WORKSHOP "Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells"

Development of novel Pd-alloy membranes based on improved supports

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CIEMAT

CONTENTS:

Properties and critical parameters

Supported Pd –based membranes for H2 selective separation

Preparation of supports and selective layers:

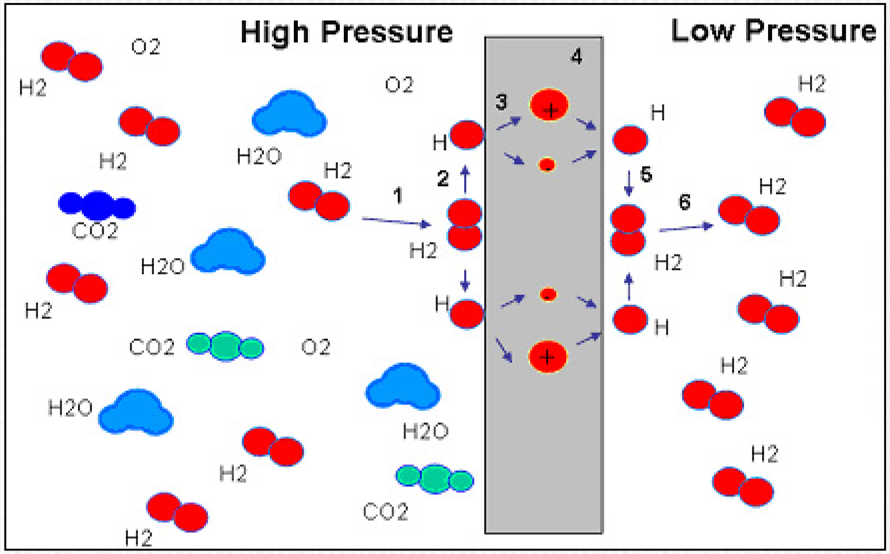
- *Calcination*
- *Dip-coating*
- *ELP*
- *Magnetron Sputtering*

First results: membrane thickness and deffect-free supports

Dense metallic membranes

Pd-based DENSE membranes

- Solution-diffusion mechanism of atomic hydrogen
- Catalytic activity for dissociation and re-associaton of molecular H_2
- Theoretically infinite selectivity
- No energy consumption



- Discovery: Graham (1866)
- First patents: PdAg (1956), PdRu (1966) PdCu and PdAu (1967-1969)

➢ Metallurgical methods (self-supported membranes)

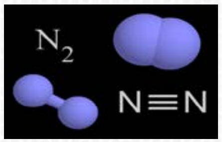
- Supported membranes: first steps Uemiya (1990)
  - ➢ Substrate (Ceramic, Methallyc)
  - ➢ Geometry (planar, cylindrical)
  - ➢ Composite (multiple layers)
  - ➢ Thin selective film self-supported on top of support

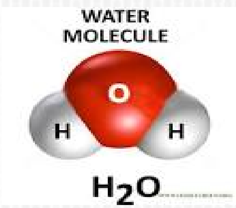
TWO MAIN PROPERTIES:

- PERMEABILITY: High H2 flux
- SELECTIVITY: Only H2

Dense supported metallic membranes

Effects of concomitant species in the gas mixtures





Hurdles

Adsorption

Depletion

Deactivation

Polarisation

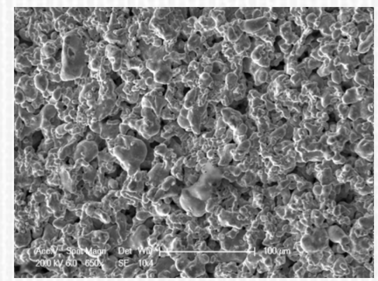
Undesired Reactions

REDUCE PERMEABILITY

Effects of presence of Defects

During fabrication

During operation

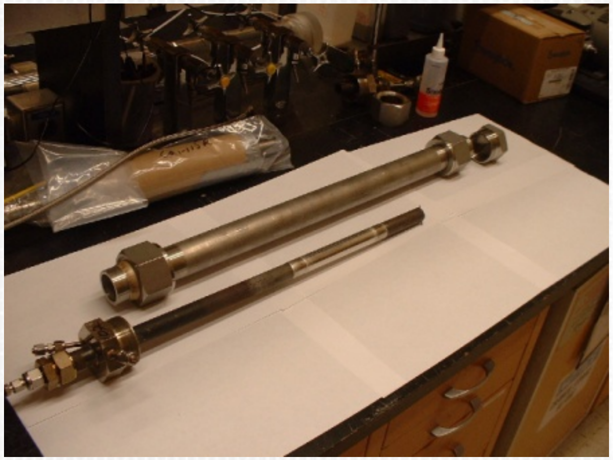


Causes:

- Intermethalic diffusion
- Shear stress
- Thermal or mechanical failure

REDUCE SELECTIVITY

Dense metallic membranes
Previous works at Ciemat



Semi commercial membranes
CHRISGAS project

Membrane
Dense Pd layer over porous SS support
Tubular O.D. =2,54 cm; L= 15 cm
Membrane surface area: 0.01216 m^2
Welded to a SS-316 tube
Membrane-tube assembly L=70 cm
Independent oven

Feeding system:
MFC H_2 (5 l/min), N_2 (15 l/min), CO (5 l/min), CO_2 (5 l/min), H_2O (25 cc/min)
Gas preheater +Vaporiser
MFMs Permeate & Retentate
Cooling & Venting System
PCVs Permeate & Retentate
Gas Analysis: Micro-GC

