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ADVANCED **PO**WER CONVERSION TECHNO**L**OGIES BASED ON **O**NBOARD AMMONIA CRACKING THROUGH NOVEL MEMBRANE REACTORS

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Palladium membranes

Winter School 2025
Eindhoven, 27-28 January

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Content

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- Membranes for H_2 separation
- Why Palladium?
- Membrane preparation
- Properties
- Membrane performance
- Applications/EU projects

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Membranes for H_2 separation

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Membranes for gas separation

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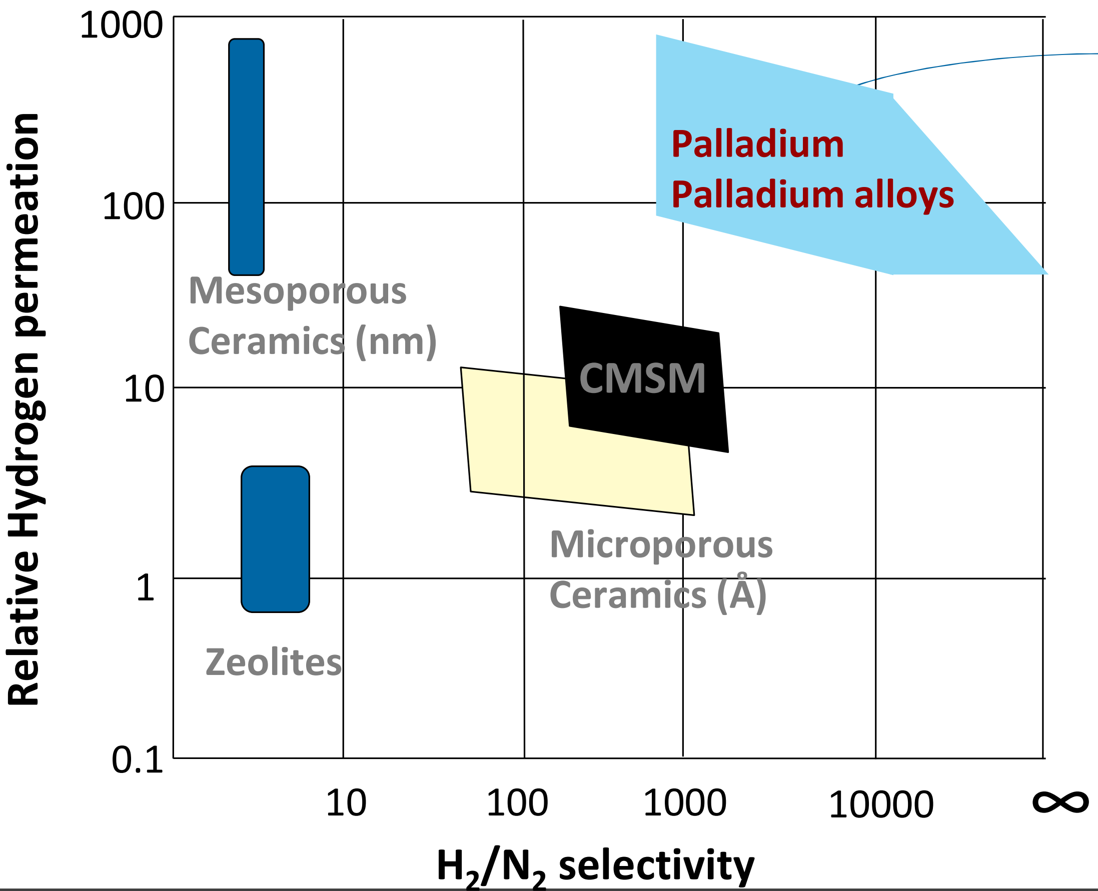
- Membrane classification
  - Nature
    - Synthetic
      - Inorganic
        - Ceramic, metallics, carbon, zeolites, glass etc.
      - Organic
    - Biological
  - Structure
    - Symmetric
    - Asymmetric
  - Geometry
    - Tubular
    - Hollow fiber
    - Flat sheet
  - Transport mechanism
    - Dense
      - Solution diffusion
      - Facilitated transport
    - Porous
      - Knudsen, molecular sieving, Surface Flow etc.

