13th International Conference on Catalysis in Membrane Reactors

Preparation and hydrogen permeation studies of ultrathin palladium and carbon membranes

D. ALFREDO PACHECO TANAKA[1], MARGOT A. LLOSA TANCO[1], JOSE MEDRANO[2], JON MELENDEZ[1], EKAIN FERNANDEZ[1], MARIA NORDIO[2], MARTIN VAN SINT ANNALAND[2] FAUSTO GALLUCCI[2].

July 10-13 2017. Houston, Texas

1 tecnalia Inspiring Business

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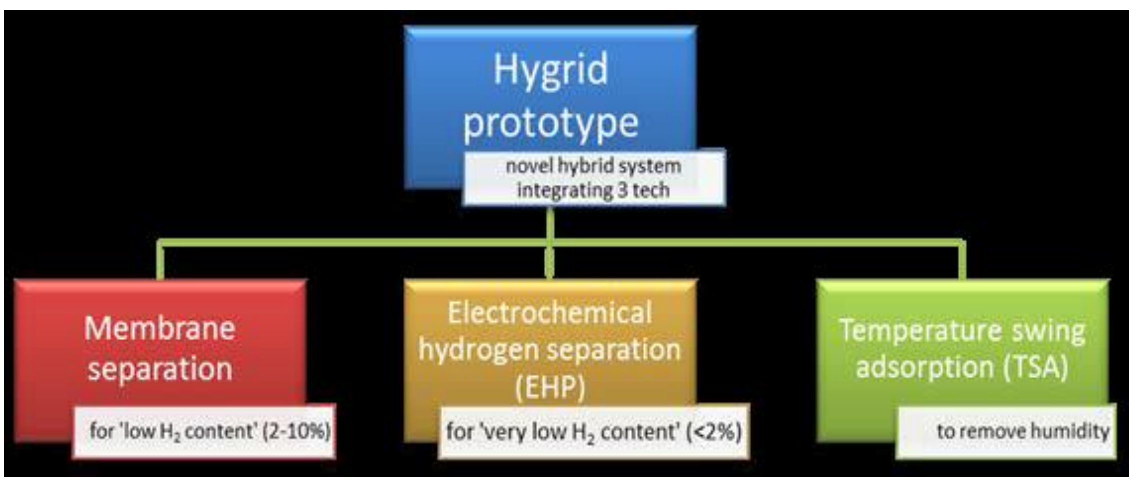
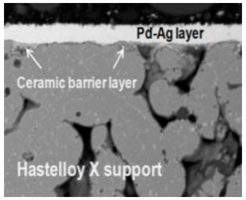
Objective

Developing of an advanced high performance, cost effective separation technology for direct separation of hydrogen from natural gas networks

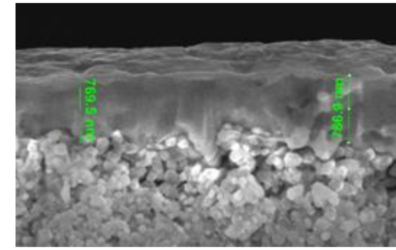


Thin



(3-5 µm thick)

Ultra thin



(≈1 µm thick)

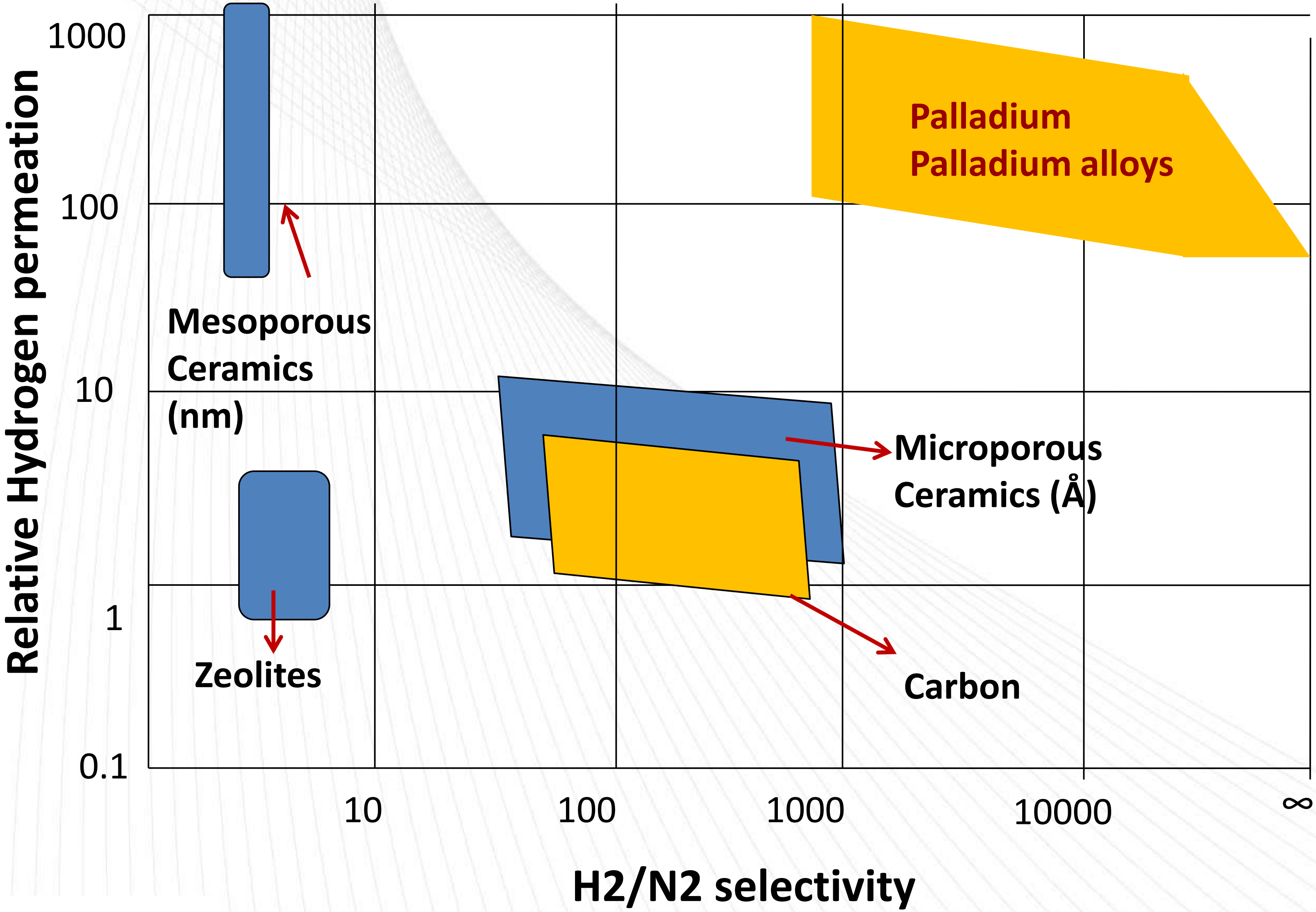
Thin and ultra thin supported Pd/Ag membranes