ELP membranes
HENRECA project

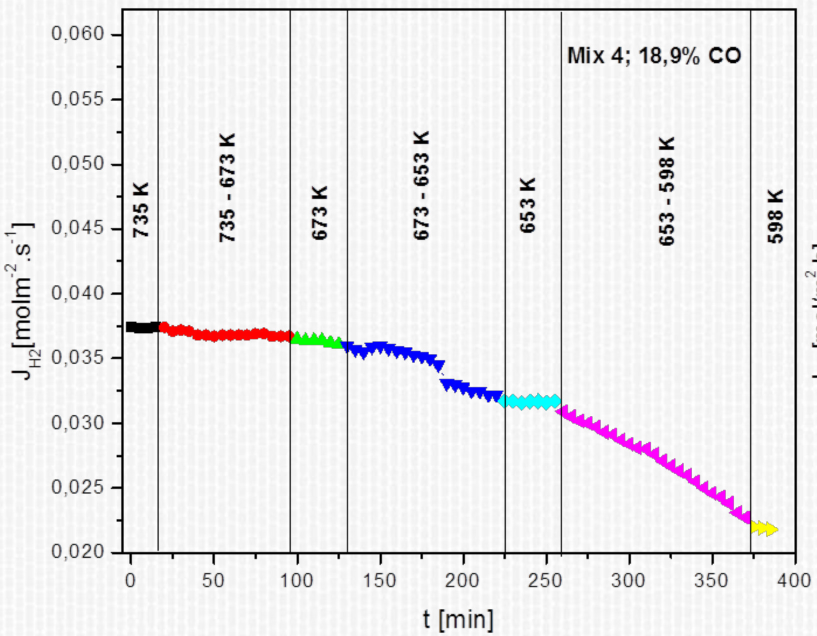
Membranes
Dense Pd layer over porous SS support
Tubular O.D. = 1,25 cm; L= 15 cm
Membrane surface area: 0,00319 m2
Welded to a SS-316
Independent oven

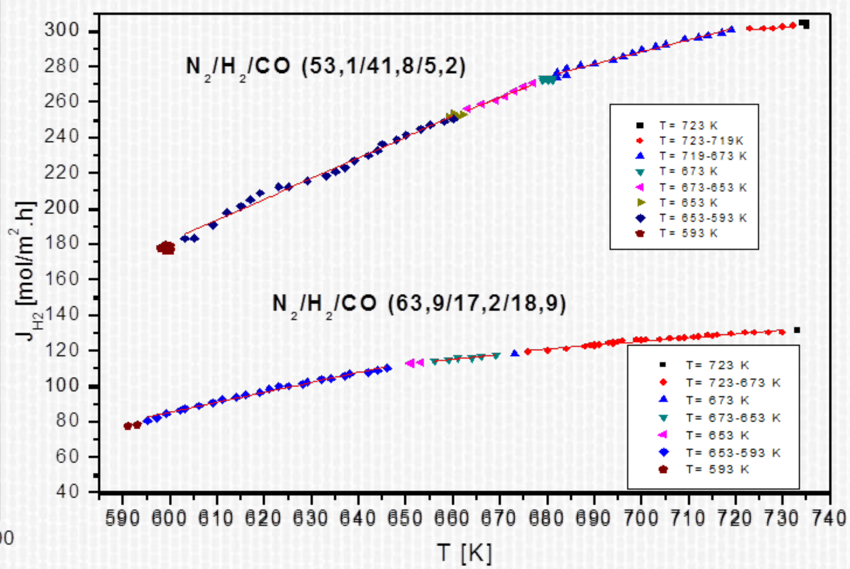
Previous work:
- Barreiro, M.M.; Maroño, M.; Sánchez, J.M., Applied Thermal Engineering 74 (2015) 186-193
- J.M. Sánchez, M.M. Barreiro, M. Maroño, Fuel 116 (2014) 894-903
- M. Maroño, J.M. Sánchez-Hervás, E. Ruiz, International Journal of Hydrogen Energy 35 (2010) 37-45

Dense metallic membranes. Semi-commercial membrane. Previous works at Ciemat

In completely selective Pd membranes effect of concomitant species reduces H2 permeation

H_2 permeation in presence of carbon monoxide





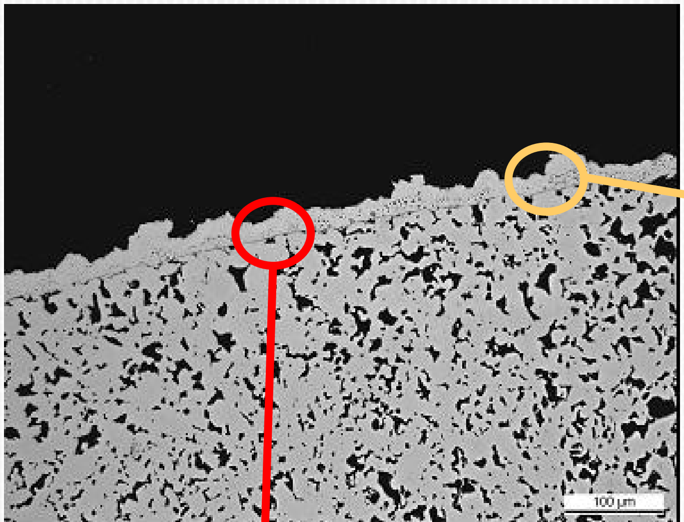
Temperature, however, has a significant effect on hydrogen permeation

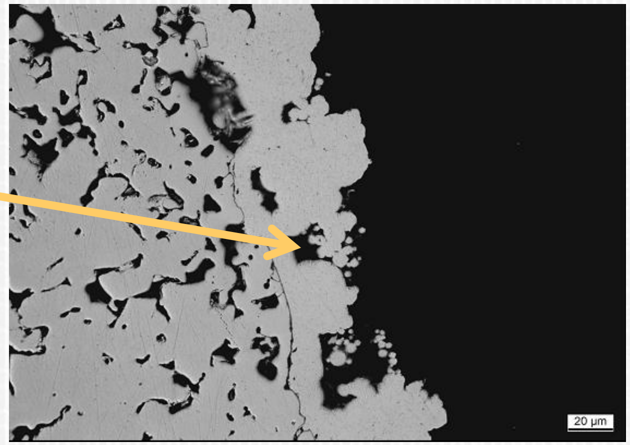
Drop in H_2 permeation particularly noticeable when temperature was lowered from 653 K to 593 K

Absence of secondary reactions: The analysis of the retentate stream was very stable at all temperatures

It is reversible. When subjected to pure hydrogen, permeation is fully restored.

