# Electrical resistivity and linear expansion of a hydrogenated Pd/Ag permeator tube

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**Abstract.** The Pd-Ag-H system is of particular importance with respect to the separation and purification of the hydrogen gas. Pd-Ag alloys have high selectivity for hydrogen gas permeation and thus are suitable for manufacturing hydrogen selective membranes. Accordingly, among the technological properties many authors have studied the electrical resistivity and linear expansion of the Pd-Ag-H system, but no data are available in a wide range of temperature and hydrogen pressure. During this activity, the solubility, the linear expansion, the resistivity and the permeability of a Pd/Ag (with Ag 25% wt) permeator tube has been measured in both hydrogenated and non-hydrogenated conditions. The experiments have been carried out in a temperature and in a lumen hydrogen partial pressure range of 50-400 °C and 0-400 kPa, respectively.

## 1. Introduction

Hydrogen selective membranes are important for technological processes such as separation of hydrogen from gaseous mixtures, purification of hydrogen for fuel cell applications and chemical reactions in membrane reactor [1]: they are even used in hydrogen isotope storage, extracting, purification and separation processes [2].

Palladium membranes have been development for ultra-pure hydrogen separation because of their high selectivity. However, they have problem of hydrogen embrittlement, a phenomena in which dissolved hydrogen tends to cause an elongation of the metal lattice as a consequence of the hydrogen uploading thus leading to the membrane failure after repeated thermal and hydrogenation cycles. In order to avoid the embrittlement, alloying of Pd with group IB metals such as silver is generally made. Another advantage of alloying is that the mechanical strength in pure hydrogen atmosphere is higher [3]. In general, a Pd-membrane becomes brittle after certain cycles of $\alpha \rightarrow \beta$ transformations due to the accompanied lattice expansion. For example in palladium-silver alloys, the lattice has already been expanded by the silver atoms, and the Pd-Ag lattice is less influenced by hydrogen uploading and then less brittle than the pure Pd lattice [4]. An optimal value of the hydrogen permeation rate is reached for a silver content around 25 wt. %.

During this activity the electrical resistivity and the linear expansion of a 25 % wt Pd/Ag permeator tube has been measured under both hydrogenated and non-hydrogenated conditions. The experimental measurements have been carried out in a temperature and in a lumen hydrogen partial pressure range of 50-400°C and 0-400 kPa, respectively.

## 2. Experimental

A Pd-Ag tube of wall thickness 200 μm and length of 12.8 cm has been produced by extrusion. The hydrogen permeator has been obtained by joining via brazing at the ends of the Pd-Ag tube a stainless steel tube and a steel plug. The obtained permeator was assembled inside a membrane module in a finger like configuration (Fig. 1): the membrane tube was gas tight fixed to one end of the module in order to permit its elongation and contraction due to the hydrogenation cycles. In this way, any mechanical stress on the thin wall tube was avoided. In the finger like configuration the feed stream entered the membrane lumen via a stainless steel tube inserted inside the Pd-Ag membrane.