D. ALFREDO PACHECO TANAKA[1], JON MELENDEZ[1], EKAIN FERNANDEZ[1], MARIA NORDIO[2], FAUSTO GALLUCCI[2]

Poster

ULTRA-THIN PALLADIUM-SILVER MEMBRANES FOR PURE HYDROGEN PRODUCTION AND SEPARATION: MODELLING AND EFFECT OF SWEEP GAS

Membranes for hydrogen separation



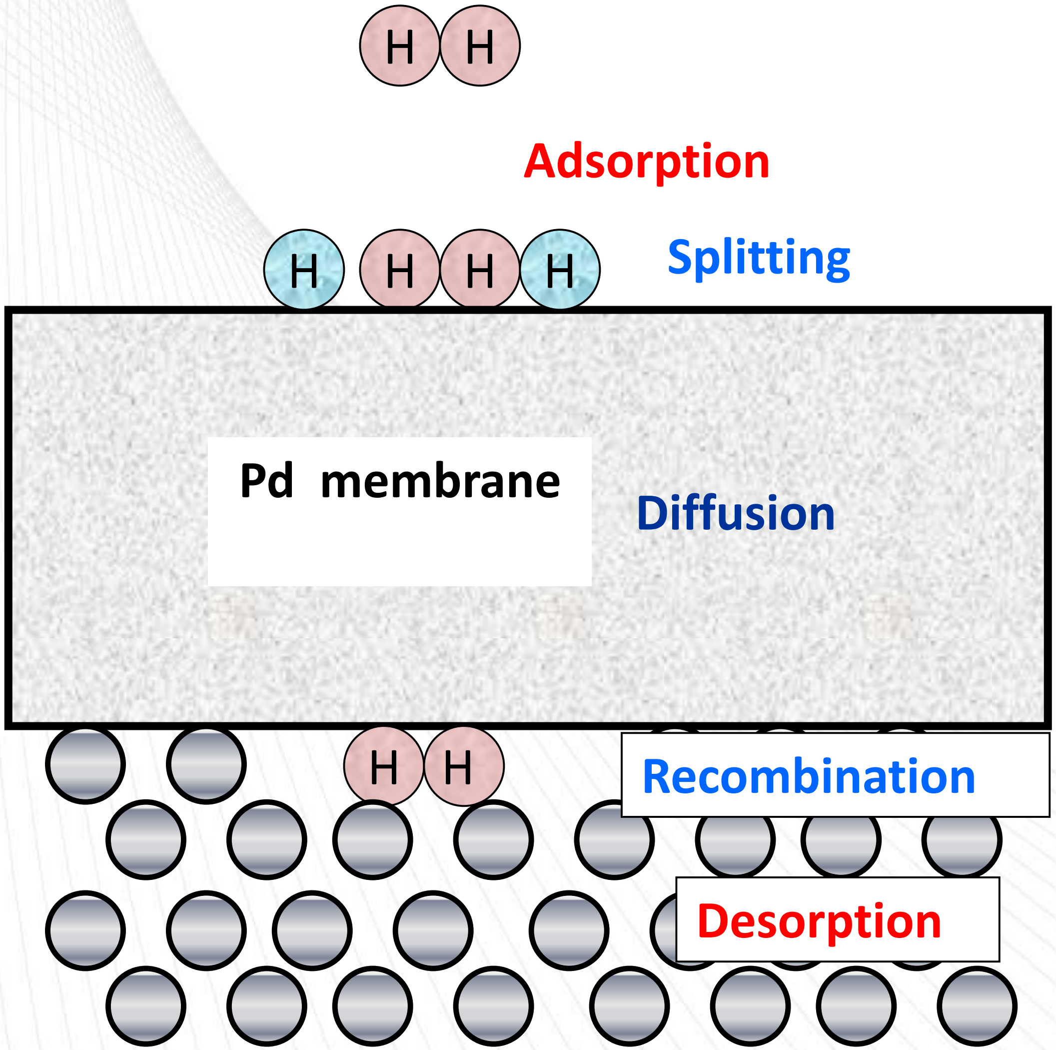
HyGrid FCH

H2 permeation in Pd membranes

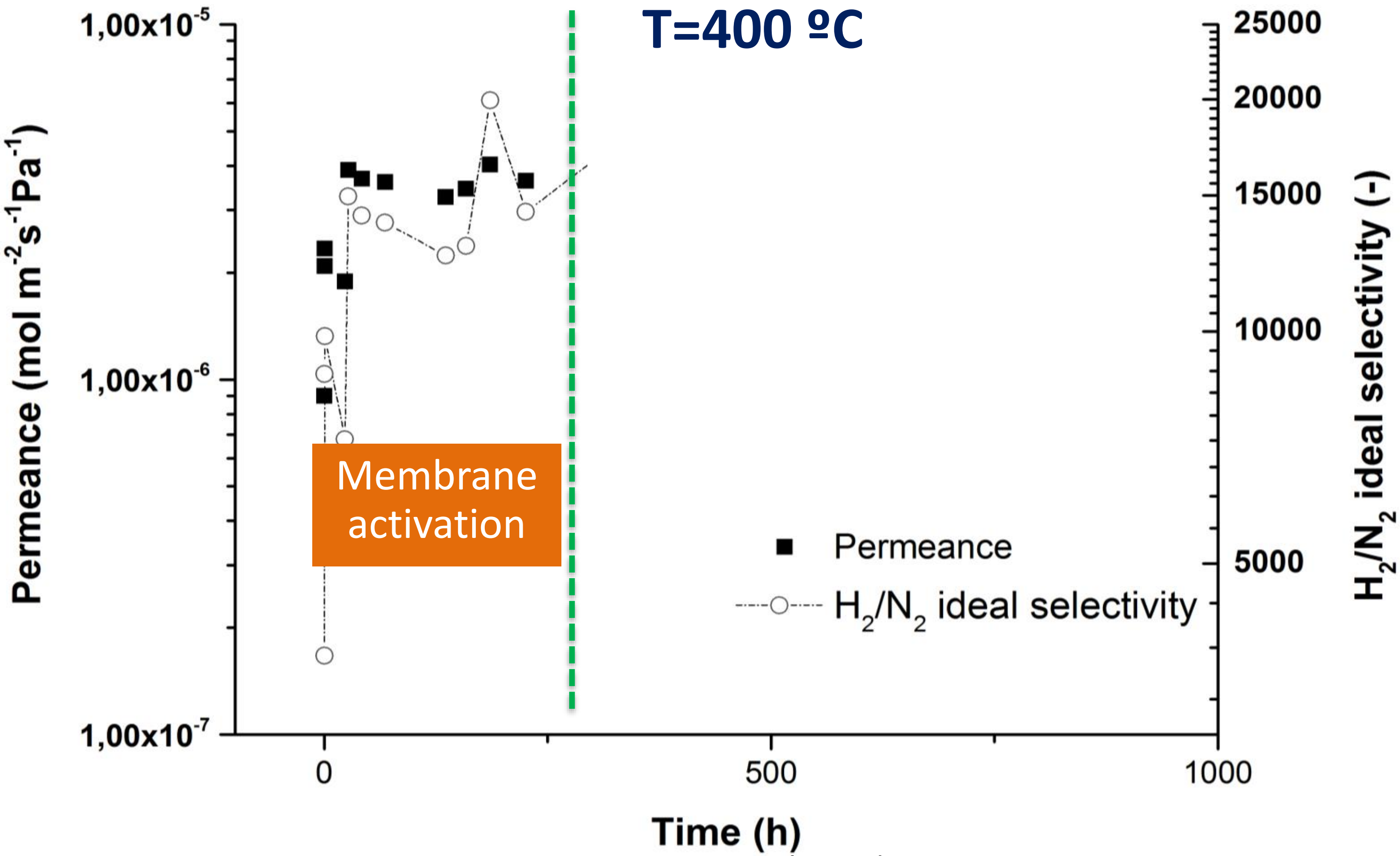
Ultra-thin membranes

-Surface interference
- H_2 splitting

resistance of support

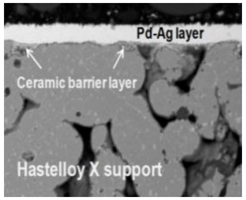


Ceramic supported Pd-based (3-4 µm thick) membrane



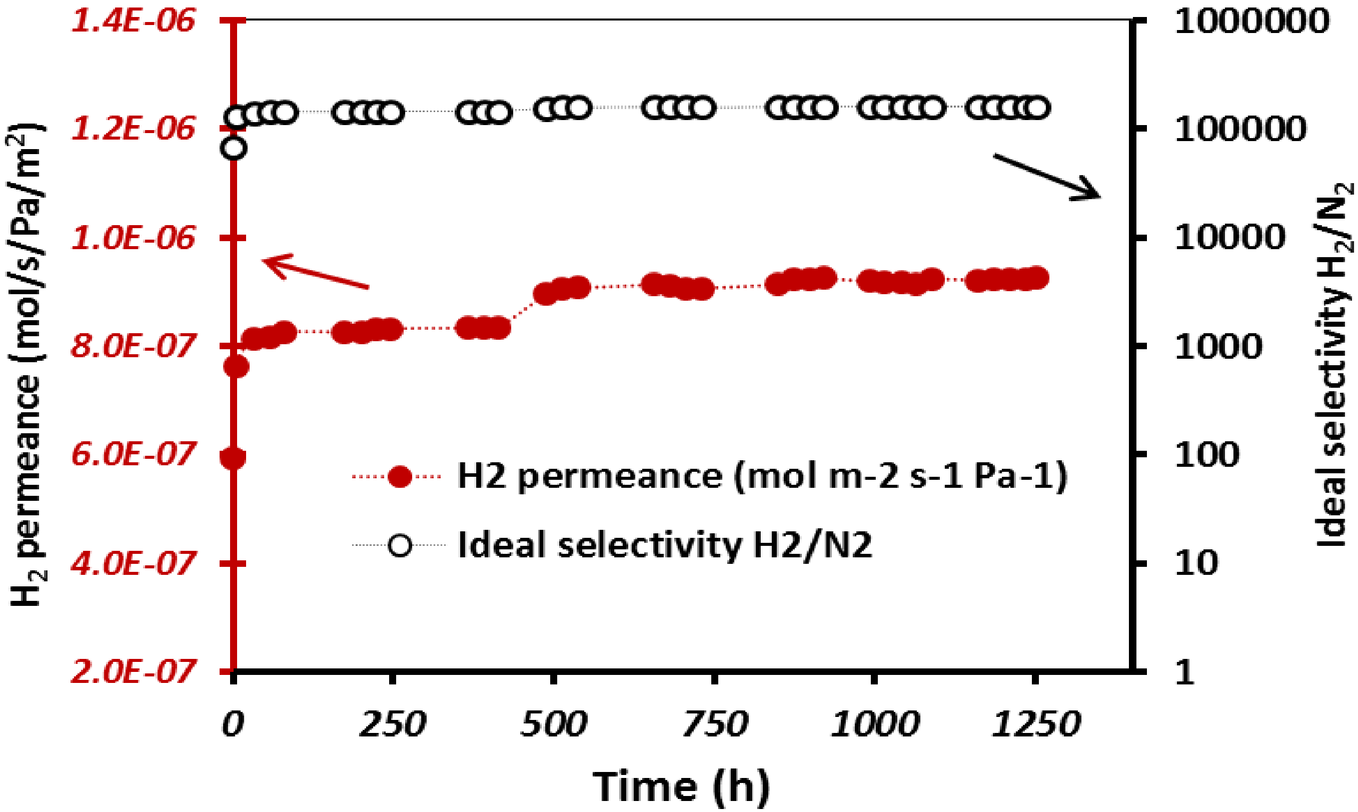
Helmi et al., Molecules 21 (2016) 376

Metallic supported Pd-Ag membranes



(5 µm thick)

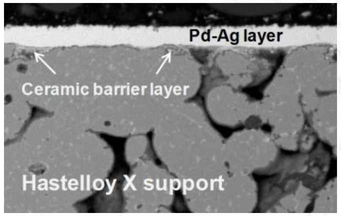
Long term permeation test at 400 °C



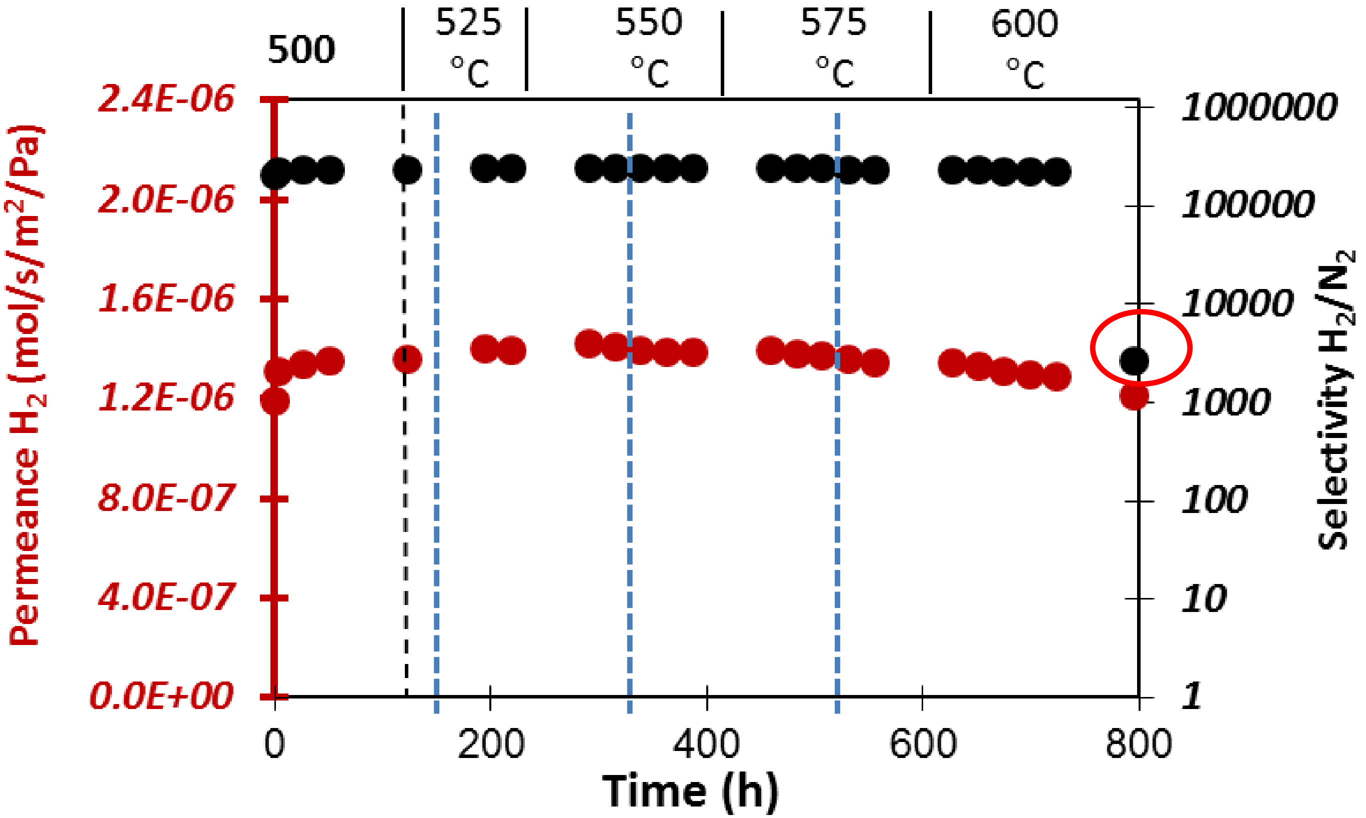
- H_2 permeance 400 ºC: **0.9 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1}**
- H_2/N_2 ideal selectivity 400 ºC: **>150,000 for >1200 h**

Medrano et al., Int. J. Hydrogen Energy 41 (2016) 8706-8718

Metallic supported Pd-Ag membranes



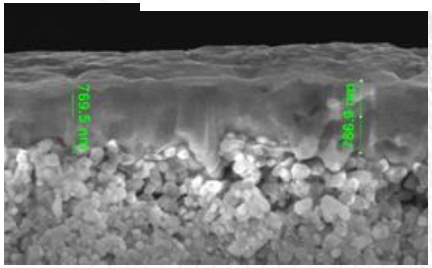
Long term permeation test at more than 500 °C



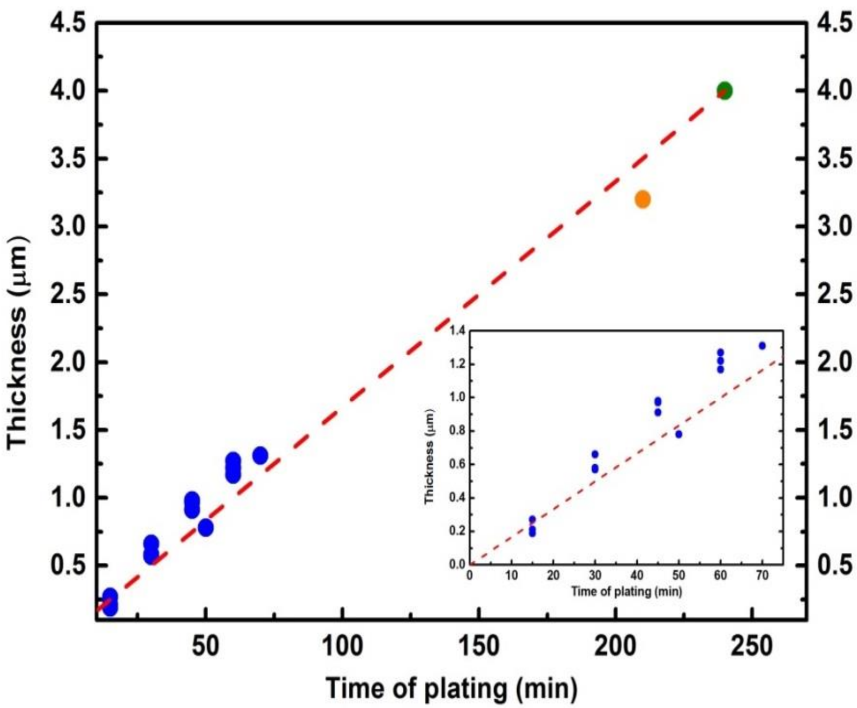
- **At >500 ºC** and after >800 h, **H_2/N_2 ideal selectivity** dropped to from 223000 to **2650**