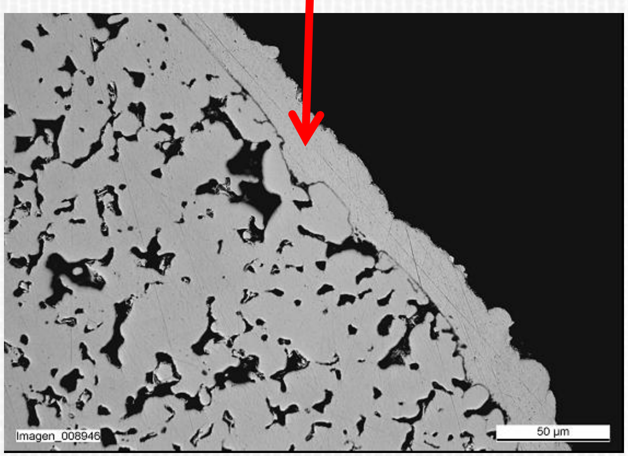
Dense metallic membranes. Direct deposition of Pd by ELP. Previous works



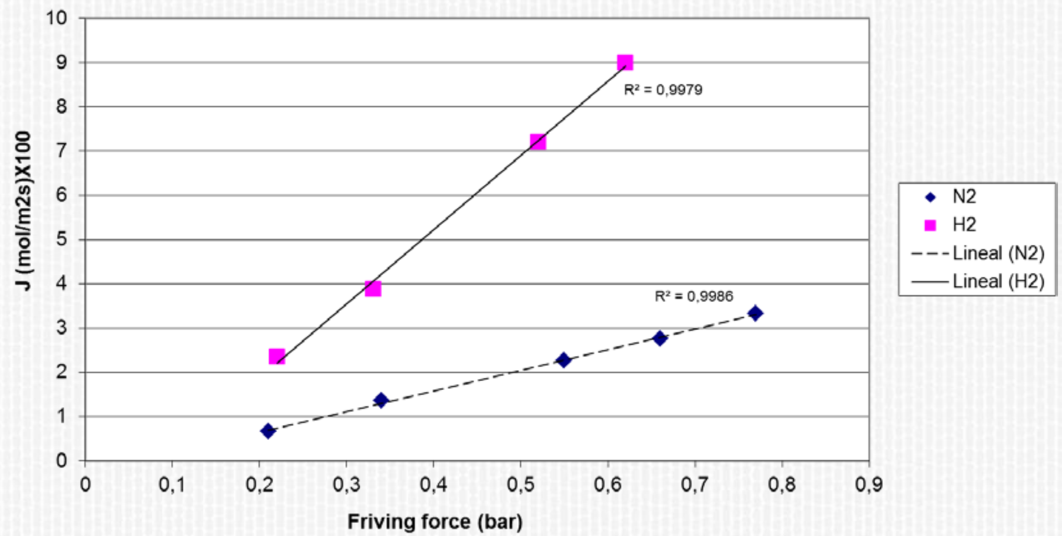


Presence of DEFECTS

Causes significant losses in selectivity

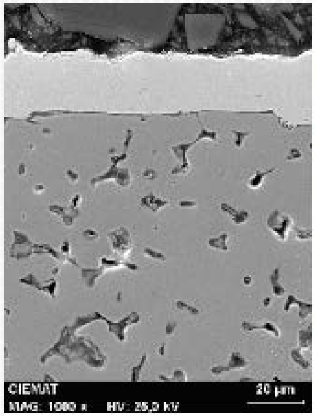


H_2 and N_2 flux at 320 ºC. Gas feed flow: 750 ml/min

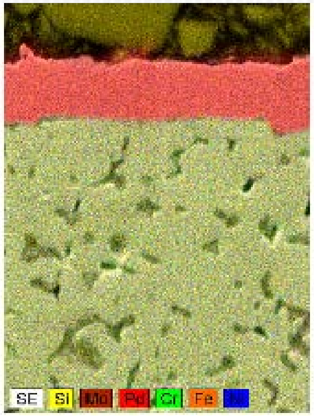


Dense metallic membranes. Direct deposition of Pd by ELP. Previous works

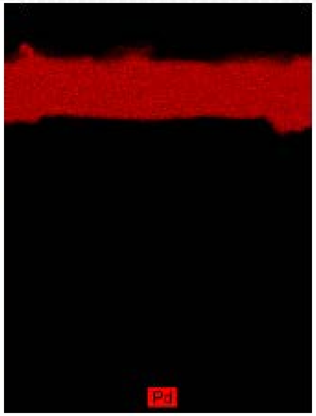
Intermethallic diffusion of support components