The experimental apparatus used to characterize the membrane is shown in the scheme of figure 2. A mass flow controller sends the hydrogen feed stream into the lumen side, while a nitrogen flux of 500 N cm$^3$ min$^{-1}$ is used as sweep gas in the shell side. The membrane module is heated by a direct current supply system; the elongation and the resistivity are measured with an optical microscope and a multimeter, respectively.
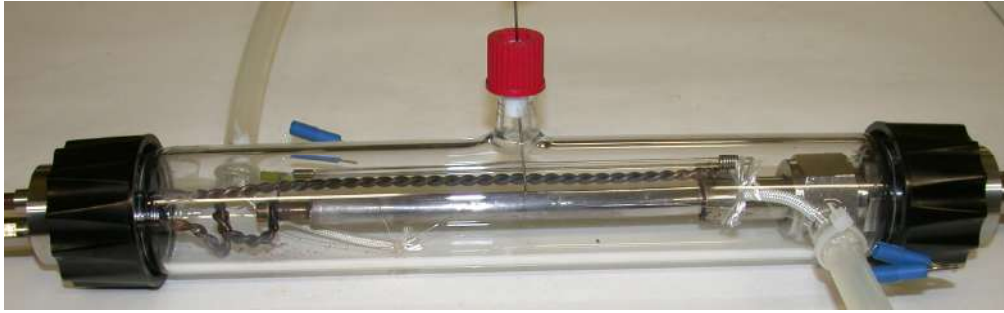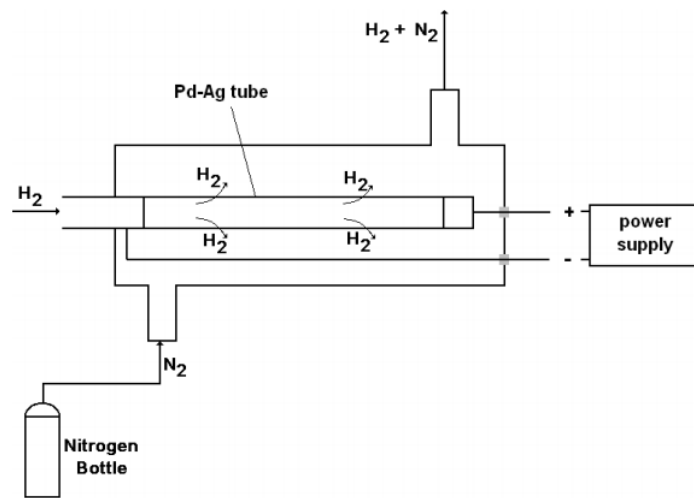
**Fig. 1**. - Pd-Ag permeator tube.



**Fig. 2.** - Scheme of the experimental apparatus.

## 3. Results and discussion

*3.1 Hydrogen Solubility*
The hydrogen solubility, in the investigated operative conditions, has been assessed by applying the Sieverts' law:

$$S = K_s p^{0.5} \qquad (1)$$

where $K_s$ [5] is the solubility constant:

$$K_s = 0.182 \exp\left(\frac{19598}{RT}\right) \qquad \text{(mol m}^{-3}\text{ Pa}^{0.5}\text{)} \qquad (2)$$

and p the hydrogen partial pressure into the metal lattice, assessed as the arithmetic mean between the hydrogen partial pressure in the lumen side ($p_{H2,\,lumen}$) and the hydrogen partial pressure in the shell side ($p_{H2,\,shell}$).

In figure 3 the effects of temperature and hydrogen lumen pressure on the solubility are reported. By increasing the temperature, the hydrogen solubility decreases for all the hydrogen lumen pressures investigated, although the solubility gap between the various lumen pressures is much larger at low temperature. Particularly, these results show that the hydrogen loading into the Pd-Ag membrane significantly occurs below 150-200 °C where the hydrogen permeation is quantitatively modest as reported below (section 3.4).
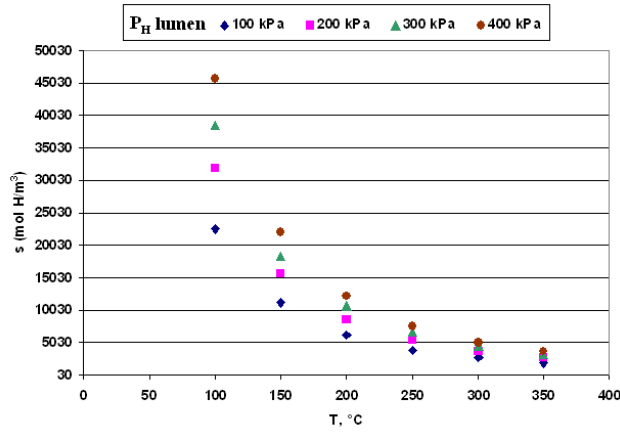
**Fig. 3.** - Hydrogen solubility in Pd-Ag membrane versus temperature for different hydrogen lumen pressure.