Pd-based supported membrane

Membranes for H_2 separation



Why Palladium?

Defect free Pd membrane:
∞ selective to H_2

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Why Palladium?

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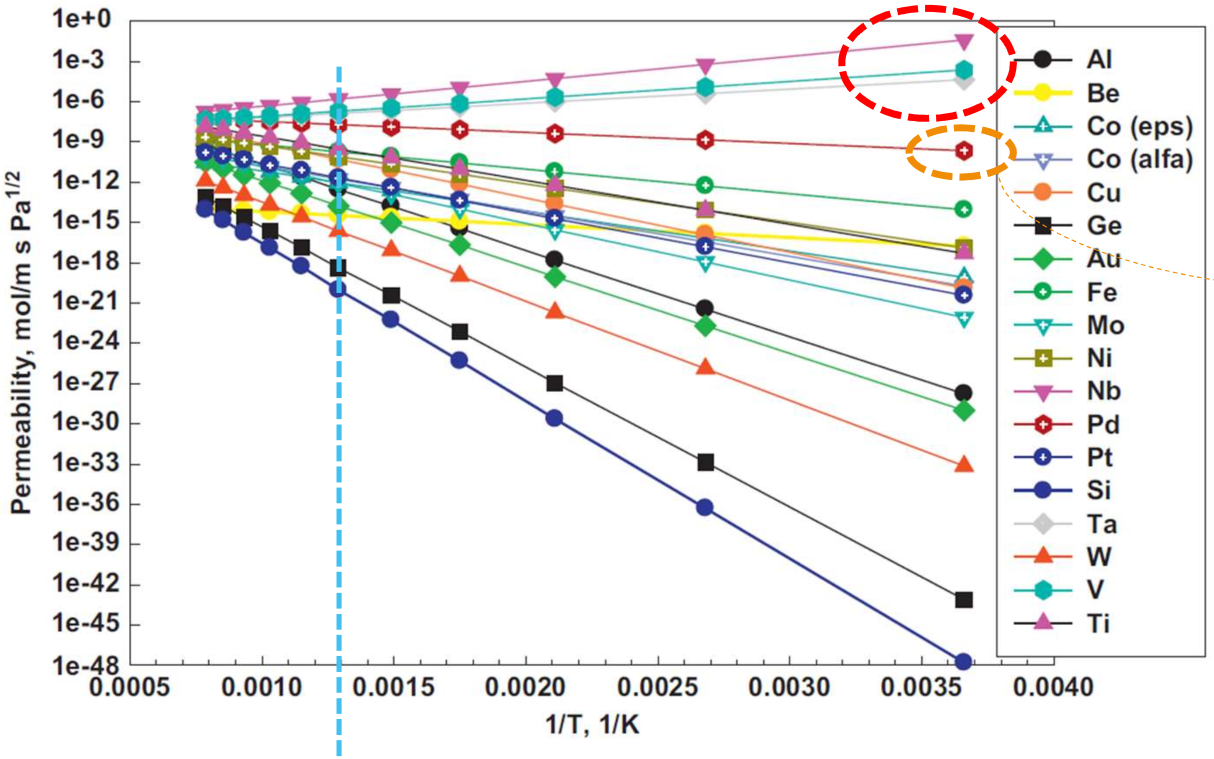
Why Palladium?

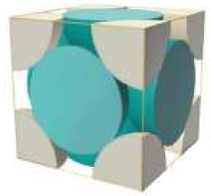


Nb
V
Ta

Pd

Strong surface resistance to hydrogen transport

BCC



FCC

Metal	Crystal structure	H_2 permeability at 500 ºC ($mol/m \cdot s \cdot Pa^{0.5}$)
Nb	BCC	$1.6 \cdot 10^{-6}$
Ta		$1.3 \cdot 10^{-7}$
V		$1.9 \cdot 10^{-7}$
Fe		$1.8 \cdot 10^{-10}$
Pd	FCC	$1.9 \cdot 10^{-8}$
Pt		$2.0 \cdot 10^{-12}$