Medrano et al., Int. J. Hydrogen Energy 41 (2016) 8706-8718

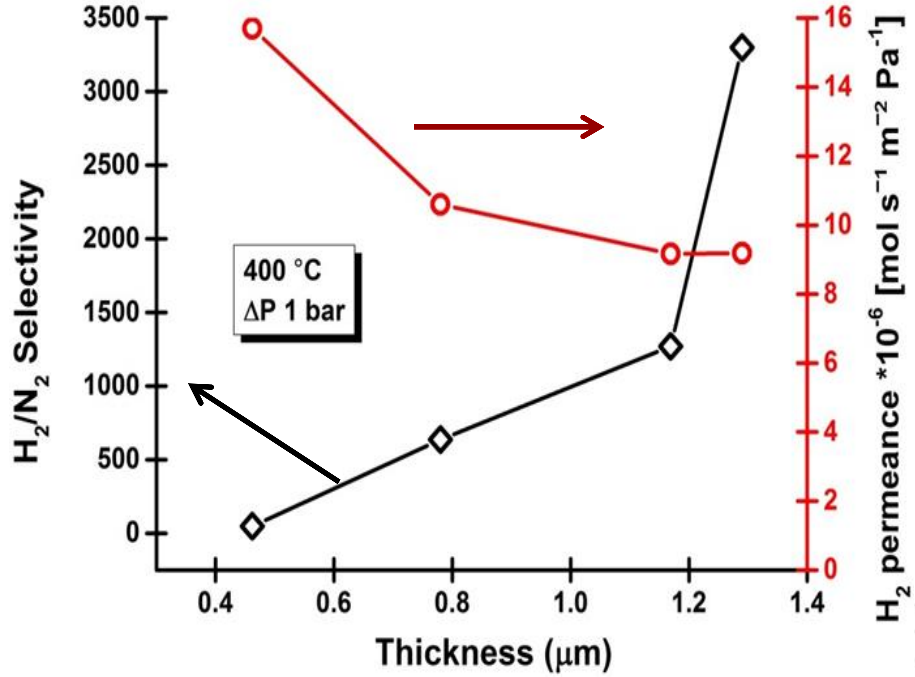
Ultra-thin Pd-Ag membranes ≈ 1µm



Thickness vs plating time



H_2/N_2 selectivity and H_2 permeance vs thickness



Melendez et al., Journal of Membr. Sci. 528 (2017) 12–23

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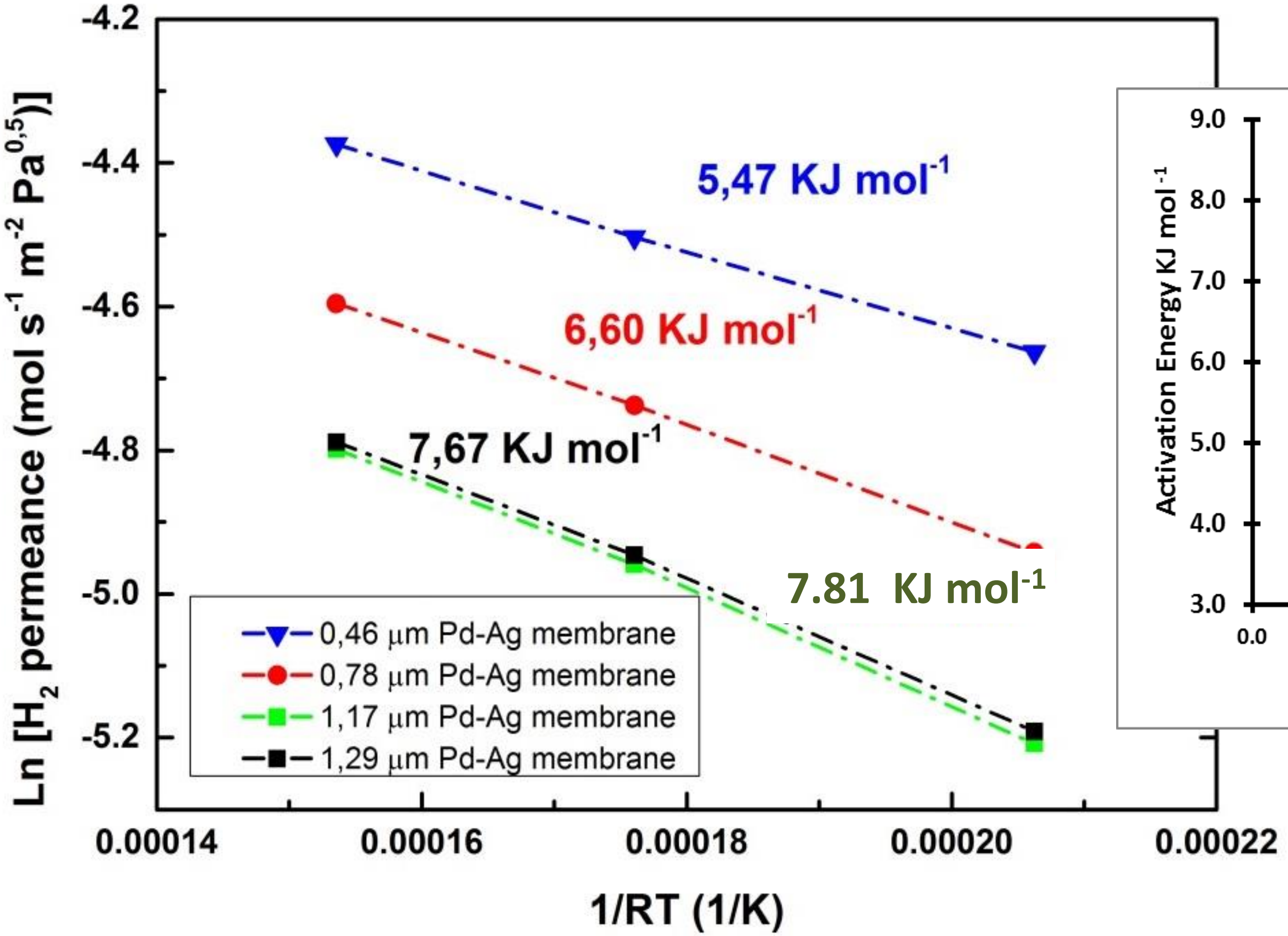
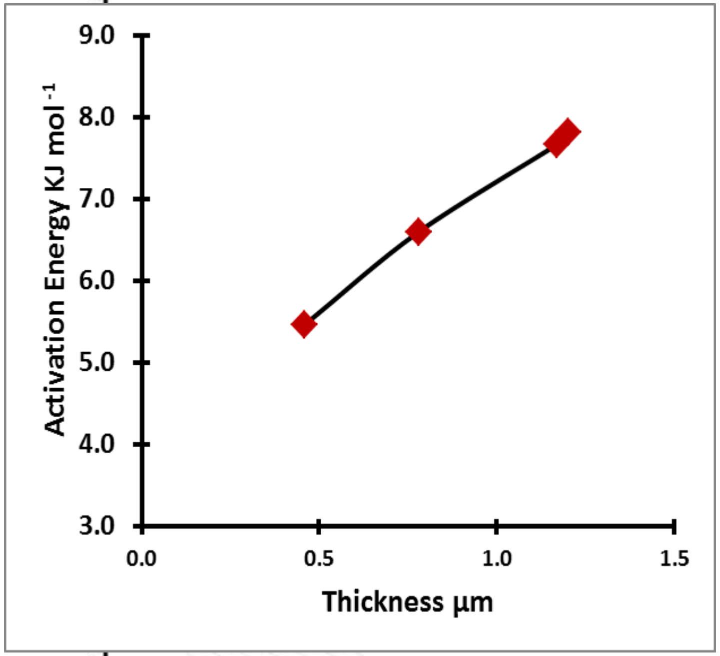
HyGrid