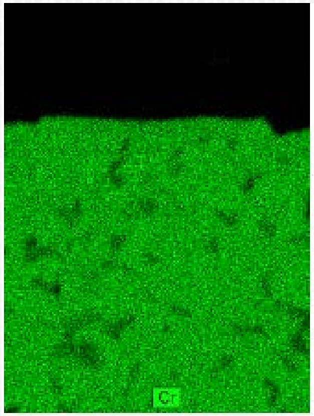
Mapping-x1000-1.jpg



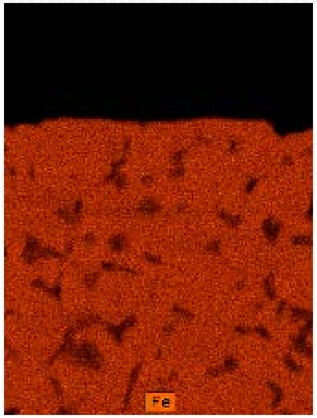
Mapping-x1000-All elements.jpg



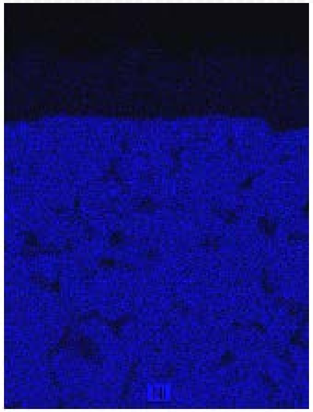
Mapping-x1000-Pd.jpg



Mapping-x1000-Cr.jpg



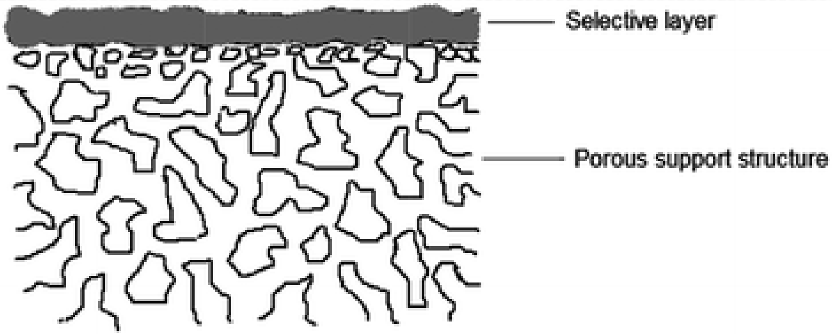
Mapping-x1000-Fe.jpg



Mapping-x1000-Ni.jpg

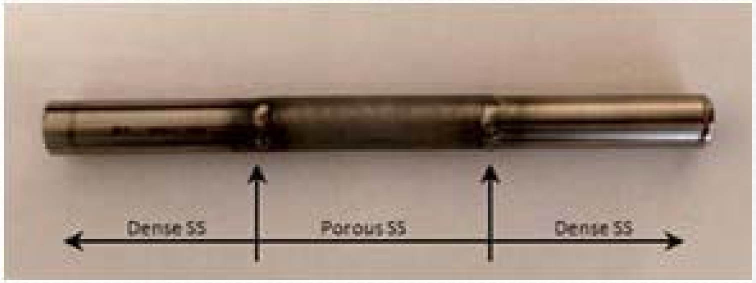
<u>SEM analysis:</u>

Suitable tool for identifying problems of intermethallic diffussion



Supported Pd –based membranes for H2 selective separation. New Developments : Types of Supports

Metallic supports: Tubular

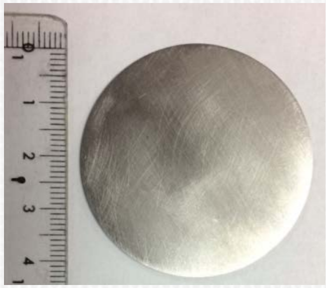


- 0.1-0.2 µm SS316
- Provided by Mott corp.
- Diameter: 0,5 in
- Welded to dense SS tubes

Ceramic supports

- 0,1 µm Al_2O_3 / 15 nm ZrO_2
- Provided by CTI SA
- Diameter: 10 mm
- Glazed ends

Metallic supports: Planar



- 0.1 µm SS316
- Provided by Mott corp.
- Diameter: 1,7 in

Supported Pd –based membranes for H2 selective separation Methods

Support preparation

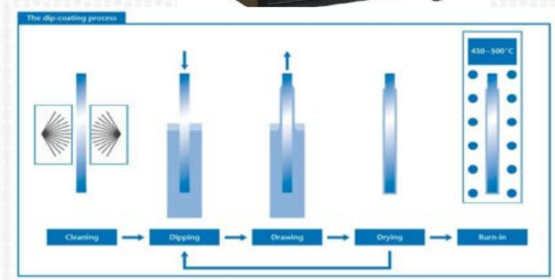
Selective layer deposition

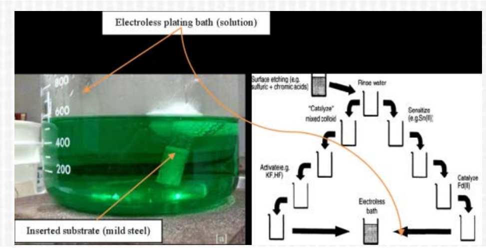
Calcination

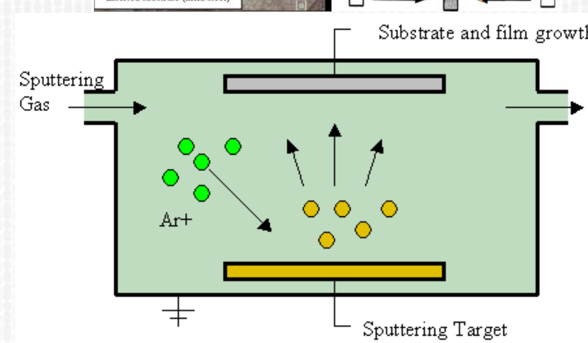
Dip-coating

ELP-PP

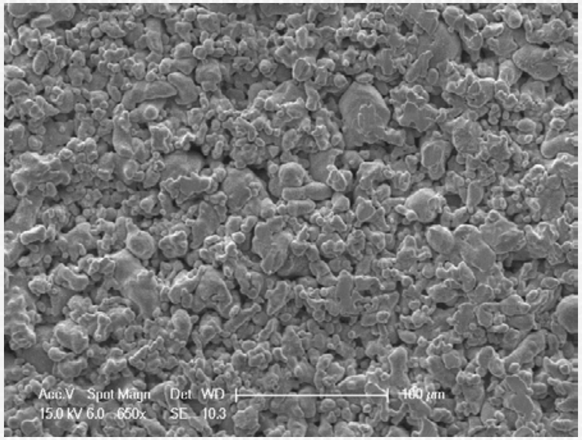
Magnetron Sputtering







Preparation of supports: CALCINATION



Oxides form a very thin layer that mimics that of the support surface but reduction of total permeation through the pores of the support is observed.