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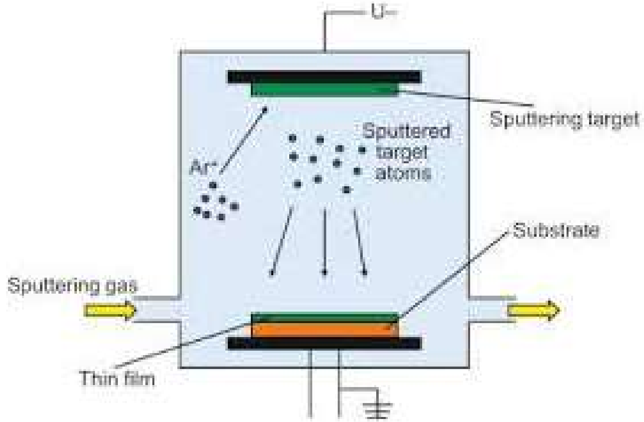
Membrane preparation

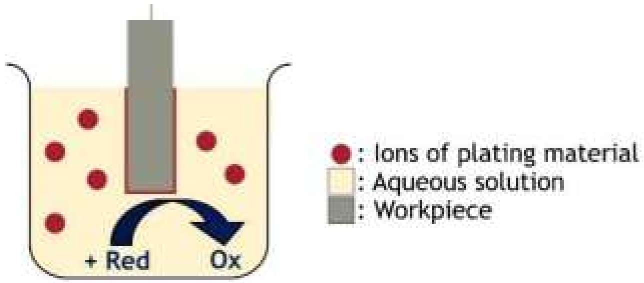
Membrane preparation

- Fabrication techniques (supported membranes)

Dry techniques
- **PVD** (Plasma vapor deposition)
- **CVD** (Chemical vapor deposition)



Wet techniques
- **ELP** (Electroless plating)
- **EP** (Electroplating)



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Membrane preparation

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➢ Fabrication techniques (supported membranes)

Technique	Pros	Cons
PVD	• Used for many metals • High deposition rate • Control of thickness and composition of alloys • No liquid wastes	• Expensive equipment • Influence of support geometry (shadowing)
CVD	• Complex geometries	• Low deposition rate • Toxic reactants • Small-scale (complex to scale-up)
Electroless plating	• High deposition rate • Complex geometries • Cheap equipment • Simple operation • Ease of scale up	• For limited number of metals • Limited number of elements in the alloy (ternary alloy difficult)
Electroplating	• High deposition rate	• Support must be conductive • Need of electricity • Mainly used for pure metal (not alloys)

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Membrane preparation

APOLO

- Importance of the support

$$H_2\,flux = J_{H_2} = \frac{P_e^0}{\delta} e^{-\frac{E_a}{RT}} \left(P_{ret}^n - P_{perm}^n\right)$$

P_e^0 : Pre-exponential factor of H_2 permeability ($mol\ m^{-1}\ s^{-1}\ Pa^{-n}$)
δ: Membrane thickness (m)
n: n-value f(limiting step)

Self-supported
- Thick
- Low hydrogen permeation
- High cost of Pd

Supported
- Thin layer (defect free)
- High hydrogen permeation
- Alloy with other metals (Ag, Cu…)

H_2 flux inversely proportional to the thickness

↓

↑H_2 flux &↑H_2 selective

↓

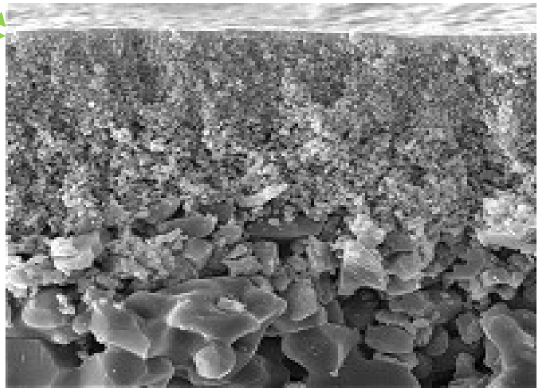
Defect free thin membrane (supported)

Membrane preparation

➢ Importance of the support

Support
- Morphology
  - Symmetric (high mass transfer resistance)
  - Asymmetric
- Material
  - Ceramic
  - Metallic

Outer layer:
α-Al_2O_3; 100 nm pore size



http://www.inopor.com/en/index.html

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Membrane preparation

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- ✓ Low mass transfer resistance
- ✓ Small pore size
- ✓ Smooth surface