## 3.2 Linear Expansion

To measure the linear expansion of the membrane a metal cylinder sustained in a pyrex tube has been attached on the free-end of the membrane: the metal cylinder was able to move inside the pyrex tube. In this way the movement of the metal cylinder followed the elongation of the membrane, while the pyrex tube having negligible thermal expantion coefficient has been used as a reference. An optical microscope fixed on the described experimental apparatus has been used to measure the displacement of the metal cylinder, i.e. the linear expansion of the membrane. Figure 4 represents a particular of the experimental set-up viewed by the microscope.
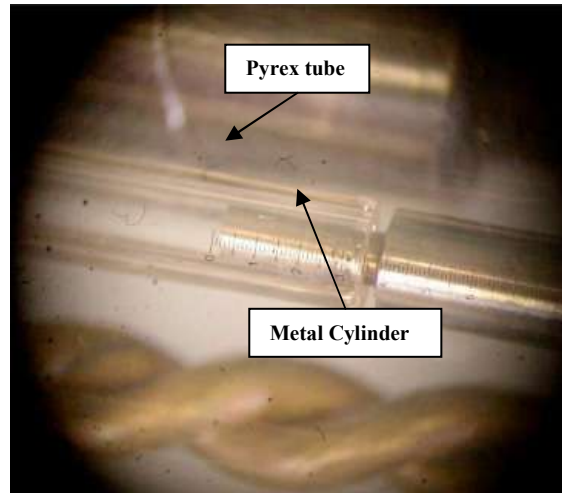


**Fig. 4.** - Particular of the membrane viewed by the optical microscope.

Figure 5 described the linear expansion ε of the Pd-Ag membrane in different conditions.

$$\varepsilon = \frac{\Delta l}{l_0}$$

(3)

Where Δl is the difference between the final and the initial ($l_0$) length of the membrane tube.

In particular the linear expansion can be considered by the sum of two contributions: the thermal and the hydrogen uploading contribution. In order to put into evidence these contributions, in figure 5 the grey points are referring to the linear expansion measured under nitrogen atmosphere (hydrogen partial pressure equal to zero), that means only thermal contribution, while the other points are related to the total linear elongation (both thermal and loading contribution).
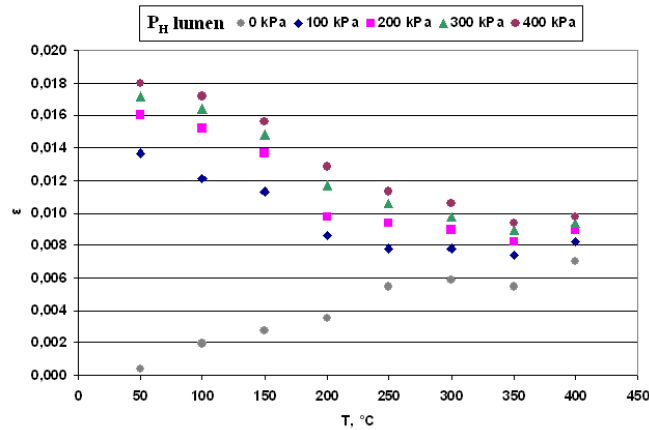
**Fig. 5.** - Linear elongation of the Pd-Ag membrane tube in a temperature range between 50-450 °C at different lumen hydrogen partial pressures, from 0-400 kPa.

According to the literature, the linear expansion related to the thermal contribution increases by increasing the temperature: in particular at 50 °C the elongation is almost zero, while at 400 °C it is about 0,7%. Under the hydrogenated conditions, the linear elongation decreases by increasing the temperature for each lumen hydrogen partial pressure investigated. Even in this case the gap between the measurements at low temperature is larger than the gap related to the measurements at high temperatures, in particular at 400 °C the gap is almost negligible.

This phenomenon agrees with the assessed hydrogen solubility values: at low temperature maximum hydrogen solubility (uploading) corresponds to the maximum elongation.