Calcination temperature is critical to keep a minimum required flow (DOE values) → 600°C

Pieza	T (°C)	ΔP (bar)	J_{N_2} (mol/m²s)	J_{H_2} (mol/m²s)	α_{H_2/N_2}	$\downarrow\Delta J_{N_2}$ (%)	$\downarrow\Delta J_{H_2}$ (%)
PSS-01	-	0,5	0,30	0,79	2,7	-	-
		1,0	0,72	1,78	2,5	-	-
PSS-01-550	550	0,5	0,21	0,59	2,9	29	25
		1,0	0,49	1,37	2,8	32	23
PSS-01-600	600	0,5	0,12	0,31	2,7	59	61
		1,0	0,27	0,73	2,7	62	59
PSS-01-650	650	0,5	0,09	0,25	2,7	70	68
		1,0	0,21	0,57	2,7	71	68

Supported Pd –based membranes for H2 selective separation

Electroless Plating technique for Pd deposition

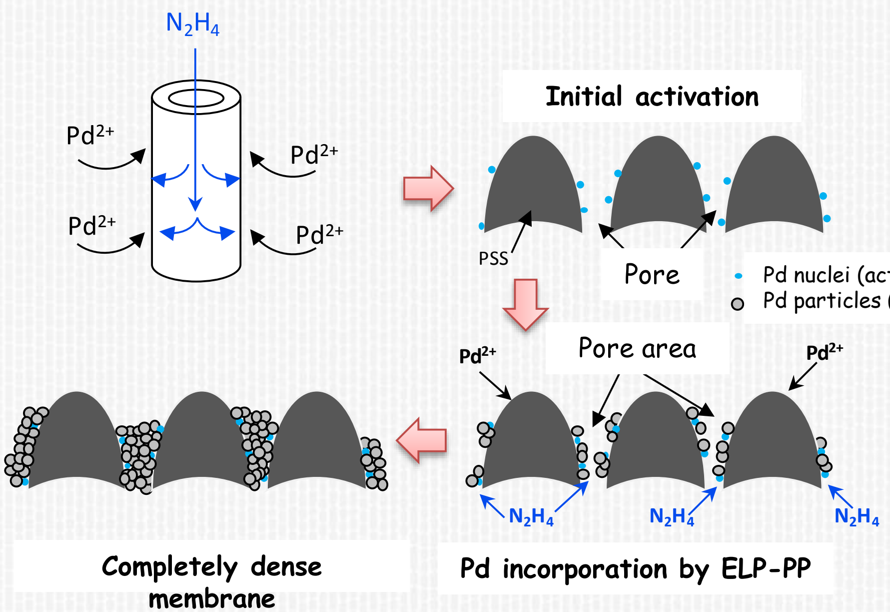
Reactions involved in ELP-PP process

$$2\,Pd(NH_3)_4^{2+} + 4\,e^- \rightarrow 2\,Pd^0 + 8\,NH_3 \qquad \text{R. Reducción}$$

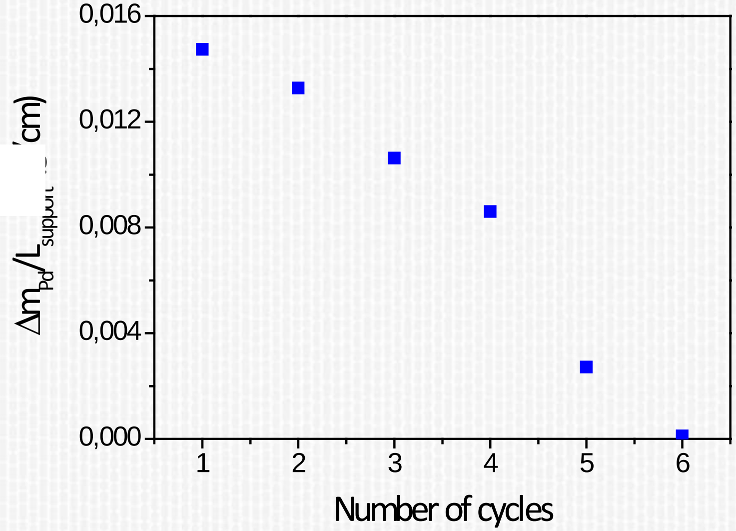
$$N_2H_4 + 4\,OH^- \rightarrow N_2 + 4\,H_2O + 4\,e^- \qquad \text{R. Oxidación}$$

$$2\,Pd(NH_3)_4^{2+} + N_2H_4 + 4\,OH^- \rightarrow 2\,Pd^0 + 8\,NH_3 + \uparrow N_2 + 4\,H_2O \qquad \text{R. Global}$$

ELP-PP process scheme



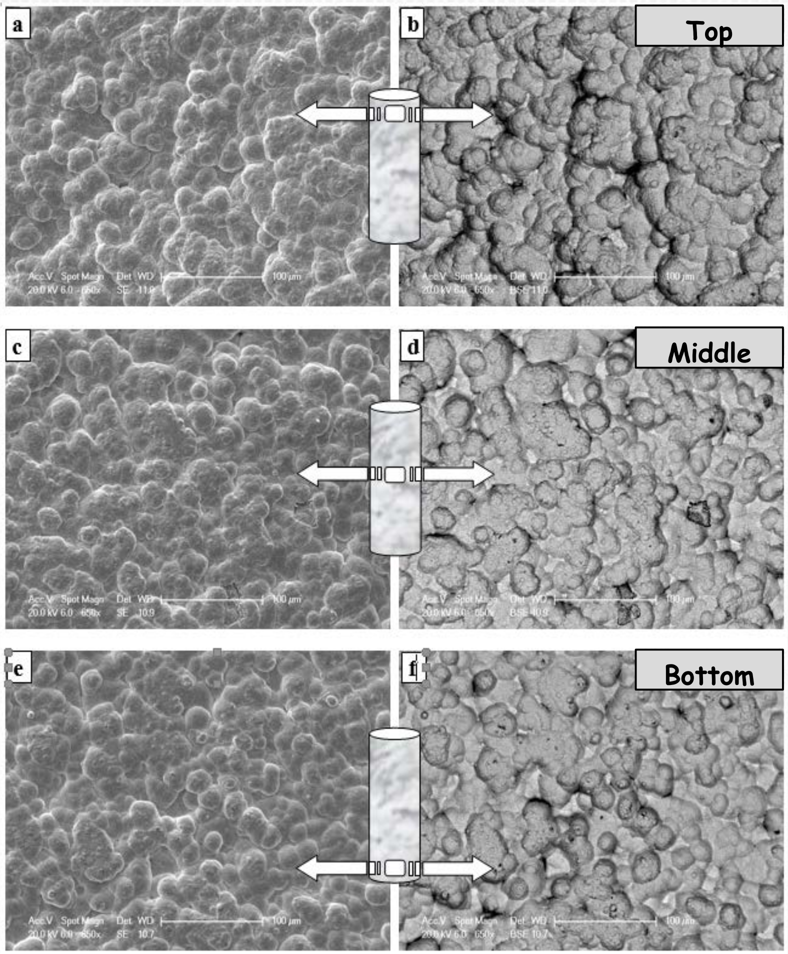
Weight gain of Support after ELP-PP cycles



