these stresses could involve formation of cracks and holes with loss of selectivity of the Pd–Ag tube. This configuration of the membrane module has been also studied in a Pd–Ag membrane reactor using a stainless steel module [23]. In a previous membrane module, both the ends of the permeator were connected to the module and the elongation of the Pd–Ag tube was compensated by using a flexible coupling [24].

### 2.2. Experimental apparatus

The experimental apparatus consists of a hydrogen generator, a nitrogen gas bottle, mass flow meter and controllers, pressure gauges, thermocouples and a heating system (see Fig. 3). The hydrogen stream feeding the membrane lumen is coming from the hydrogen generator Packard mod. 9400. It produces hydrogen by electrolyzing deionized water. The purity of the hydrogen produced has been verified by the gas chromatograph Chrompack mod. Micro GC using the columns CP-COX and Molsievies 5A. The GC analysis on the feed stream has shown the presence of very low percentages of oxygen and nitrogen into the hydrogen feed stream.

The nitrogen coming from a gas bottle is sent to the shell side of the membrane module in order to recover the permeated



Fig. 2. The membrane module.

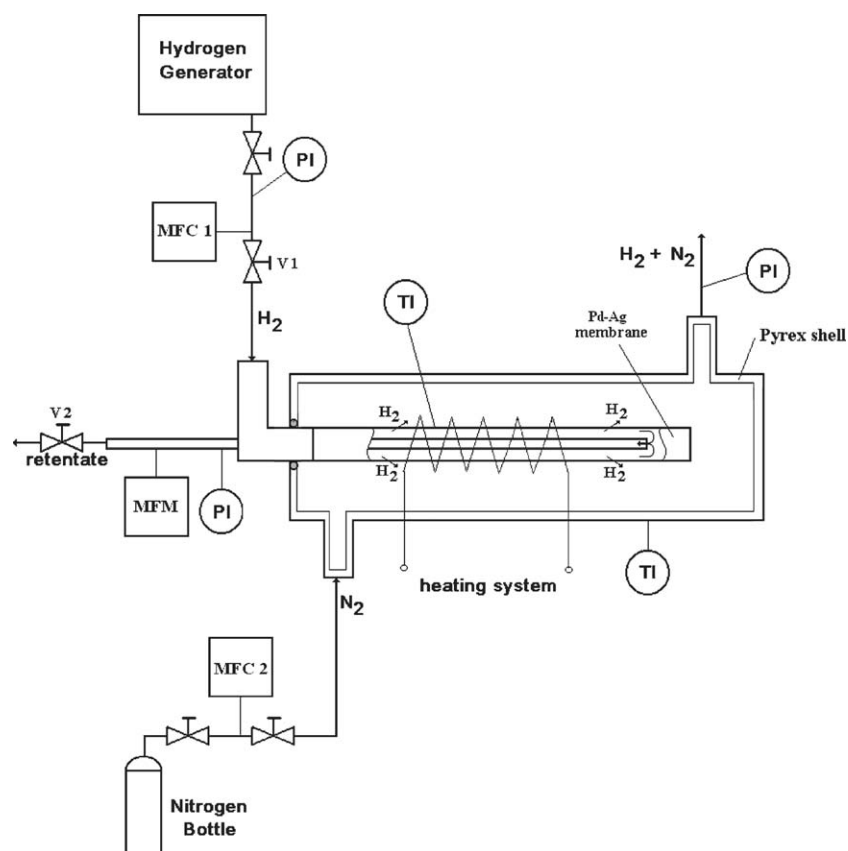


Fig. 3. Scheme of the experimental apparatus. MFC1 and MFC2, mass flow controllers; MFM, mass flow meter; V1, shut-off valve; V2, throttle valve; PI, pressure gauges; TI, thermocouples.

hydrogen. The mass flow controllers MFC1 and MFC2 regulate the hydrogen feed and nitrogen sweep streams, respectively. The mass flow meter MFM measures the retentate stream leaving the membrane lumen. This gas stream contains the non-permeated hydrogen and the impurities present in the feed. Three pressure gauges (PI) measure the pressure at the inlet and the outlet of the membrane tube and at the shell outlet; a shut-off valve (V1) is present on the hydrogen generator line while the throttle valve (V2) on the retentate line permits adjusting the pressure inside the membrane. Isothermal conditions are assured by a remote-controlled heating system based on a platinum coil wire wrapped around the membrane tube.