### 3.3 Electrical Resistivity

The electrical resistivity is a Pd-Ag property alloy affected by the hydrogen loading: measurements of this parameter have been carried out under different hydrogenation conditions and temperatures. A DC current has been applied to the ends of the membrane tube through a power supply (HP 6573A) while a multimeter (HP 3458A) has been used in order to measure the voltage in different points of the membrane. The electrical resistivity has been then assessed via the Ohm law.

The connection between the multimeter and the membrane has been realized with Pt wires attached on the membrane surface (Fig. 6).
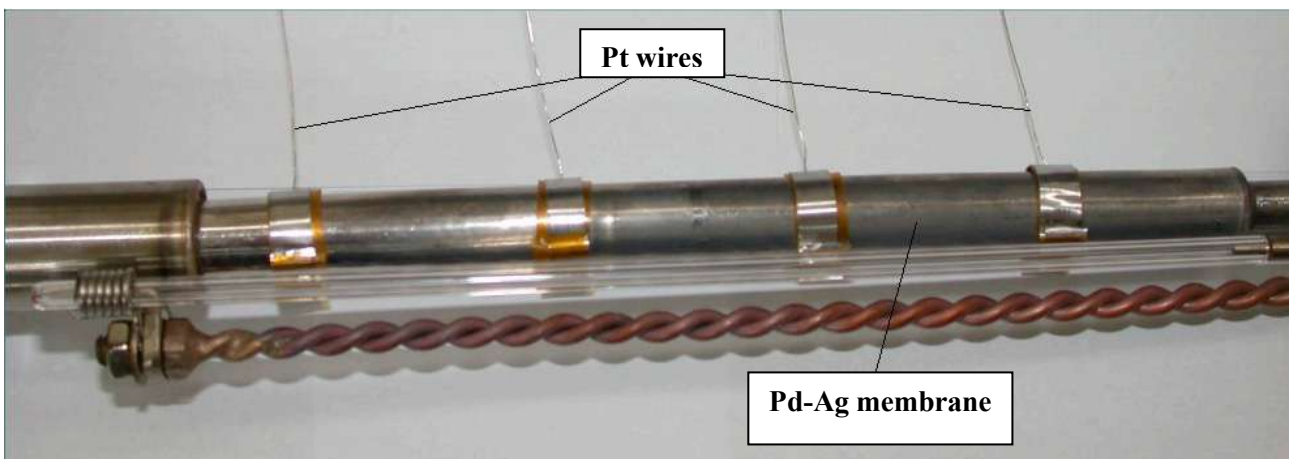


**Fig. 6.** - Particular of the palladium wires attached onto the membrane surface for the resistivity measures.

Figure 7 reports the values of the Pd-Ag electrical resistivity in the range temperature between 100 and 400 °C, for different lumen hydrogen partial pressure. Especially, for a given temperature the electrical resistivity values change slightly for the hydrogenated material.
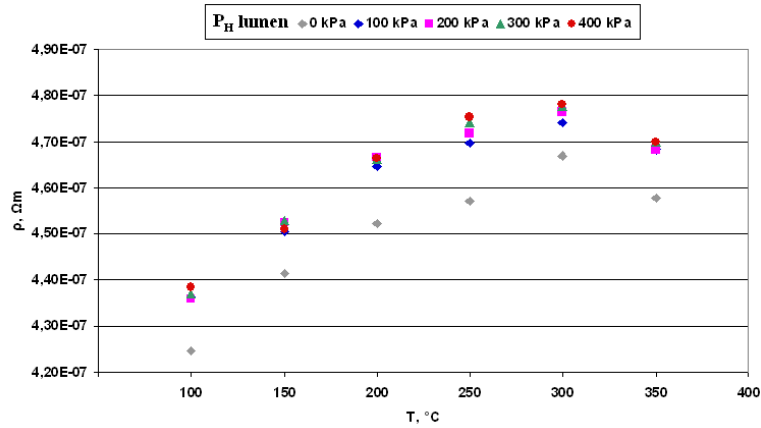
**Fig. 7.** - Pd-Ag electrical resistivity in temperature range between 100-400 °C
for different lumen partial hydrogen pressure.