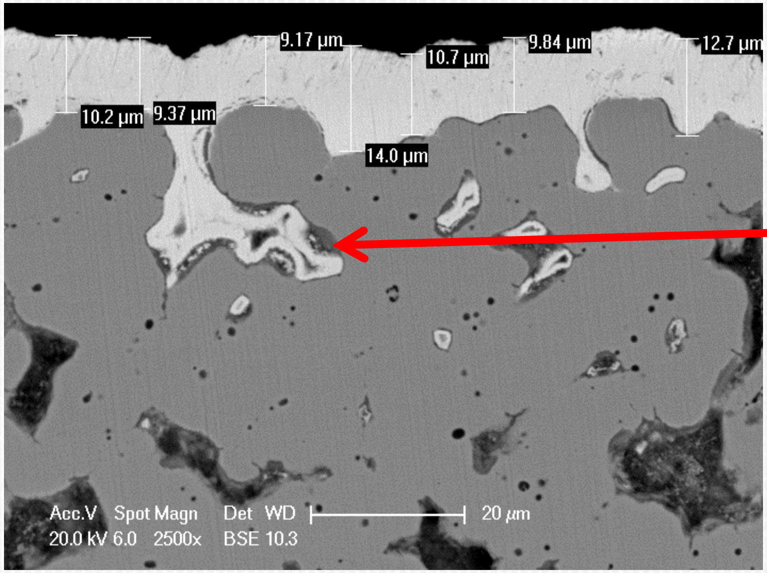
EERA European Energy Research Alliance

Supported Pd –based membranes for H_2 selective separation Palladium incorporation by ELP-PP

AMPEA Advanced Materials and Processes for Energy Applications



Homogeneous Pd deposition in vertical direction of the support with the formation of a thin layer on top

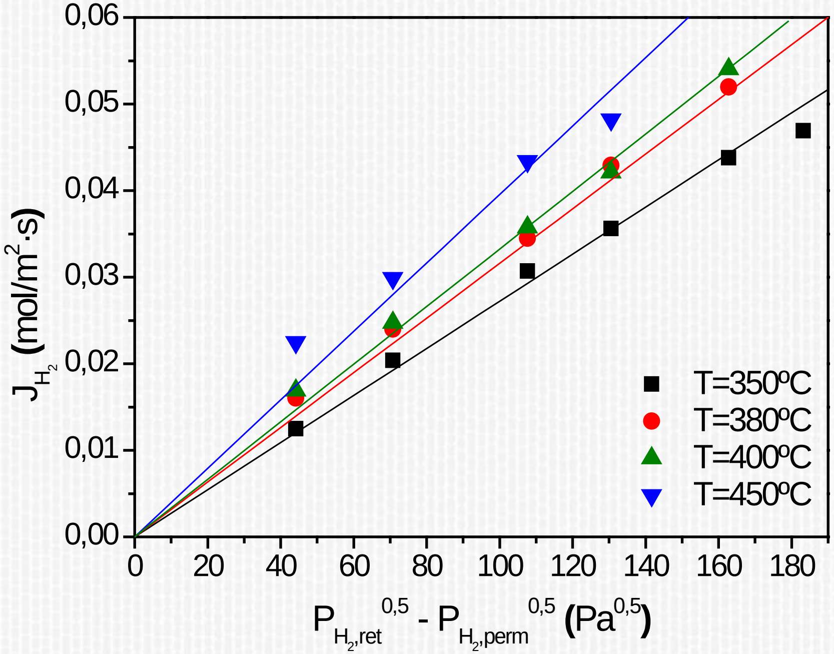


Formation of oxides by calcination

A thin external layer of circa 10 µm of Pd and the presence of the oxide layer can be observed

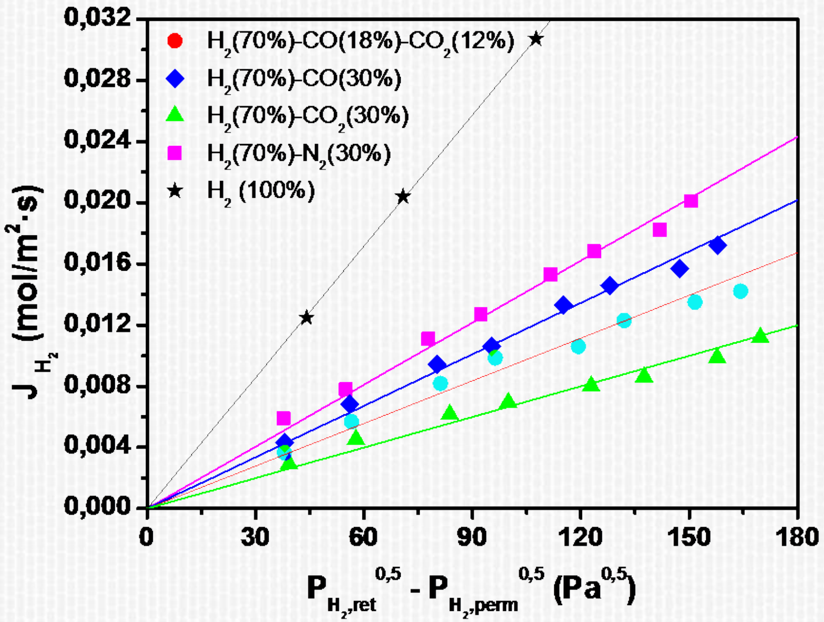
Permeation behavior

Pressure and temperature effect for pure hydrogen



Completely selective to H2
Permeation increases with Temperature following Arrhenius