→ Asymmetric ceramic support

- ✓ Easy to integrate into a reactor

→ Asymmetric metallic support

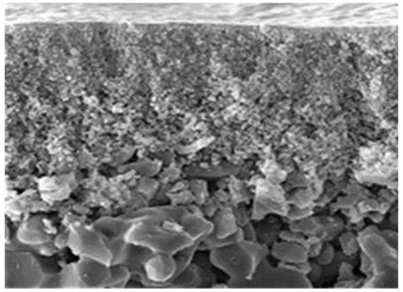
- ✓ No chemical interaction with Pd-based layer

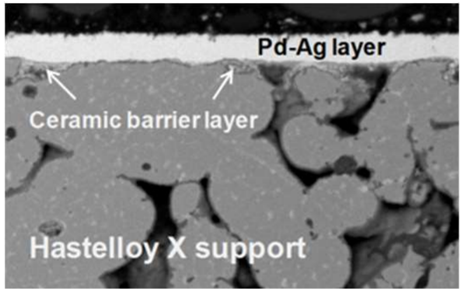
→ Ceramic support: α-Al_2O_3, ZrO_2…
Metallic support: interdiffusion barrier

Membrane preparation

➢ Importance of the support

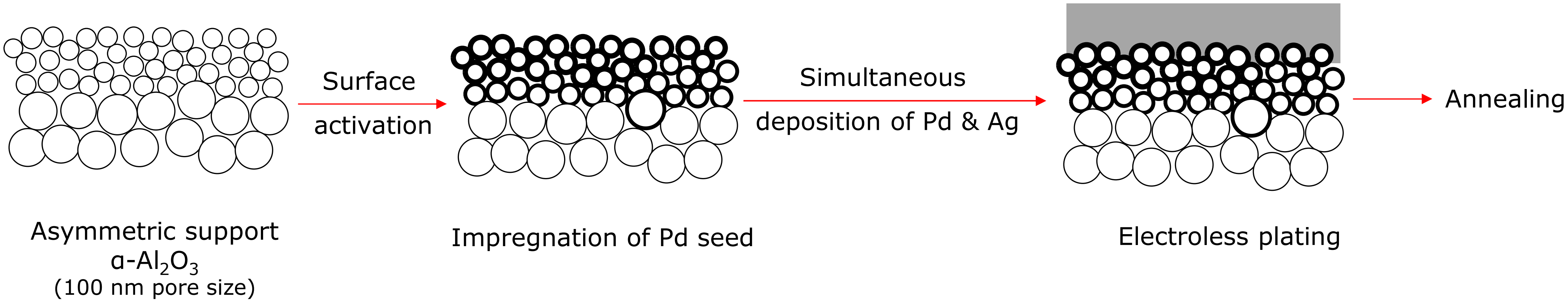
	Support material (asymmetric)	
	Ceramic	**Metallic**
Pros	• Low resolution to gas permeation • Small por size • Smooth surface • Less expensive than metallic supports	• Low resistance to gas permeation • Mechanically strong • No problem with sealing • Easy to connect to a reactor





Membrane preparation

- Deposition of thin Pd-based supported membranes (< 5 µm) (for high H_2 permeation and selectivity)



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Membrane preparation

APOLO

- Deposition of thin Pd-based supported membranes (< 5 µm) (for high H_2 permeation and selectivity)

Ceramic supported thin Pd-based membranes
(with Swagelok-graphite connectors)

500 mm

Metallic supported thin Pd-based membranes
(welded to dense metal tubes)