Activation energy of Ultra-thin Pd-Ag membranes



Ea vs thickness

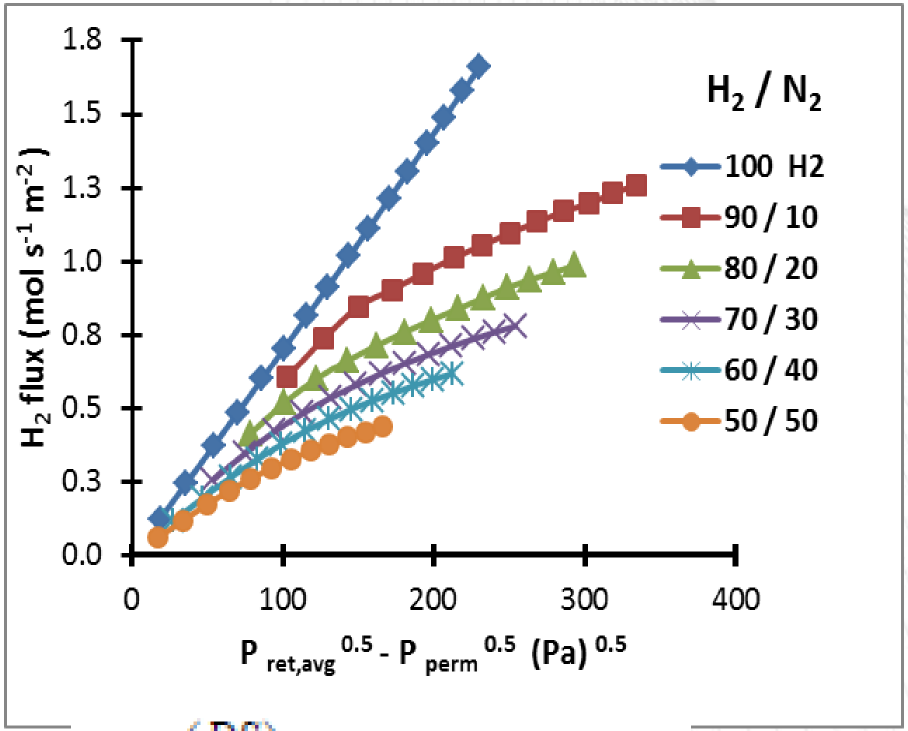


Melendez et al., Journal of Membr. Sci. 528 (2017) 12–23

H_2 flux at various gas mixtures and pressures at 400°C

Membrane thickness 1.30 um

Effect of dilution H_2 and N_2

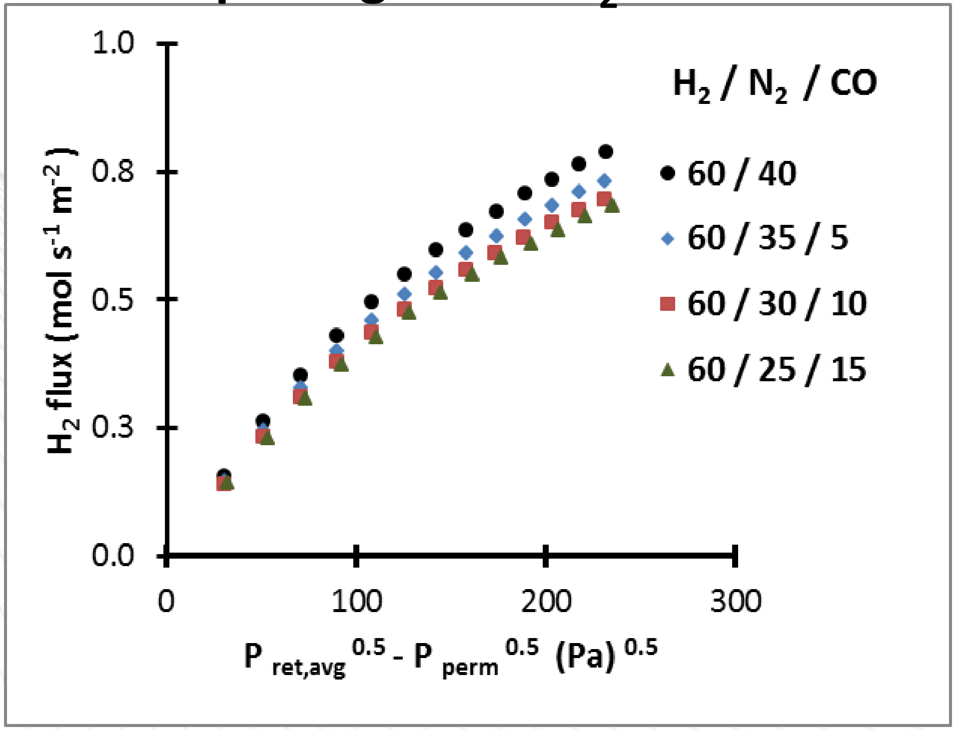


$$J = \left(\frac{DS}{l}\right) e^{-(E_a/RT)} (P_0^n - P_1^n)$$

Effect of CO

At H_2 / N_2 60/40

Replacing some N_2 with CO

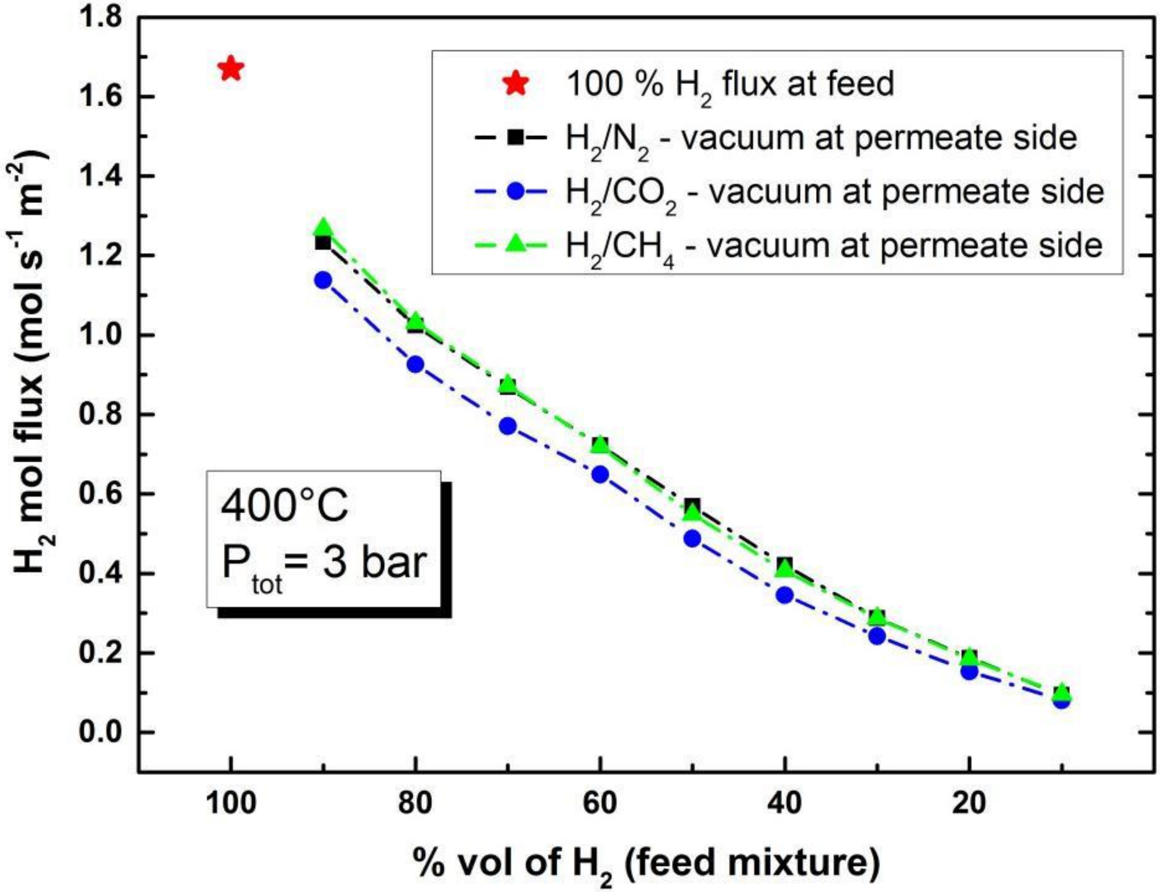


Melendez et al., Journal of Membr. Sci. 528 (2017) 12–23

H_2 flux at various gas mixtures and pressures at 400°C

Thickness 1.30 um

3 bar total pressure, vacuum at the permeate



Melendez et al., Journal of Membr. Sci. 528 (2017) 12–23

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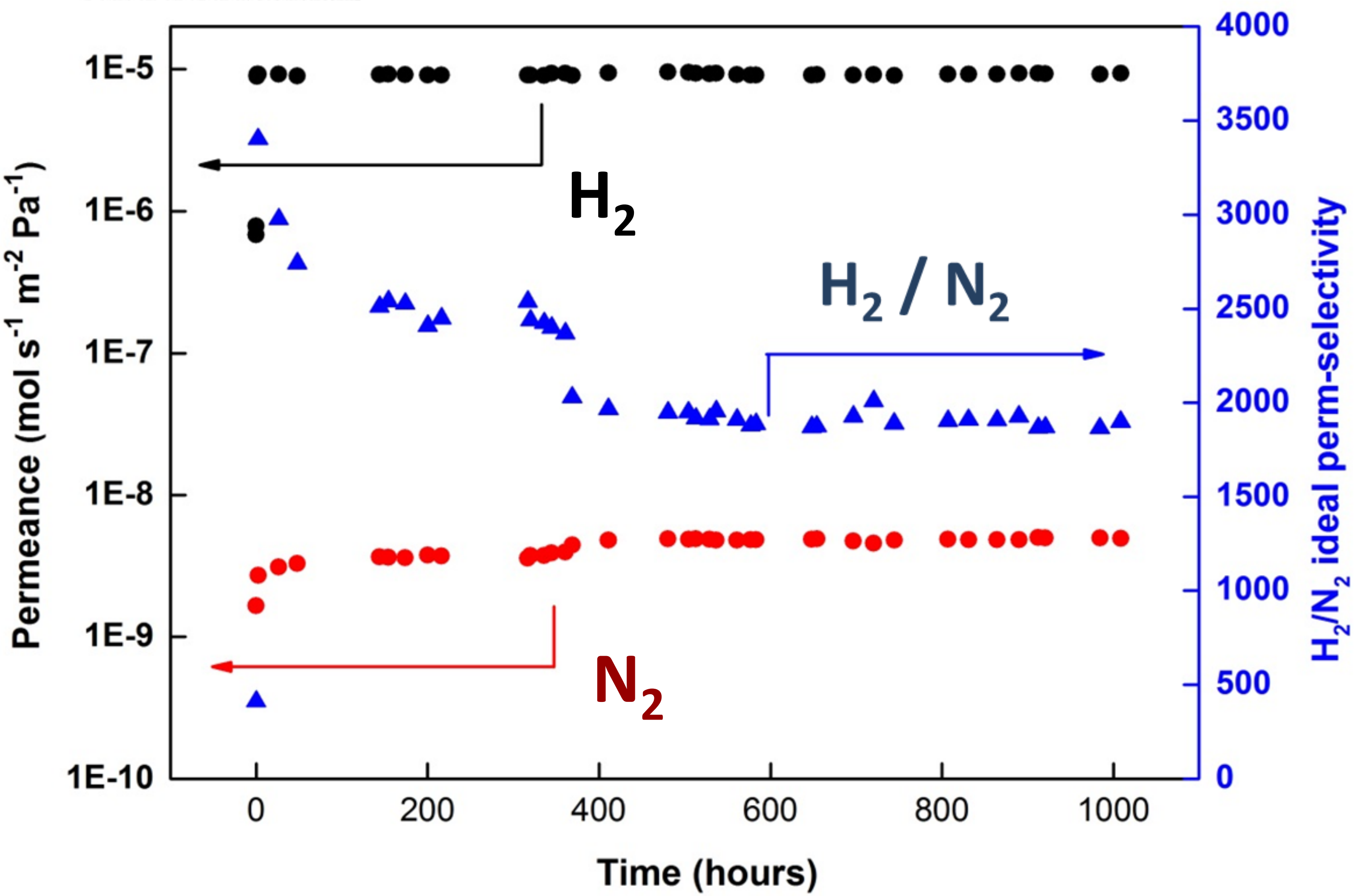
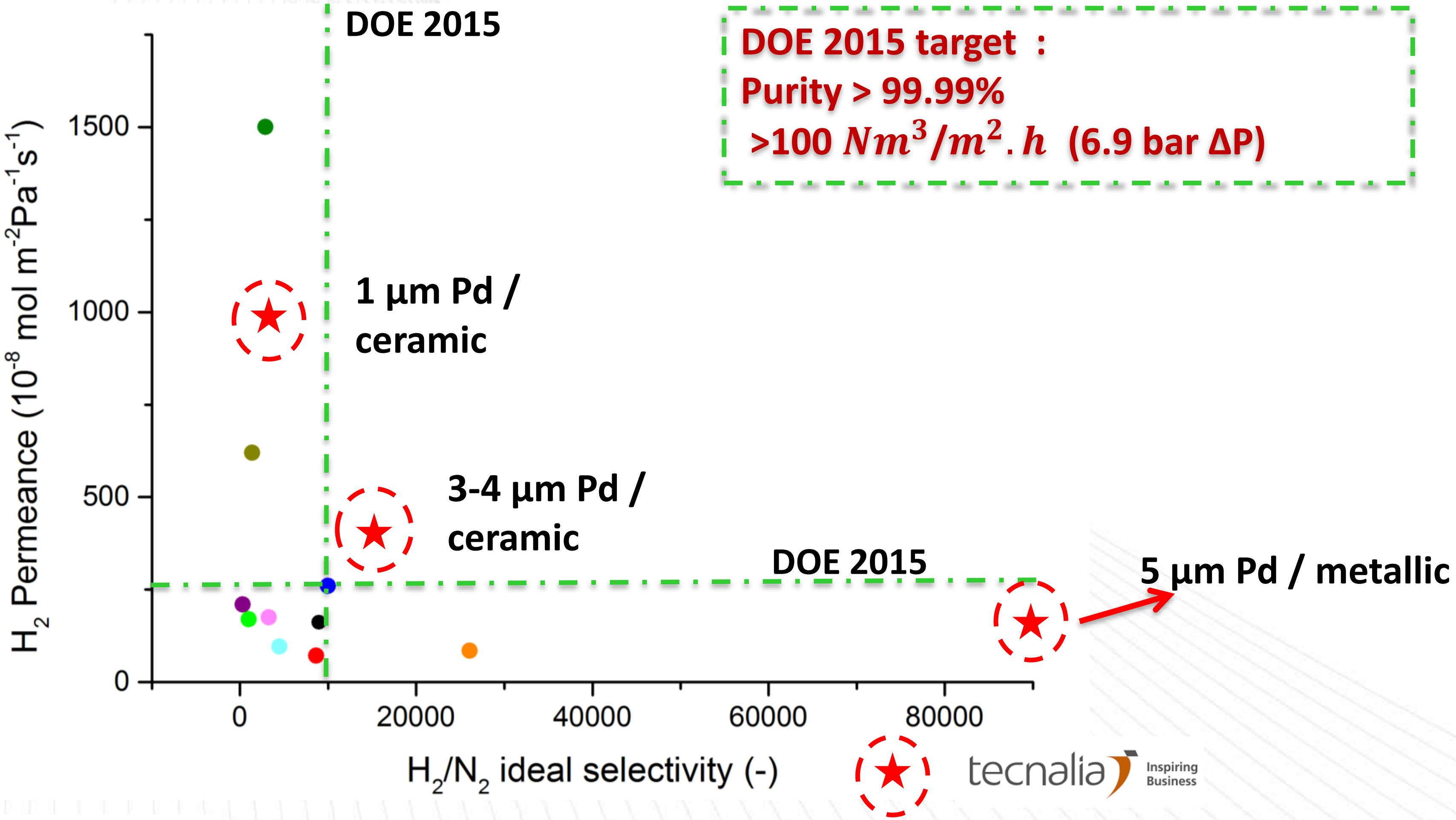
HyGrid FCH

Long term test Pd-Ag membranes ≈ 1,3 µm



Melendez et al., Journal of Membr. Sci. 528 (2017) 12–23

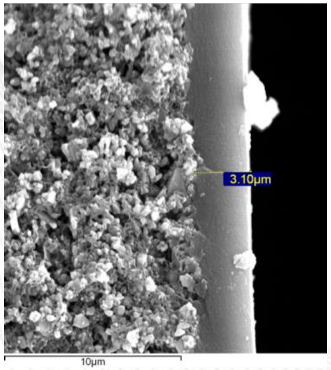
Pd alloy membrane properties at TECNALIA



DOE 2015 target :
Purity > 99.99%
>100 $Nm^3/m^2.h$ (6.9 bar ΔP)

Gallucci et al., Chem. Eng. Sci 92 (2013) 40–66

Carbon Molecular Sieves Membranes (CMSM)



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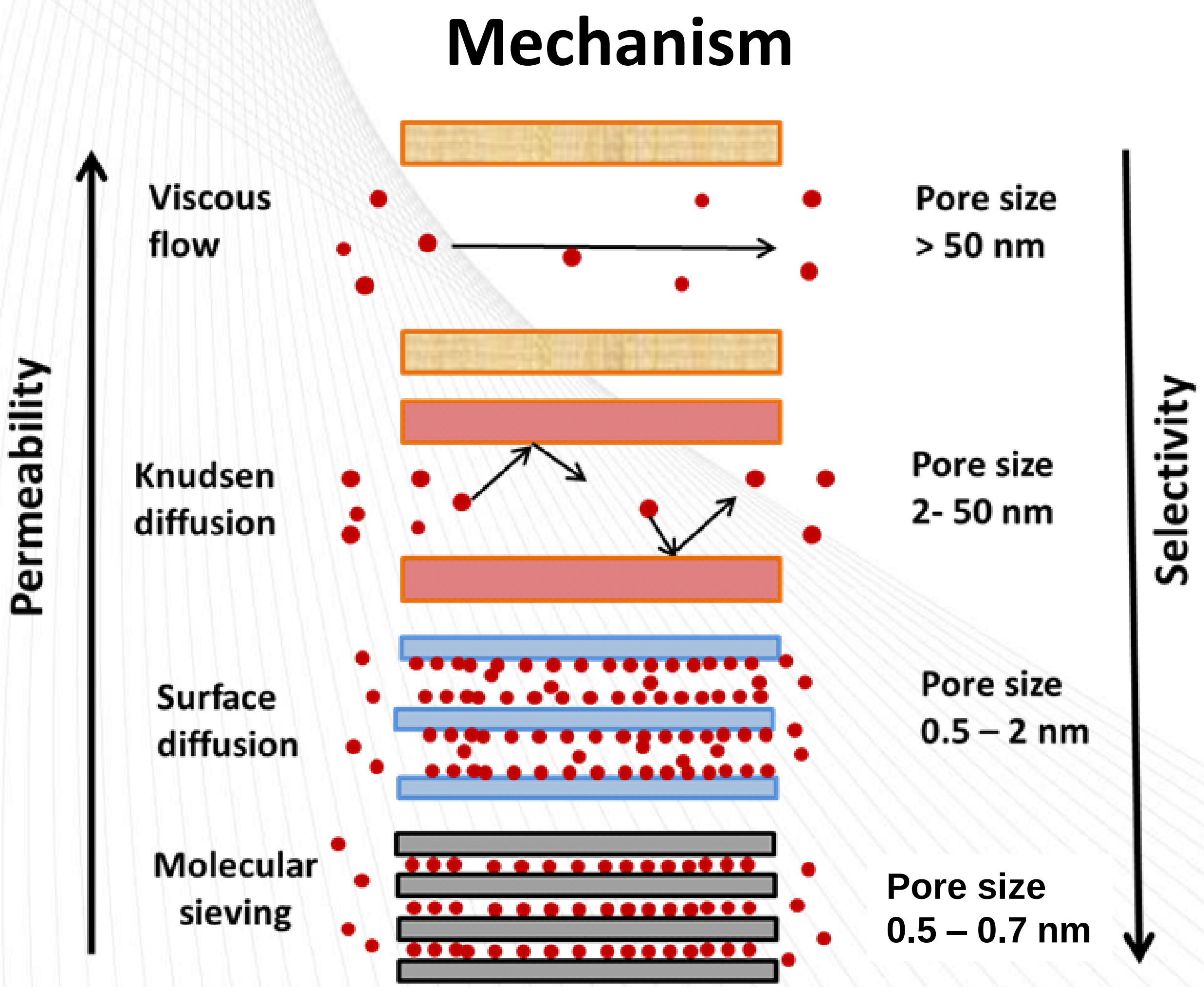
Poster