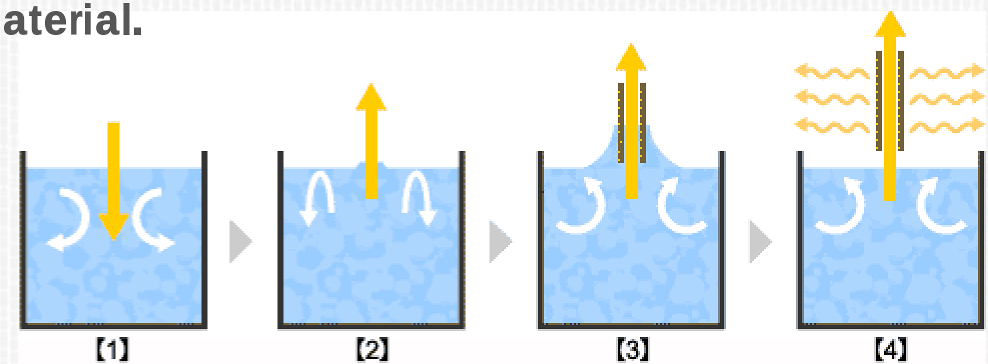
Influence of feed composition (T=350ºC)



Presence of mixtures reduces permeation, with special negative effect of CO_2

Preparation of supports and selective layers: DIP-COATING

Dip-coating is performed by a precision controlled immersion and withdrawal of a substrate into a reservoir of liquid to deposit a layer of material.



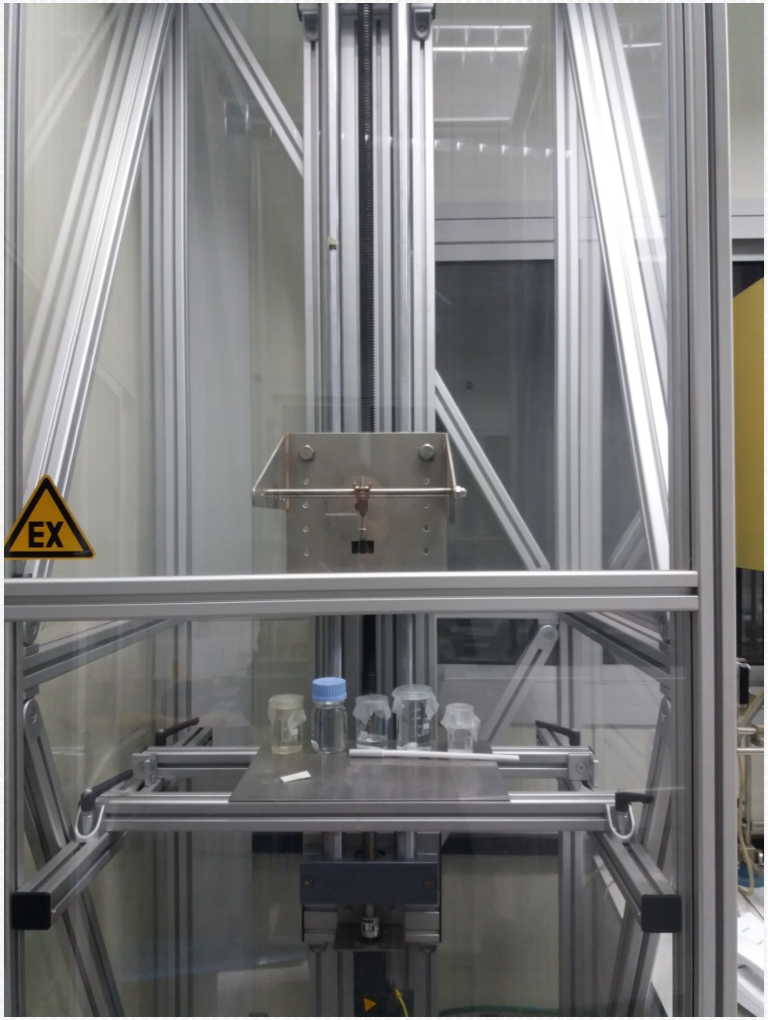
(1) Diping
(2) Wet layer formation
(3) Withdrawal
(4) Solvent evaporation

If the withdrawal speed is chosen such that the sheer rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation using:

$$h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}}$$

h = coating thickness η = viscosity
γ_{LV} = liquid-vapour surface tension ρ= density
g = gravity

Supported Pd –based membranes for H2 selective separation Dip-Coating



Advantages of dip-coating method:

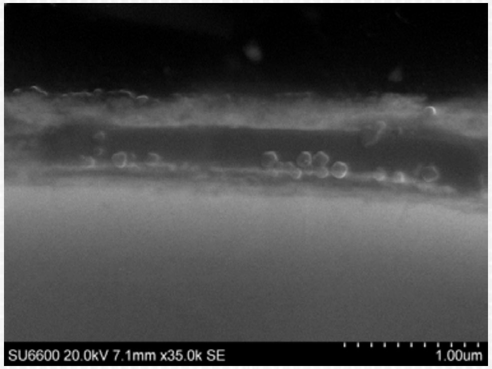
- Low capital costs
- Accurate control of film thickness and alloy composition
- Reproducibility
- Deposition of homogeneous and thin films: smoothening of surface roughness
- Stability of the solution over long periods of time
- Cheap preparation of the dipping solution

Thin and uniform many alloy films (including Pd-based) have already been deposited on top of flat surfaces.

Tubes of more than 1 meter long have been prepared by this method.