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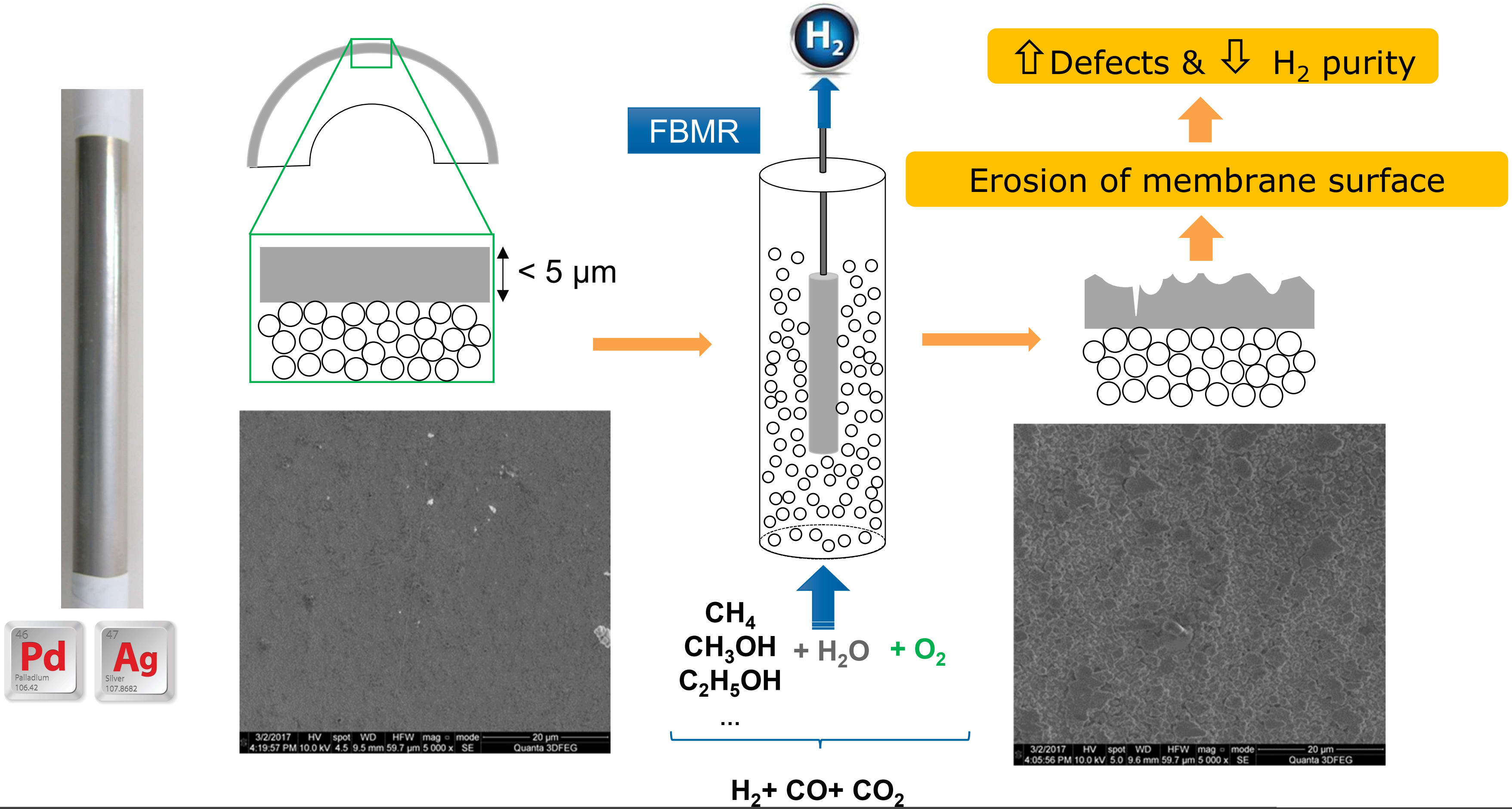
Membrane preparation