### 2.3. Membrane test

For a given temperature, the membrane tube has been characterized by measuring the transmembrane differential pressure under a controlled hydrogen feed flow rate. These tests have been performed by feeding a hydrogen stream inside the membrane (valve V1 opened, valve V2 partially closed). At steady state conditions, the hydrogen flow rate permeating through the membrane ( $F$ ) is given by the difference between the hydrogen stream fed inside the membrane ( $F_1$ ) regulated by the mass flow controller MFC1 and the hydrogen flow rate leaving the membrane tube ( $F_2$ ) measured by the mass flow meter MFM. With reference to the Sievert's law the hydrogen permeability through

the metal membrane is calculated by the formula:

$$Pe = \frac{Fd}{(\sqrt{P} - \sqrt{P_{shell}})A} \quad (1)$$

where  $Pe$  is the hydrogen permeability ( $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}$ ),  $F$  the hydrogen permeating flow rate ( $\text{mol s}^{-1}$ ),  $d$  the wall tube thickness (m),  $P$  the hydrogen pressure inside the membrane (Pa),  $P_{shell}$  the hydrogen partial pressure in the shell side (Pa), and  $A$  is the permeation surface area ( $\text{m}^2$ ).

In the formula (1) the pressure inside the membrane ( $P$ ) adjusted by means of the throttle valve (V2) has been directly measured by the pressure gauge, while, the hydrogen partial pressure in the shell side has been obtained by the calculation:

$$P_{shell} = P_T \frac{F}{F_{N_2} + F} \quad (2)$$

where  $P_T$  is the total pressure in the shell side (Pa) and  $F_{N_2}$  is the sweep gas nitrogen flow rate ( $\text{mol s}^{-1}$ ).

The membrane has been characterized in the temperature range of 150–400 °C with the hydrogen pressure inside the membrane of 100–200 kPa. The hydrogen permeating flow rates measured are varied from  $5.48 \times 10^{-5}$  to  $2.52 \times 10^{-4} \text{ mol s}^{-1}$ . In our experiments the hydrogen is recovered in the shell side by a stream of nitrogen with a flow rate of  $7.44 \times 10^{-4} \text{ mol s}^{-1}$  operating at atmospheric pressure.

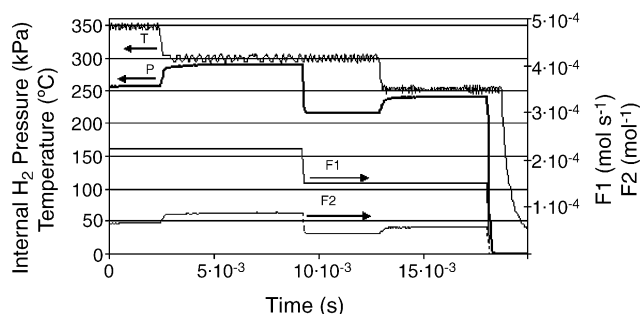


Fig. 4. Graph of a typical permeation test.

### 3. Results

During testing, the behaviour of the membrane has been investigated by varying either the temperature or the flow rate of the hydrogen feed stream. In Fig. 4, an example of a permeation test was reported. Starting with the hydrogen feed flow rate (F1) of  $2.24 \times 10^{-4}$  the initial temperature of 350 °C is decreased to 300 °C, and then the hydrogen feed flow rate was lowered to  $1.5 \times 10^{-4}$ . Finally, the temperature was set at 250 °C. Accordingly, both the internal pressure  $P$  and the retentate stream (F2) were increasing with the temperature drop. At the end of the permeation experiment the selectivity of the membrane tube was demonstrated by means of a tightness test. Correspondingly, both valves V1 and V2 were closed maintaining the high temperature and purging continuously the shell side with nitrogen. As shown in Fig. 4, the pressure inside the Pd–Ag was quickly decreasing close to zero as a consequence of the hydrogen permeation through the membrane into the shell where the hydrogen partial pressure was maintained at a low level by the sweep gas (nitrogen). The absence of cracks and holes was verified by observing the constant low value of the pressure inside the membrane.

The results of the permeation tests carried out at different temperatures were used for evaluating the hydrogen permeability according to formula (1). In the graph of Fig. 5, the permeability data collected during the experimental campaign are reported versus the inverse of the absolute temperature as indicated by

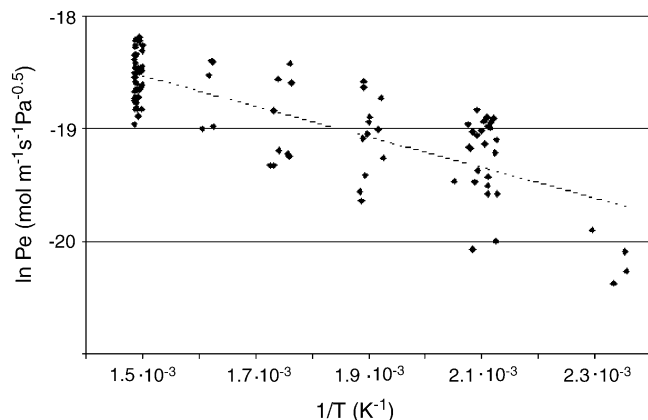


Fig. 5. Arrhenius plot of the permeability data.