BIOGAS UPGRADING WITH CARBON MEMBRANES: EXPERIMENTAL DEMONSTRATION AND BENEFITS EVALUATION

Porous membranes for gas separation



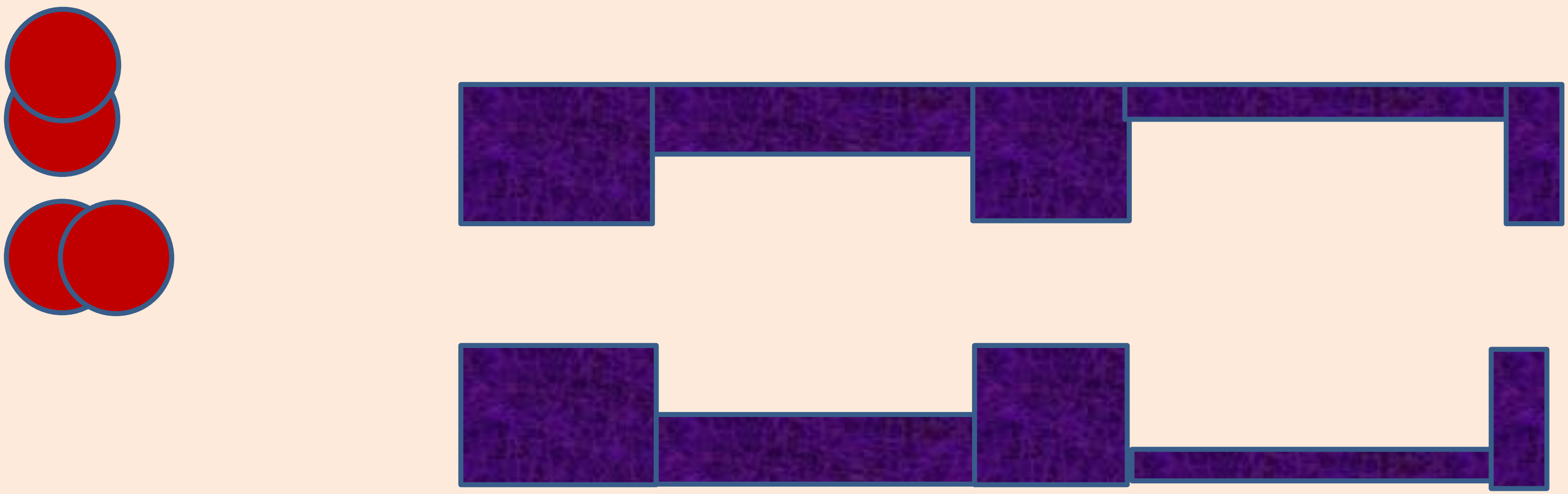
Molecular sieves membranes

Zeolite membranes

- Difficult to obtain crack-free
- Intercrystallite voids affecting selectivity

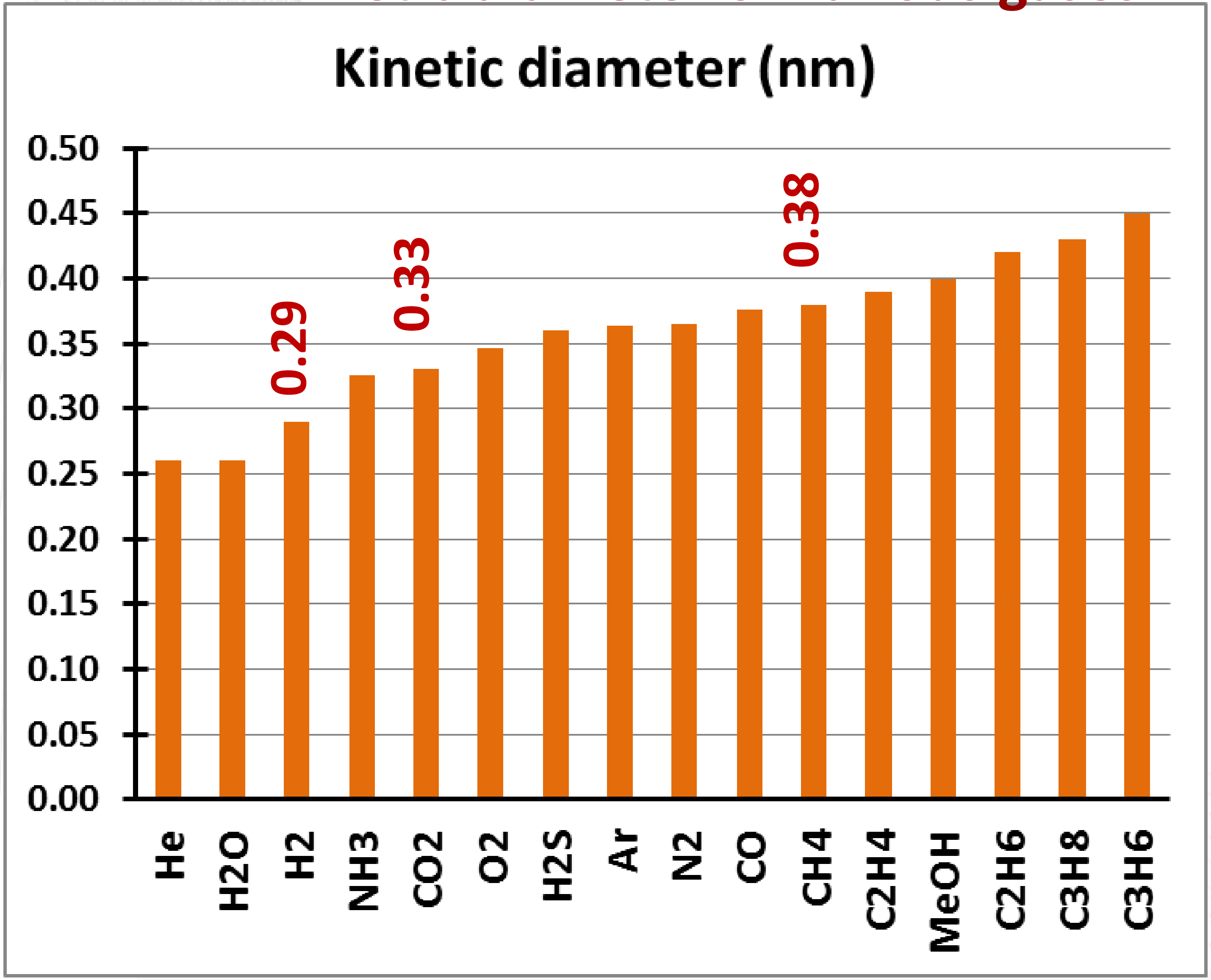
Carbon Molecular sieves membranes

Carbonization of a polymer precursor under inert atmosphere or vacuum

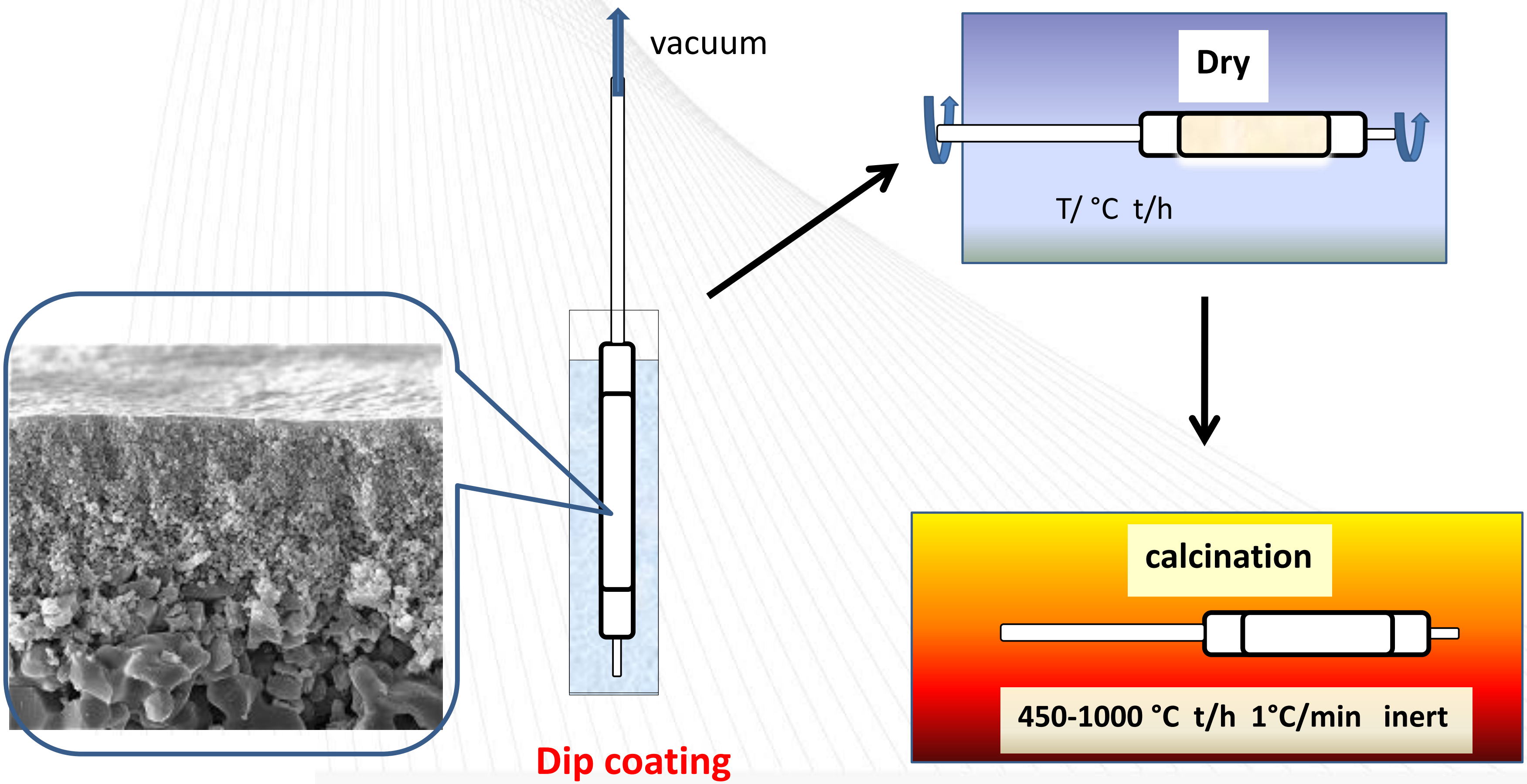


Presence of micropores and ultramicropores

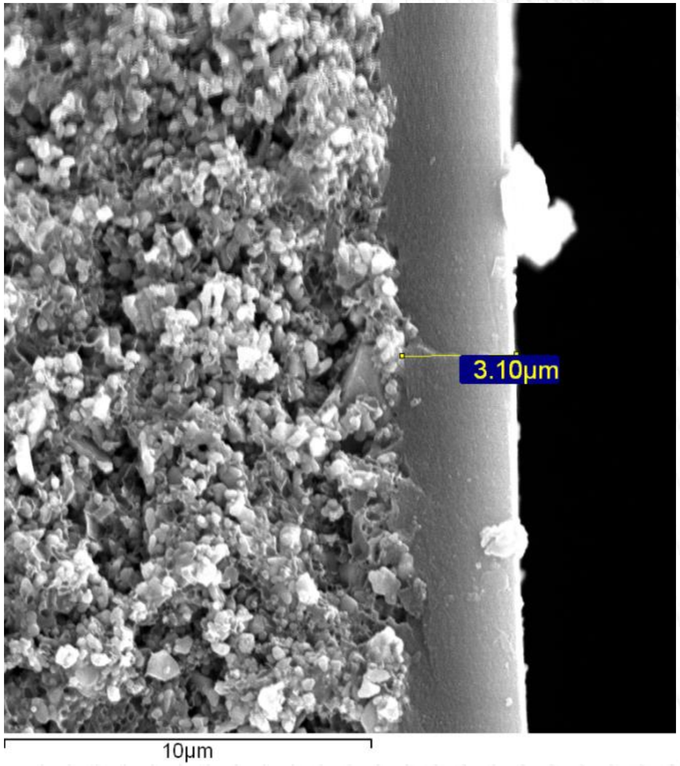
Kinetic diameter of various gases

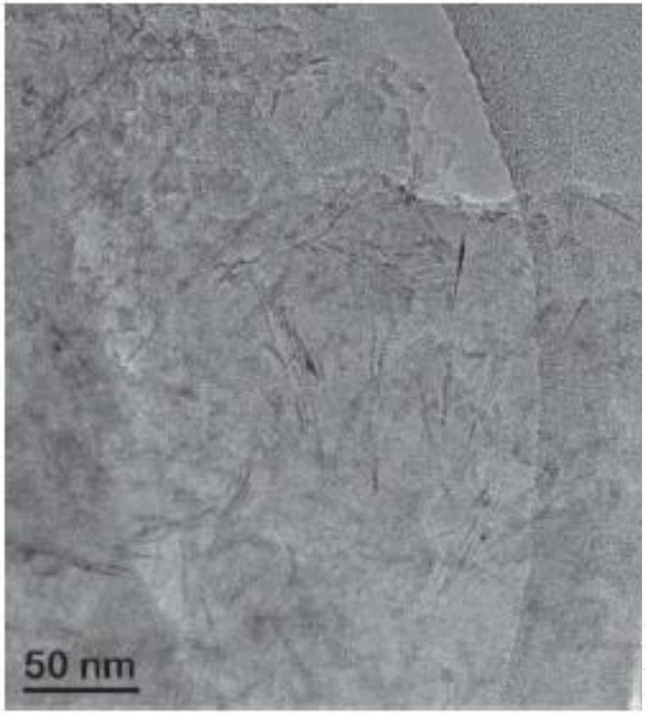


Preparation of composite-Alumina-CMSM



SEM and TEM of the Al-CMSM

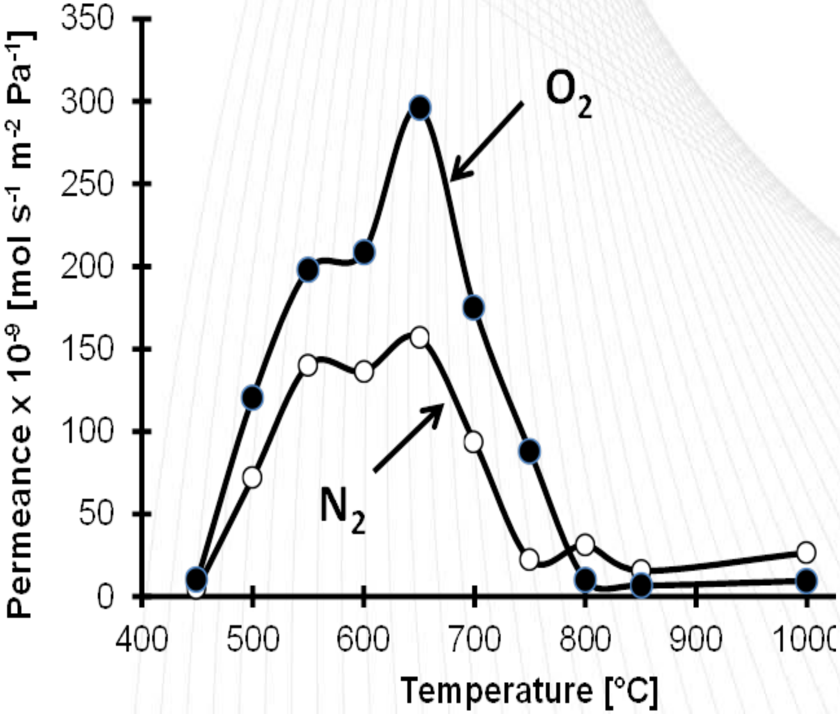




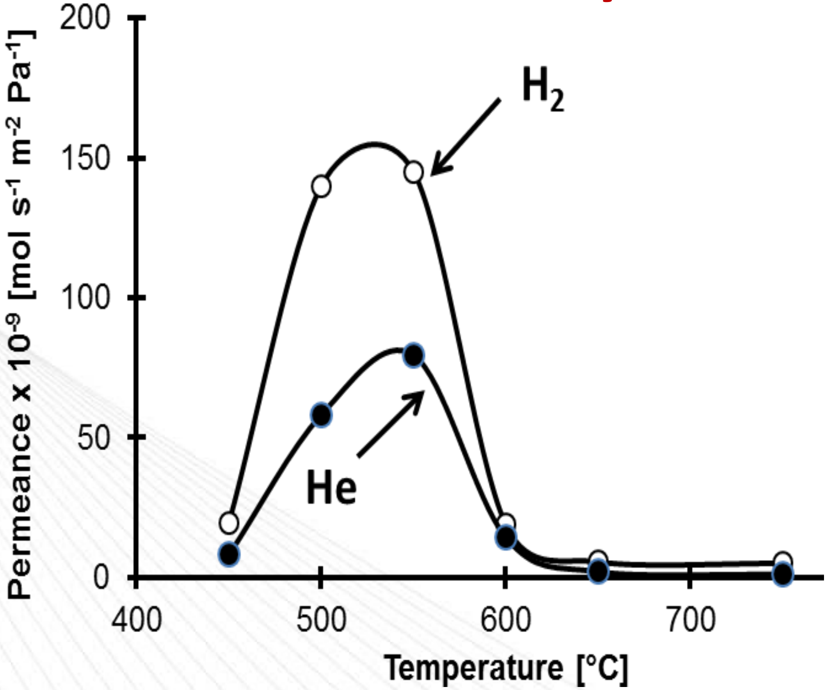
Composite phenolic resin CMSM, exeira, Campo, Tanaka, Llosa, Magen, Mendes, Carbon 49 (2011) 4348