APOLO



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Membrane preparation

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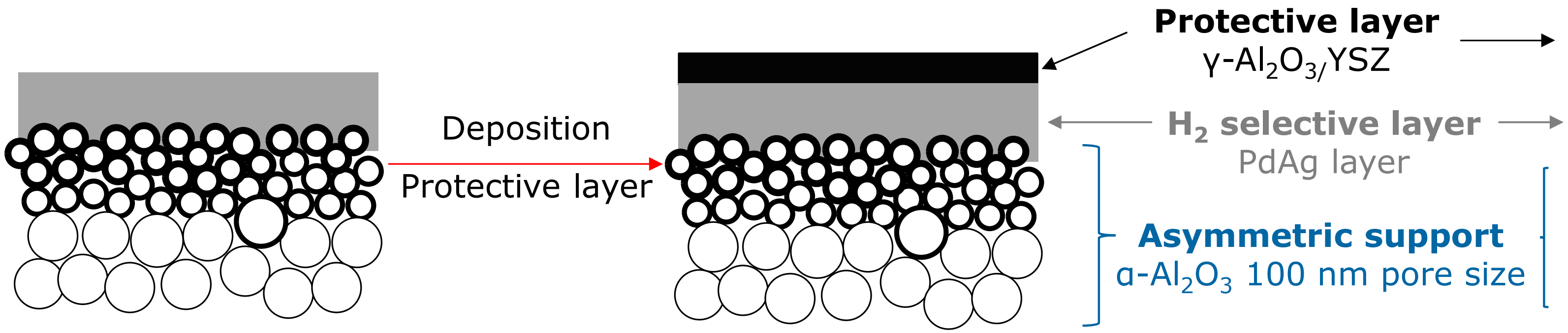
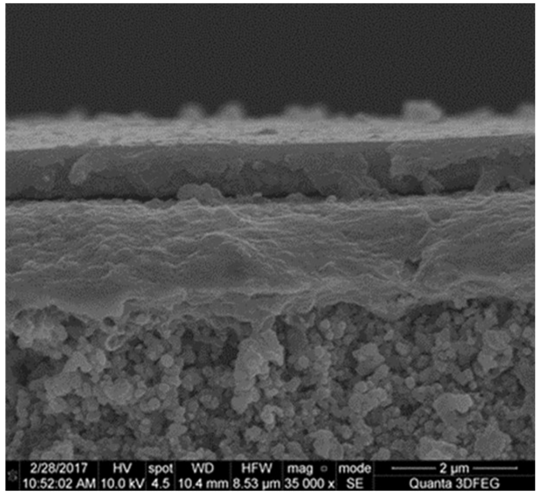
- Deposition of thin Pd-based **double-skinned (DS) membranes** (for high H_2 permeation, selectivity and **attrition-resistant**)