Table 1

Apparent activation energy and pre-exponential factor: comparison with the literature

$E_a$ (kJ mol <sup>-1</sup> )	$Pe_0$ ( $\times 10^{-5}$ mol m <sup>-1</sup> s <sup>-1</sup> kPa <sup>-0.5</sup> )	Reference
11.24	0.21	This work
33.31	1.66	[10]
29.73	7.71	[13]
15.70	2.19	[14]
15.50	2.54	[15]
18.45	1.02	[16]
12.48	0.38	[17]

the Arrhenius law:

$$Pe = Pe_0 e^{-E_a/RT} \quad (3)$$

where  $Pe_0$  is the pre-exponential factor (mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-0.5</sup>),  $E_a$  the apparent activation energy factor (kJ mol<sup>-1</sup>),  $R$  the gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is the absolute temperature (K).

Table 1 compares the experimental results in terms of  $Pe_0$  and  $E_a$  of this work with recent results present in literature. It can be seen that both  $Pe_0$  and  $E_a$  are in the range of the literature data. In particular, the results of this work are close to the ones of Itoh and Xu [17].

The analysis of the experimental data shows a larger spread of the permeability values at low temperature and, particularly, at 150 °C the hydrogen permeability through the palladium–silver alloy is equal or lower than  $2.0 \times 10^{-9}$  mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-0.5</sup>.

The scatter of the experimental data shown in Fig. 6 are the consequence of poisoning effects due both to the manufacturing procedure (rolling, brazing) and the exposure of the membrane to the laboratory air (CO, CO<sub>2</sub>, etc.) when the membrane tube was removed from the module. Especially, the spread of the permeability data is higher at temperatures below 200–250 °C, accordingly to the literature on this issue [20,21].

Furthermore, during testing the Pd–Ag membrane tubes modify their surface structure and an increase of the hydrogen permeability may be resulted as reported in a previous work [20].

On the other hand, the permeability values measured in the temperature range of 350–400 °C are about  $1.0 \times 10^{-8}$  mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-0.5</sup> according to the literature [10,13–17].

As an important result, over the 12 months of testing the hydrogen selectivity was verified. The reliability of the Pd–Ag permeator is mainly due to both the manufacturing procedure



Fig. 6. Pd–Ag thin wall permeator tubes: as produced (above) and after testing (below).



and the adopted membrane module design. Particularly, the finger-like assembly of the permeator tube permits its free elongation and contraction. In Fig. 6 the Pd–Ag tube after testing (below in the picture) is compared with a tube before testing (above). The permeator tube, as a consequence of the hydrogenation and thermal cycles, has significantly changed its geometry despite the fact that has maintained its complete hydrogen selectivity.

#### 4. Conclusions

Via diffusion welding of thin Pd–Ag foils a permeator tube was manufactured. A long-term experimental campaign aimed at demonstrating its high hydrogen permeability and durability was carried out.

The tests were performed in a wide range of temperature (150–400 °C) and hydrogen pressure (100–400 kPa) in order to verify the applicability of such permeators in processes for producing pure hydrogen from hydrocarbons (i.e. reforming and partial oxidation).

At temperatures between 150 and 200 °C, a poor reproducibility of the measurements as well as low permeability values ( $2.0 \times 10^{-9} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ ) were observed. Nevertheless, at higher temperature, 350–400 °C, hydrogen permeability values around  $1.0 \times 10^{-8} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$  have been measured comparably with the literature data.

Furthermore, the long-term tests performed over a 12-month period have confirmed the capability of the thin wall permeator tube to produce high purity hydrogen. In fact, the complete hydrogen selectivity and none failure (formation of cracks, holes) were observed. This reliability is a result of both the tube manufacturing procedure and the reactor design configuration (finger-like). This arrangement presents no constraints between the permeator tube and the membrane module. In fact, in this case the Pd–Ag elongation or contraction under hydrogen loading and thermal cycling can take place without excessive mechanical stresses.

This work has demonstrated both the high hydrogen permeability and the long duration of Pd–Ag thin wall permeator tubes. These characteristics together with the reduced costs make this technology ready for producing highly pure hydrogen in energetic and industrial applications (PEM fuel cells and automotive systems, chemical industry, etc.). In the past Pd–Ag thin walled tubes have used to construct membrane reactors for the water gas shift and, recently, in our group these permeators are being tested in membrane reformers producing hydrogen from ethanol.

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