Effect of carbonization temperature

Fresh membrane



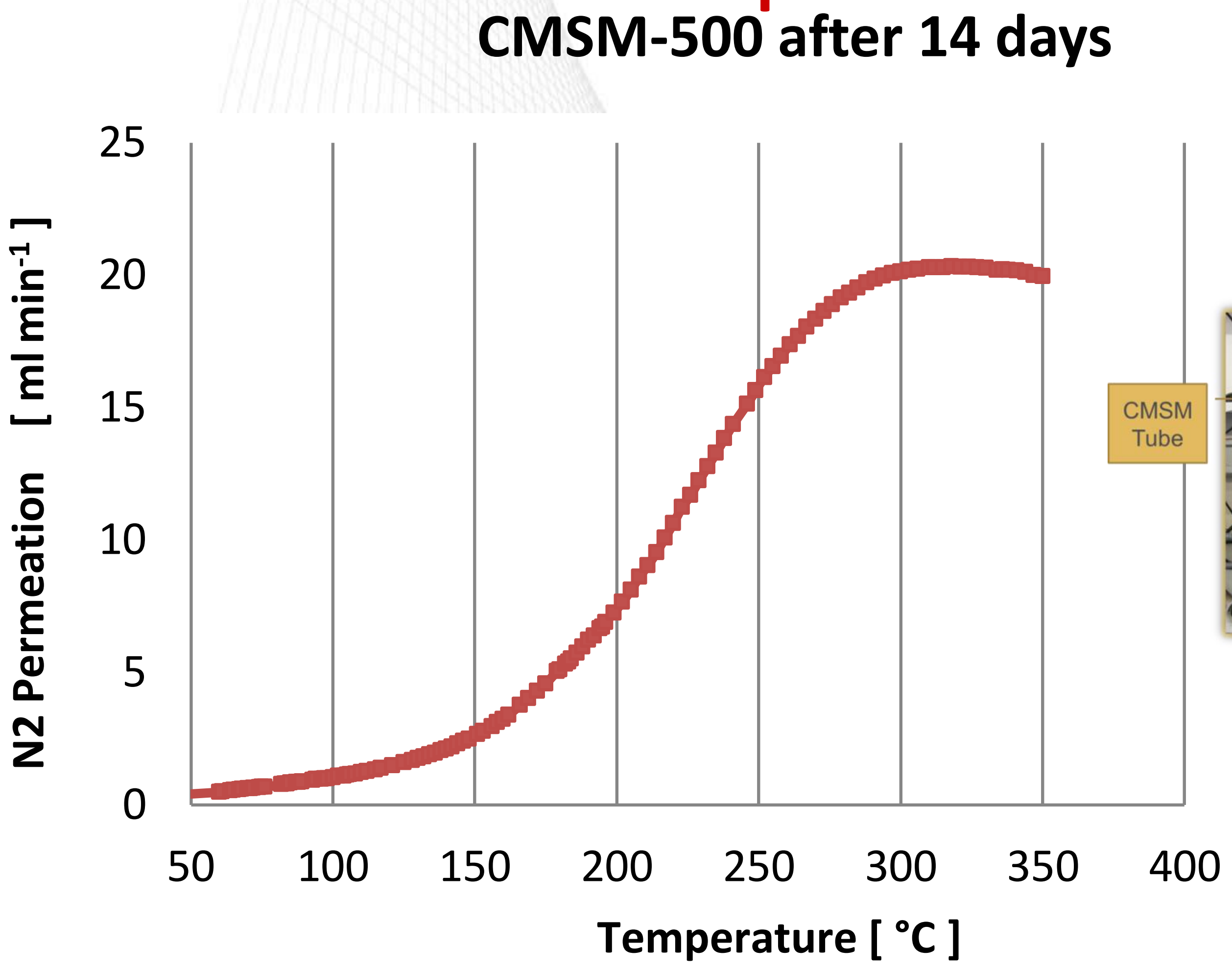
After one day

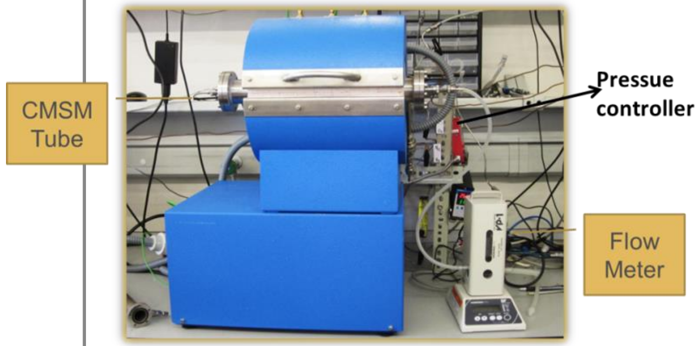


O_2 and N_2 very low flux

Llosa , Pacheco et.al Int J.hydrogen energy 40 (2015) 5653 40 (2015) 3485

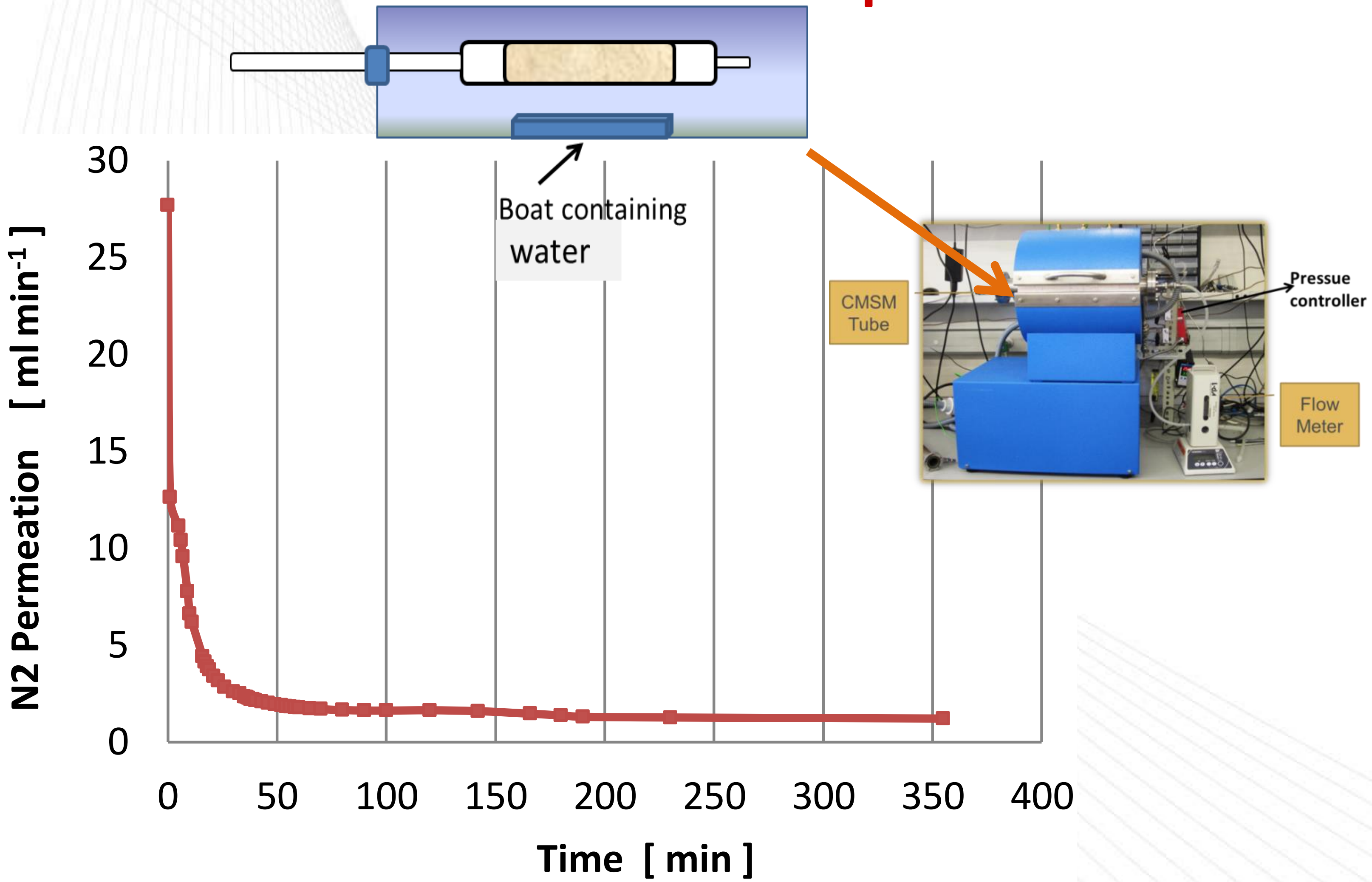
N_2 permeation of c-CMSM-500 in function of the temperature at 400 kpa





N_2 permeation of fresh membrane 66.8 ml min^{-1}

N_2 permeation at 400 kPa for CMSM-500 in function of the time of water adsorption