*3.4 Hydrogen Permeability*

Permeation tests of the Pd-Ag tube have been carried out under controlled temperature and transmembrane differential pressure conditions: pure hydrogen was fed in the lumen side in the pressure range between 100-400 kPa, while the hydrogen permeated through the membrane was collected in the shell side at atmospheric pressure by a nitrogen stream of 500 Ncm$^3$ min$^{-1}$, the investigated temperature range was 100-400 °C.

The hydrogen permeability through the Pd-Ag membrane was calculated by the formula:

$$Pe = \frac{Fd}{(\sqrt{p_{H_2,lumen}} - \sqrt{p_{H_2,shell}})A} \tag{4}$$

where Pe is the hydrogen permeability (mol m$^{-1}$ s$^{-1}$ Pa$^{0.5}$), F is the hydrogen permeating flow rate (mol s$^{-1}$), d the wall tube thickness (m), $p_{H2,lumen}$ the hydrogen pressure inside the membrane (Pa), $p_{H2,shell}$ the hydrogen partial pressure in the shell side (Pa), and A is the permeation surface area (m$^2$).

The permeability data have been collected according to the Arrhenius law:

$$Pe = Pe_0 \exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

where *Pe* is the hydrogen permeability, *Pe$_0$* the pre-exponential factor, *E$_a$* the activation energy, *R* the gas constant and *T* the absolute temperature.

By considering the hydrogen permeability values reported in figure 8, there are some considerations to underline. In fact, the activation energy (that can be visualized by the slope of the permeability values line) presents two different values, as reported in table 1. In particular the activation energy at low temperature is higher than the activation energy at high temperature thus meaning that significant hydrogen permeation through the membrane can occur only at temperature over 200 °C. As another important result, despite of the large membrane wall thickness (200 µm) the high hydrogen permeation fluxes measured demonstrated the applicability of such a membrane tube for separating ultra pure hydrogen in laboratory and industrial processes.

**Table 1.** Hydrogen permeability through Pd-Ag.

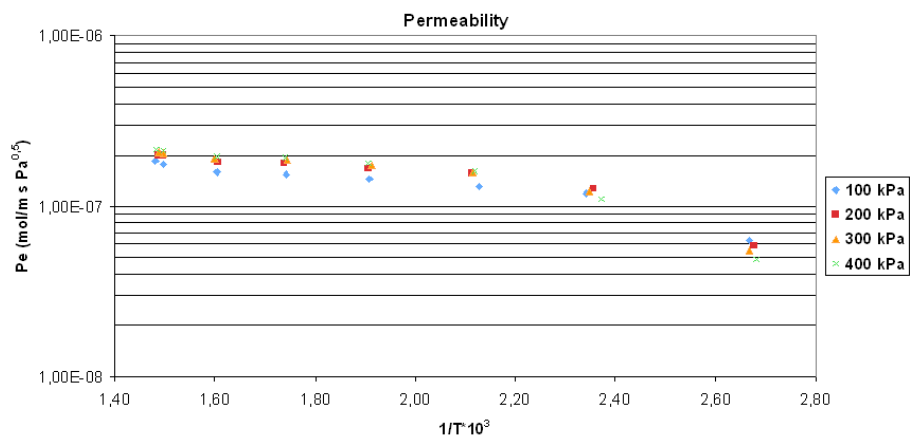| Temperature, K | Pressure, kPa | Pe$_0$, mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$ | E$_a$, kJ mol$^{-1}$ |
|---|---|---|---|
| 373-423 | 100-400 | 3.38×10$^{-5}$ | 19.7 |
| 474-673 | 100-400 | 3.43×10$^{-7}$ | 3.4 |

**Fig. 8.** - Hydrogen permeability though Pd-Ag.

## 4. References

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