Supported Pd –based membranes for H2 selective separation. Dip-Coating

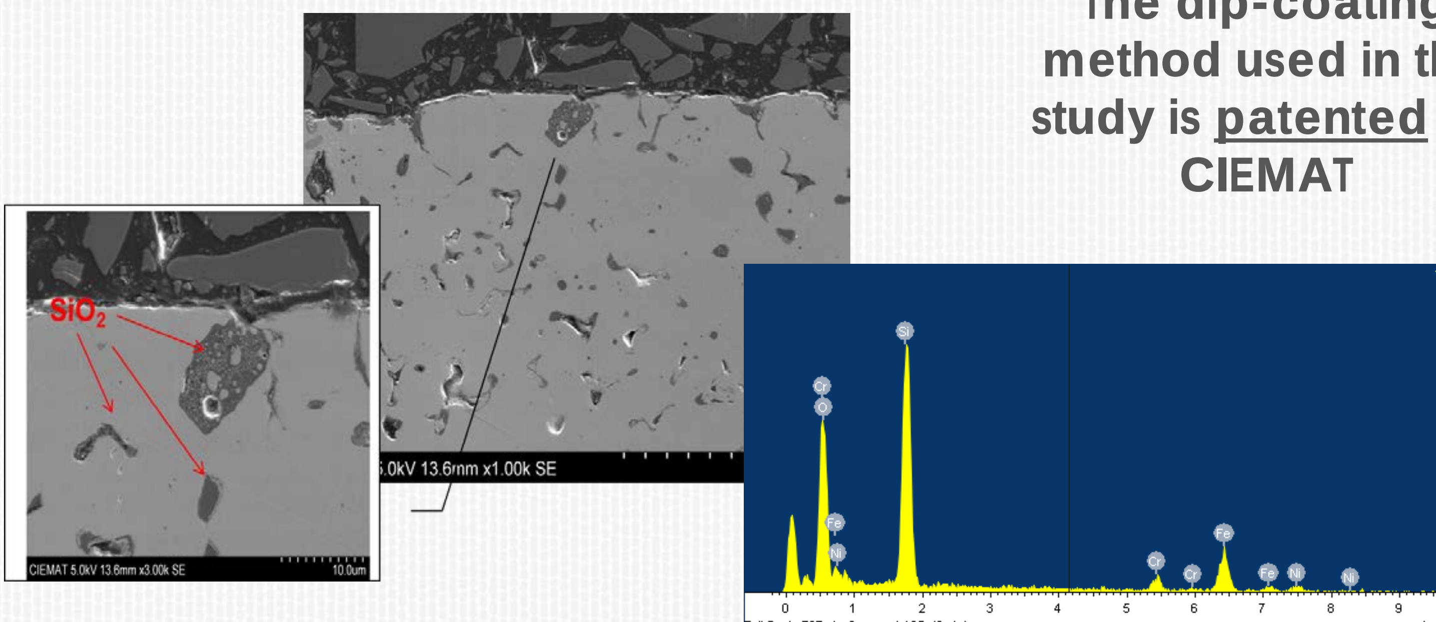
How does dip-coating method works?



SEM Images were taken to verify film homogeneity of the deposition tests, using dense and porous stainless steel supports with a layer of SiO_2.

In the photograph a thin layer (~0.3 µm) of PdAg is deposited on top of the intermetallic silica layer.

The dip-coating method used in this study is patented by CIEMAT



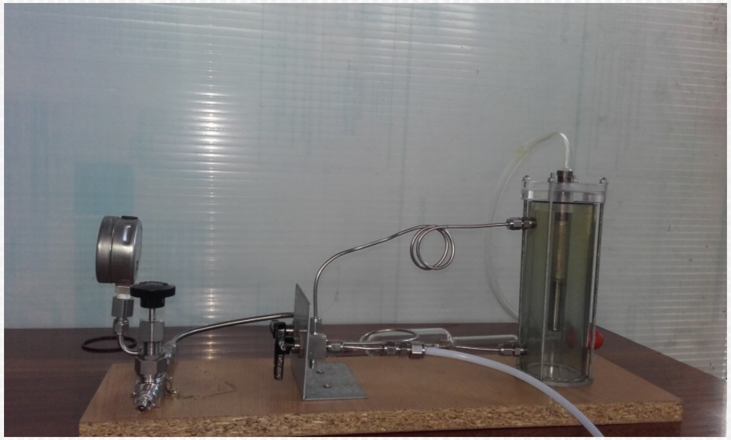
Preparation of new alloys

Magnetron Sputtering: commercial UNIVEX 450B system with confocal configuration

2 DC/1 RF SOURCES: 4" -SIZE TARGETS
SAMPLE SIZE: UP TO 6 INCHES

Procedure: combination of methods to optimize properties of supports and membranes

Early leak detection system



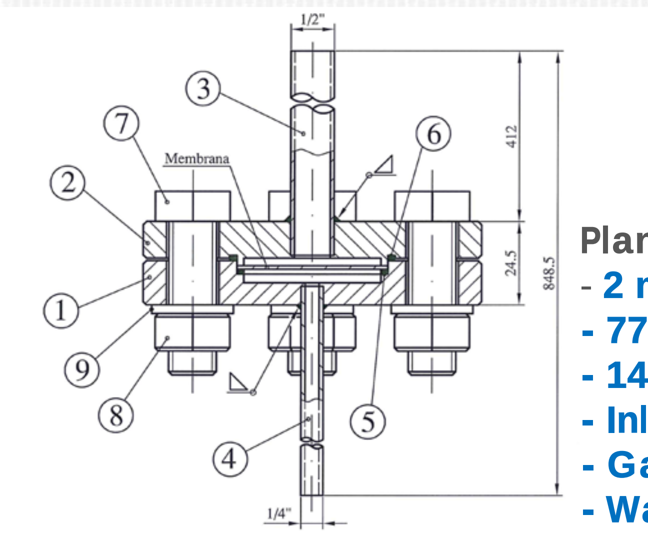
The membrane test module is based on the “Rising water test” used by Guazzone [1].

It consists on a scaled pressurized tube with He and water inlets. As the water ascends through the tube it reveals the leaks of the non-submerged section of the membrane

Now it is being modified to withstand pressures up to 5 bar by using metal fittings.

[1] Guazzone, F et al, PhD thesis, WPI (2005)

Supported Pd –based membranes for H2 selective separation Membranes permeation studies



Plant operation characteristics:

- $2\ m^3 \cdot h^{-1}$ (at standard conditions, 273 K,101 kPa)
- 773 K
- 1400 kPa
- Inlet gases H_2, N_2, CO, CO_2 and CH_4
- Gas chromatograph with TCD and a microGC
- Water recovery and analysis system

Thanks for your attention!

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