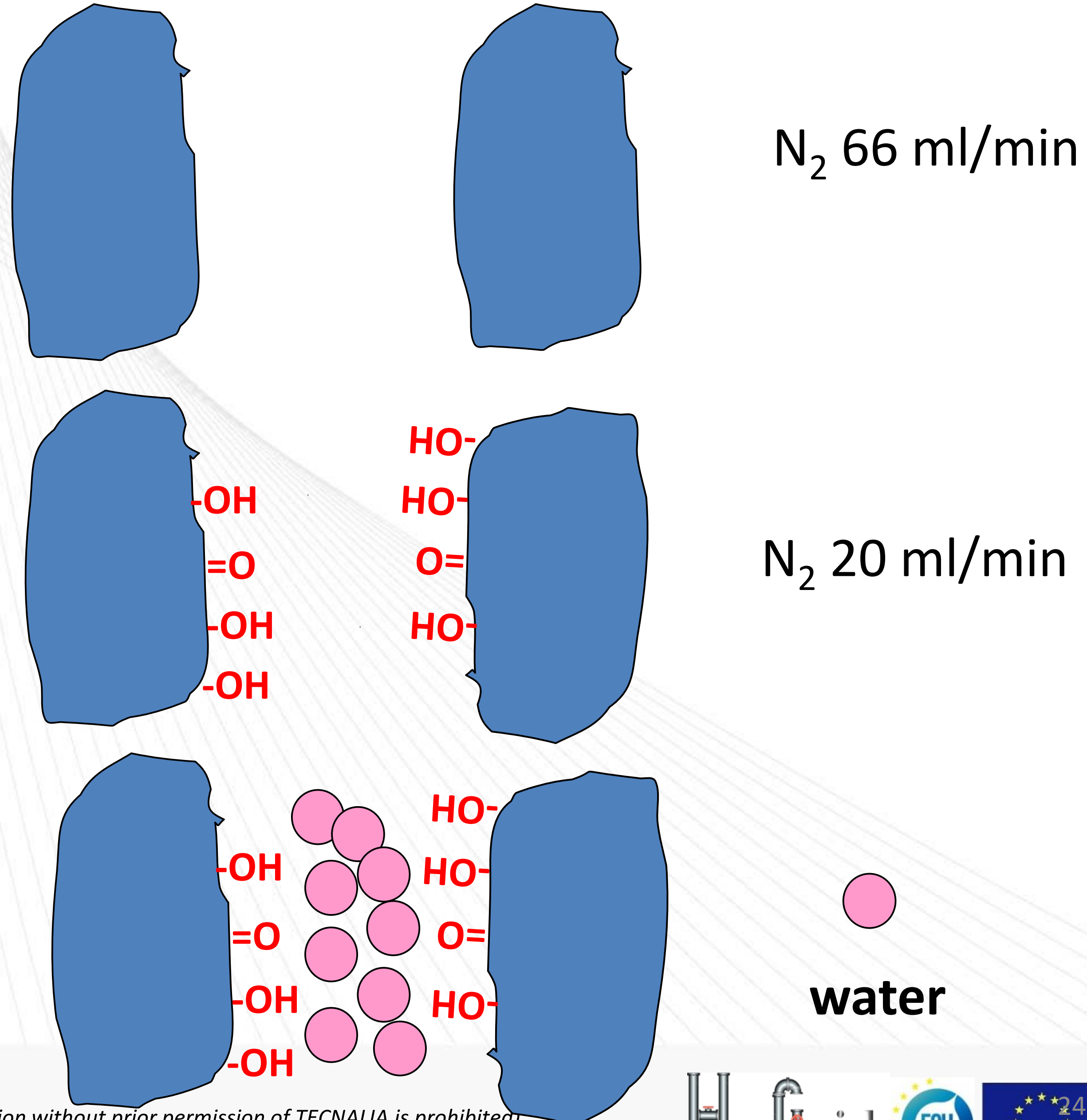


Modification on the porous

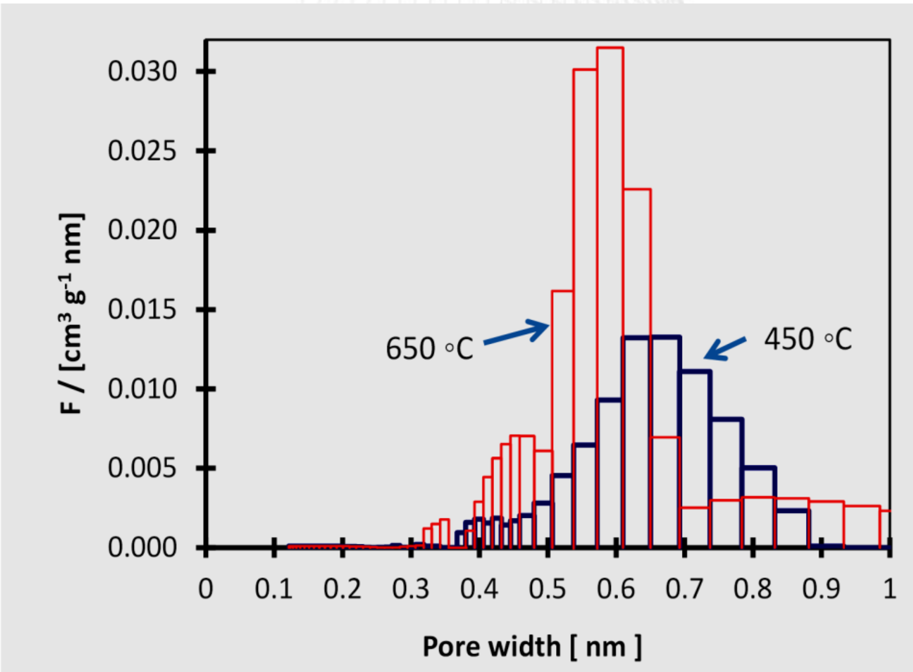
Just after carbonization

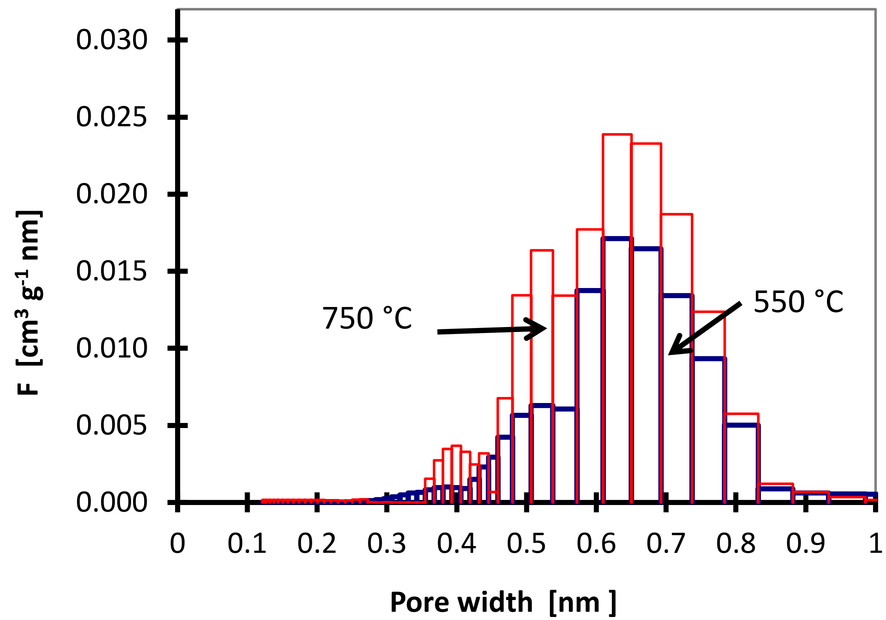
Active places react with water (water chemisorption)

Water physisorption

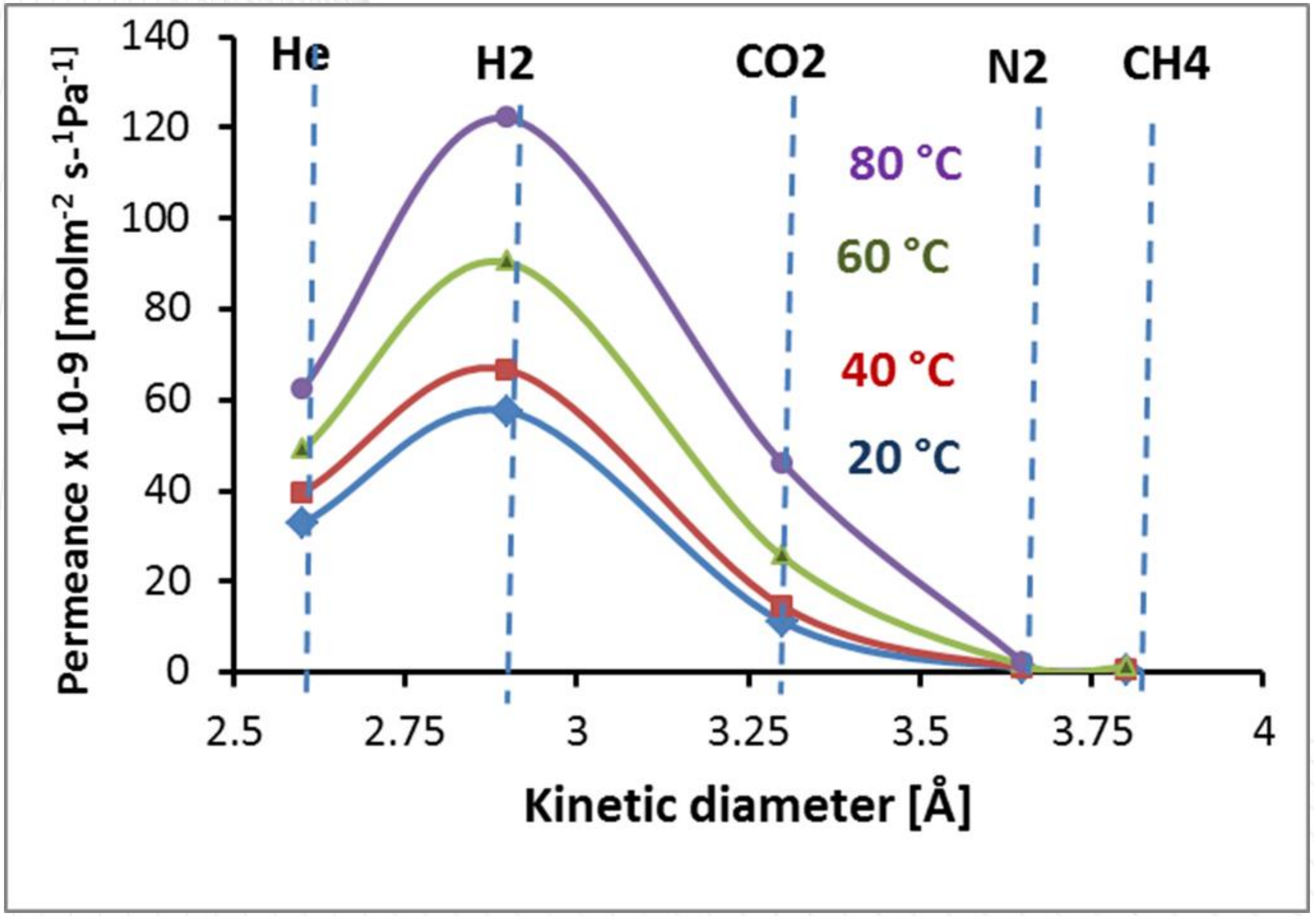


Pore size distribution at various carbonization temperatures

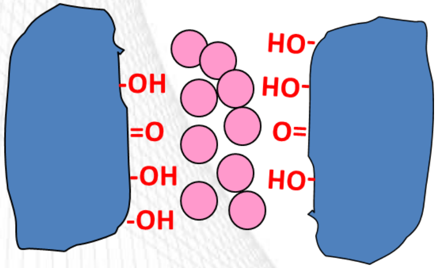


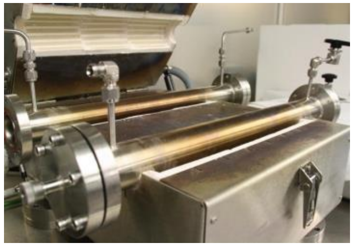


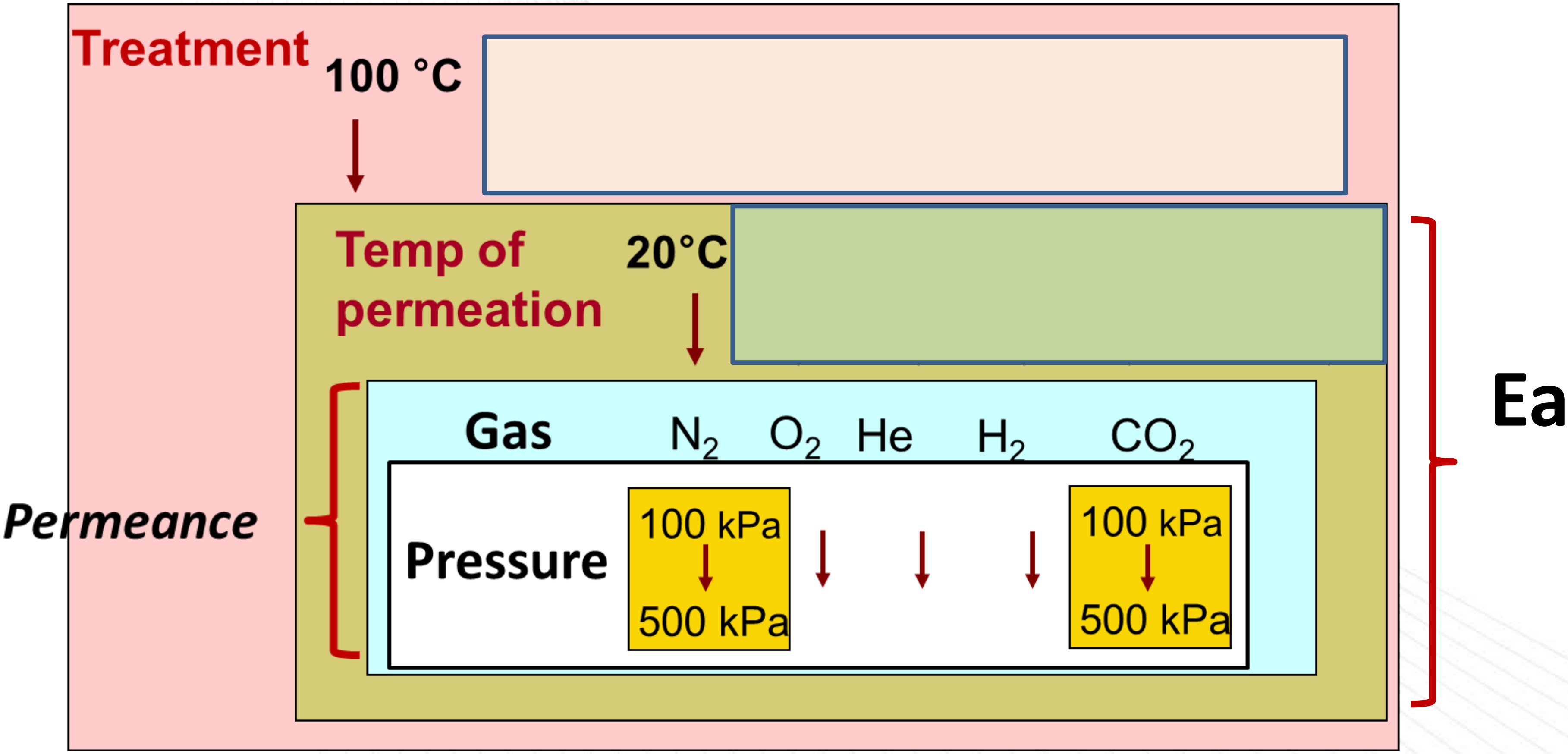
Gas permeance as a function of temperature Al-CMSM carbonized at 500 °C



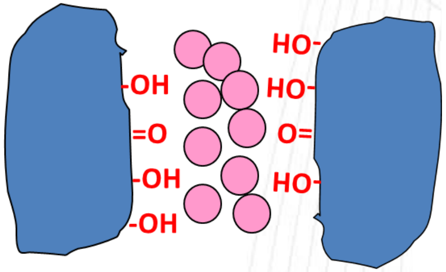
Activation Energy (Ea) at various activation heat treatments

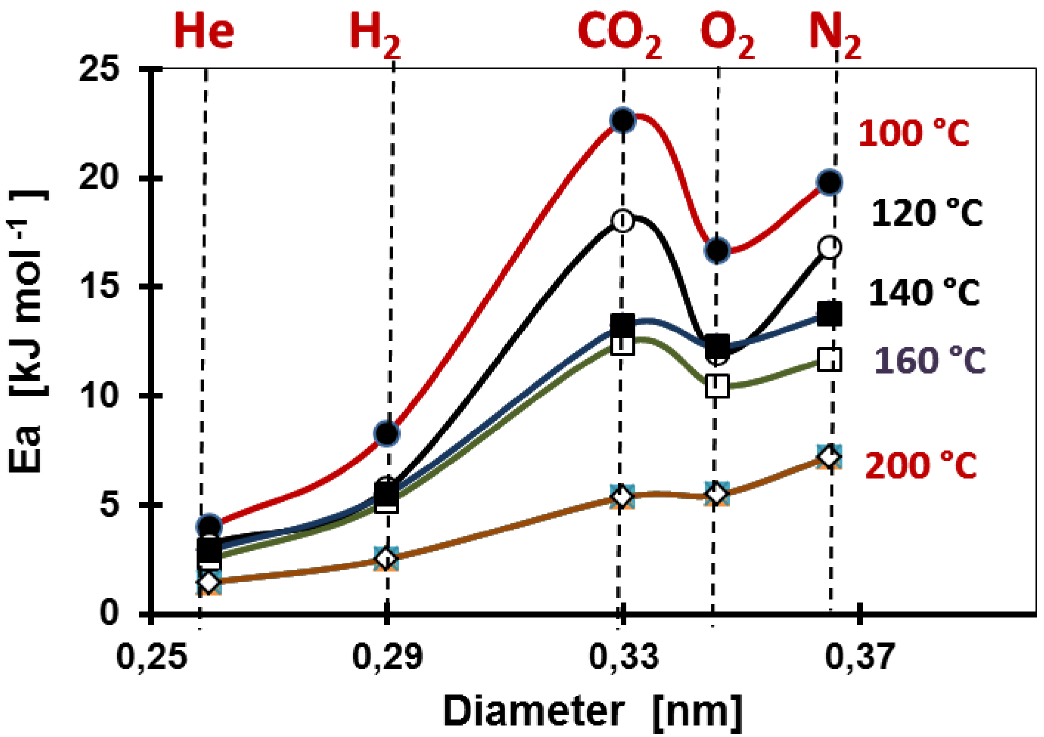






Activation energy of c-CMSM-500 membrane at various temperatures of pemeation, for various gases



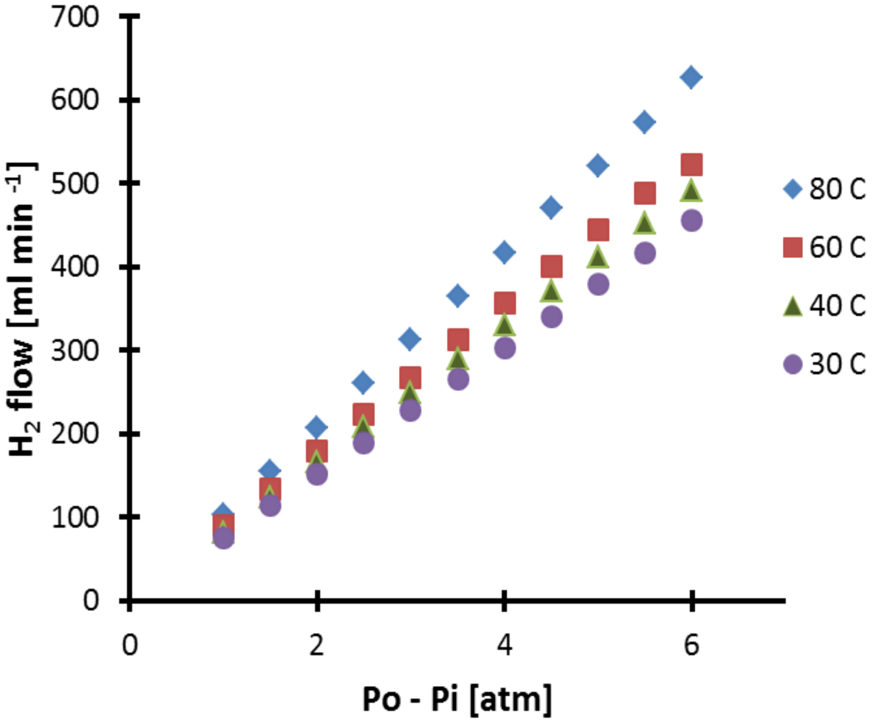


The values correspond to the average of permeation data performed at different temperatures from 40°C to 100°C

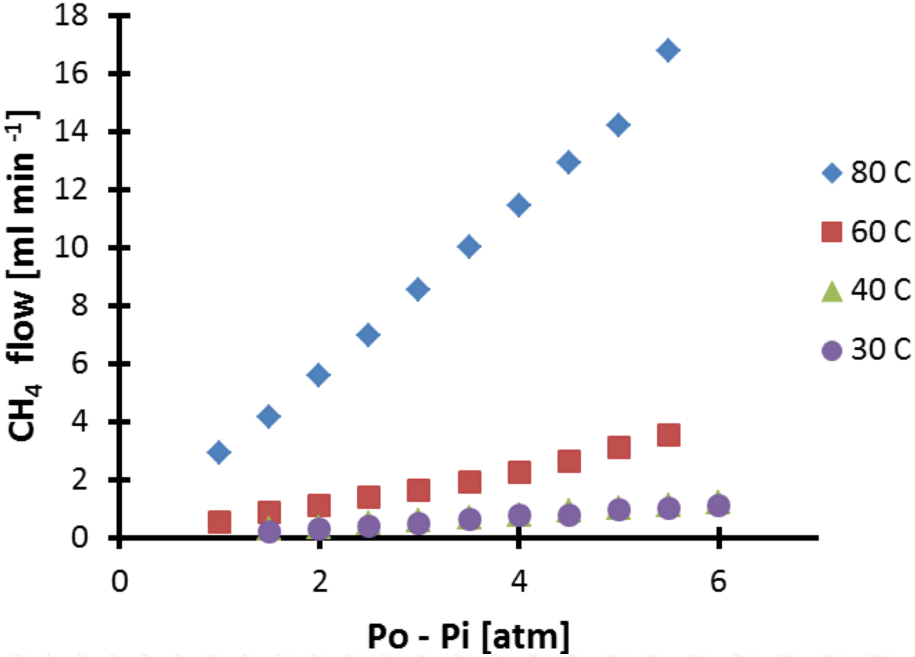
Single H_2 and CH_4 gas flow as a function of temperature and pressure

HyGrid

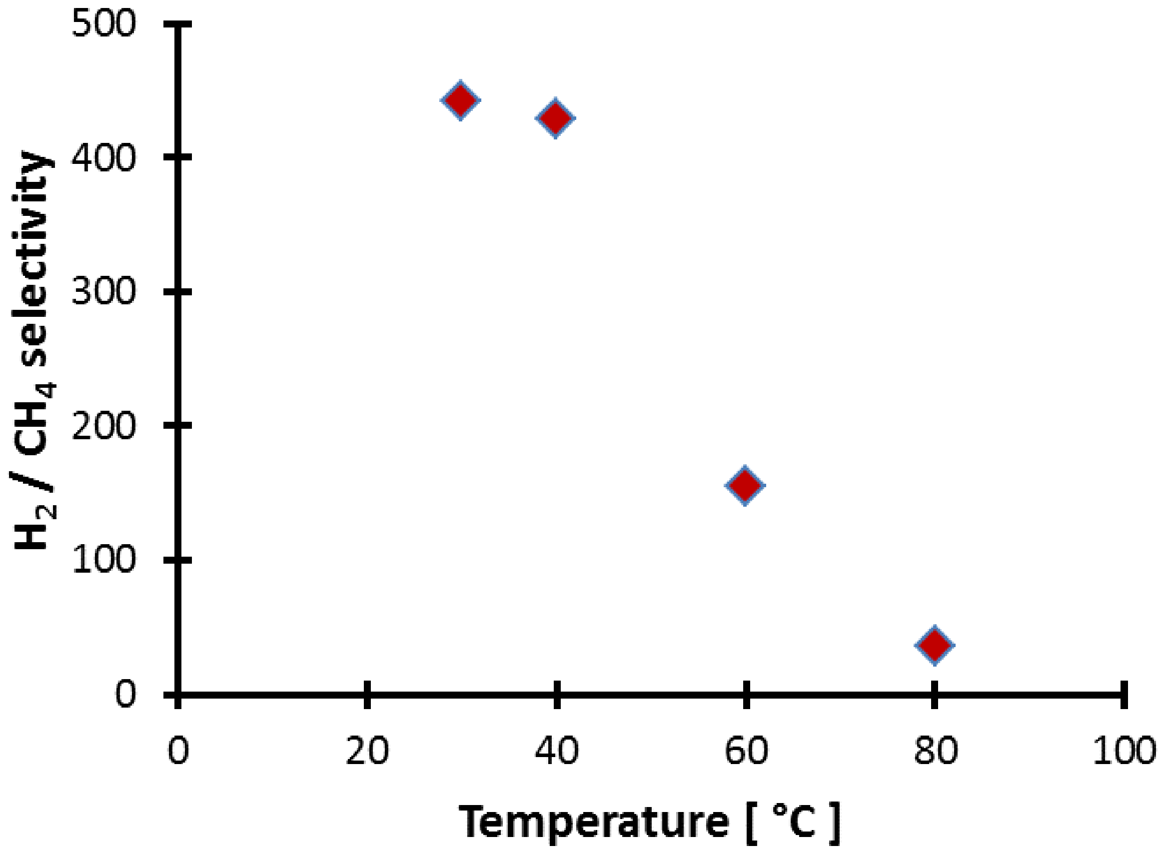
H_2



CH_4



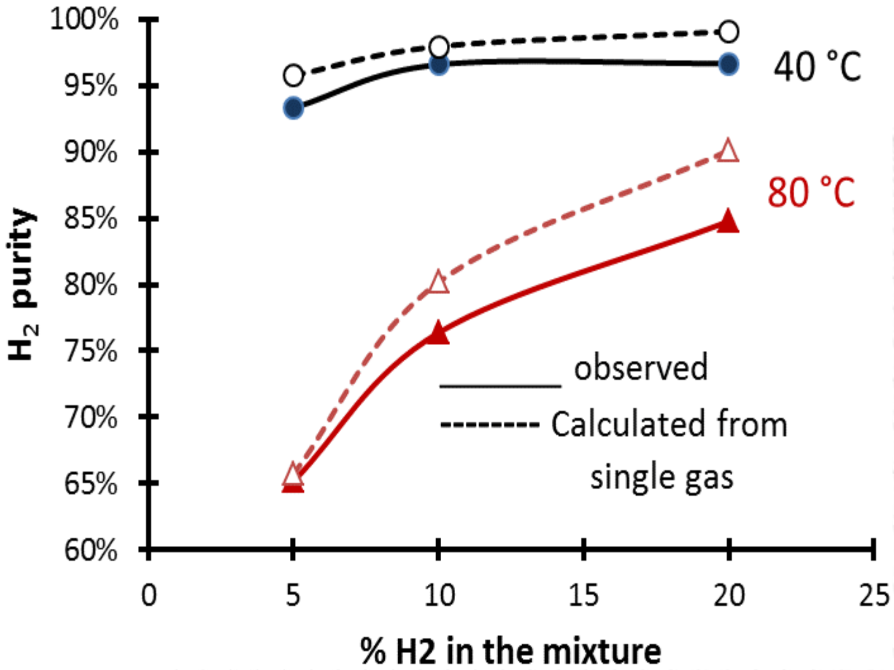
H2 and CH4 gas ideal perm-selectivity as a function of temperature



H_2, CH_4 mix gas permeation

H_2 purity (%) at various H2 contents in the mixture

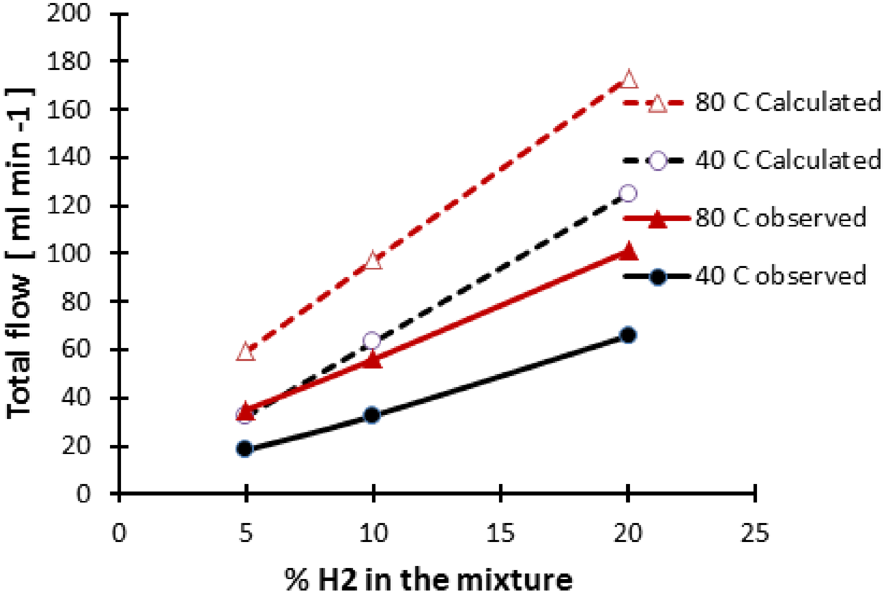
Pressure: out 7.5, in 0.01 bara, inlet 2 L min^{-1}



Testing temp (°C)	H_2 in feed mixture (%)	H_2 purity in the permeate (%)	
		Measured	**Calculated**
40	5	93.3	95.7
	10	96.6	98.0
	20	96.7	99.0
80	5	65.2	65.7
	10	76.4	80.2
	20	84.8	90.1

Total flow H2- CH4 mixed gas

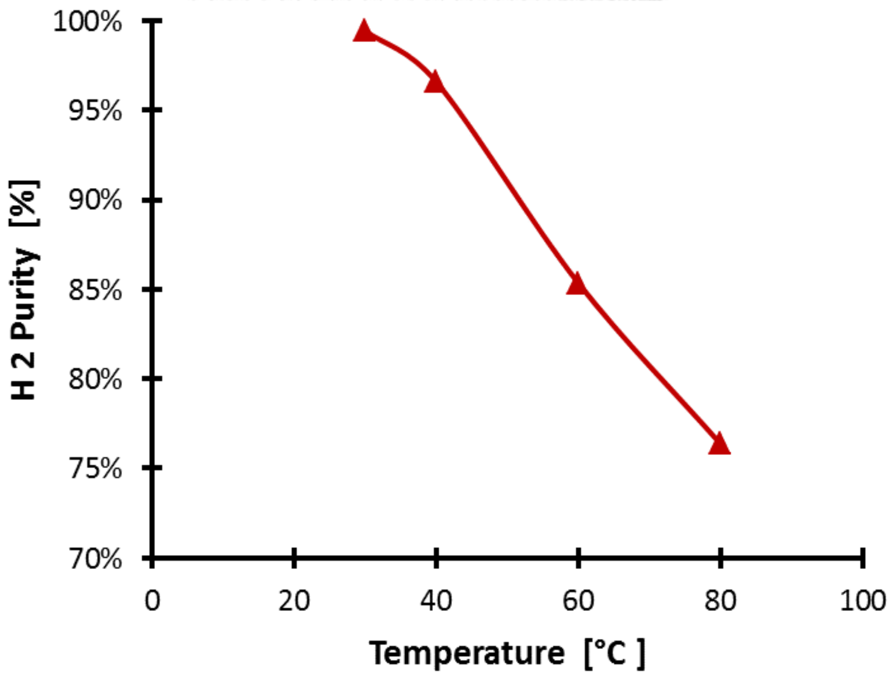
Pressure: out 7.5, in 0.01 bara, inlet 2 L min^{-1}



Testing temp (°C)	H_2 in feed mixture (%)	H_2 purity in the permeate (%)	
		Measured	**Calculated**
40	5	93.3	95.7
	10	96.6	98.0
	20	96.7	99.0
80	5	65.2	65.7
	10	76.4	80.2
	20	84.8	90.1

H_2-CH_4 mixed gas tests (10% of H_2)

(Pressure$_{out}$: 7.5 bara; Pressure$_{in}$: 0.01 bara, inlet 2 L min^{-1})



Testing temperature (°C)	H_2 purity in the permeate (%)
80	76.4
60	85.4
40	96.6
30	99.4

Exceeds the H_2 purity requirement of Grade A (98.0 %) and is close to Category 3 (99.9%).

Acknowledgements

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 700355. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and N.ERGHY.

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