Dip-coating

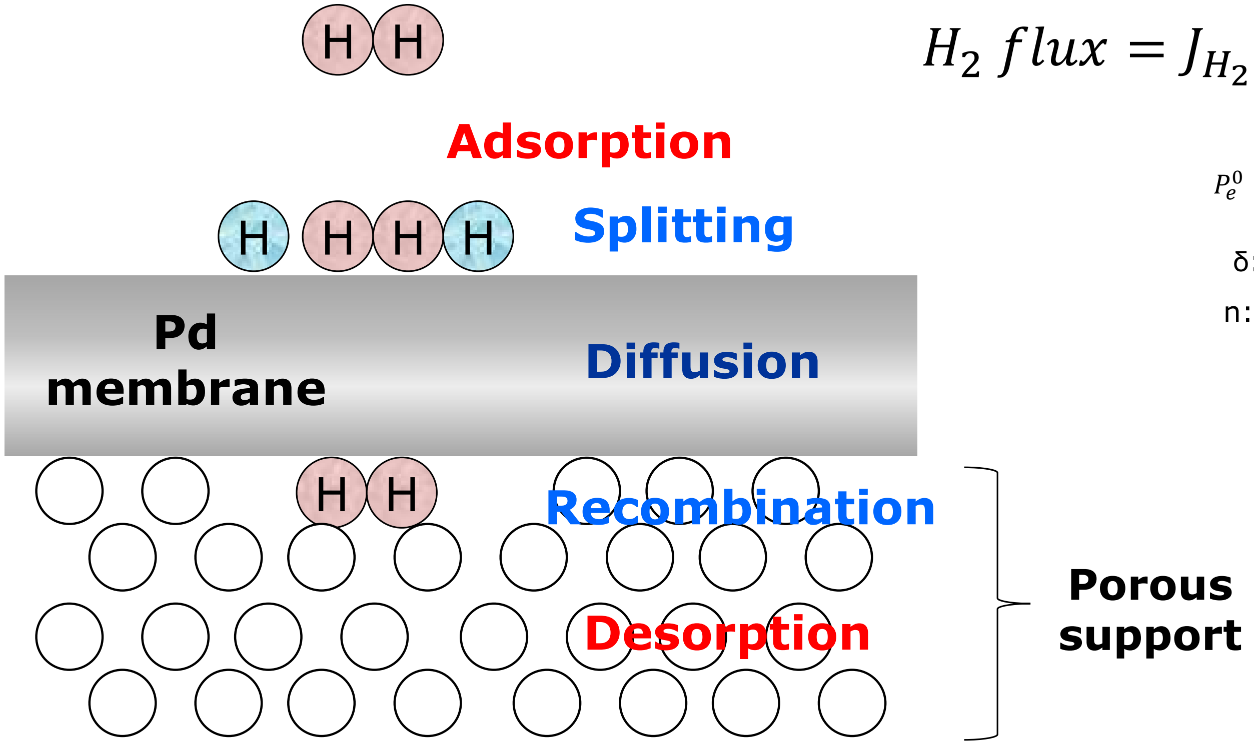


SEM image in cross section of **Pd-based DS membrane**

Properties

Properties

- Diffusion mechanism: Solution-diffusion



$$H_2\ flux = J_{H_2} = \frac{P_e^0}{\delta} e^{-\frac{E_a}{RT}} \left(P_{ret}^n - P_{perm}^n\right)$$

P_e^0 : Pre-exponential factor of H_2 permeability (mol m^{-1} s^{-1} Pa^{-n})

δ: Membrane thickness (m)

n: n-value f(limiting step)

n= 0.5 (Bulk)

n= 1 (Surface)

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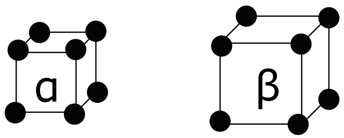
Properties

➢ Problems associated with Pd membranes

Embrittlement

α-β phase transition of PdH (<293 °C)



Sulphur poisoning

Pd_4S

Defective membranes

+Ag (up to 23%)
+Cu (up to 40%)
→ ↓ Phase transition temp.
↑ H_2 permeability
↓ Membrane price

+Au (up to 5%) → ↑ H_2 permeability

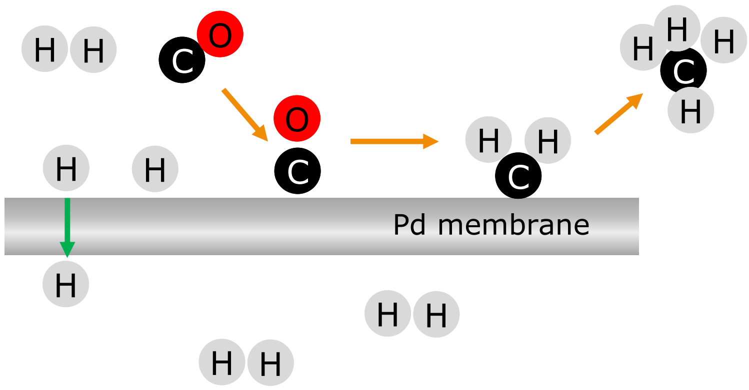
Properties

- Problems associated with Pd membranes

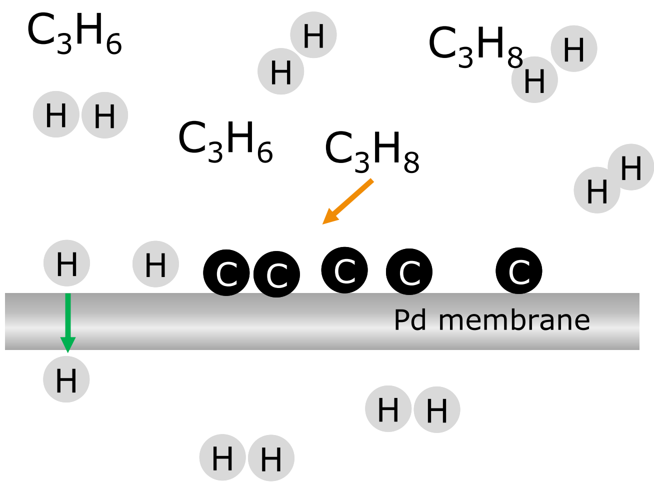
CO poisoning
(syngas)

H_2 permeation inhibition

Carbon deposition
(propane dehydrogenation)



↑ **Temp** → ↓ Poisoning



↓ **Temp** → ↓ Poisoning

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Properties

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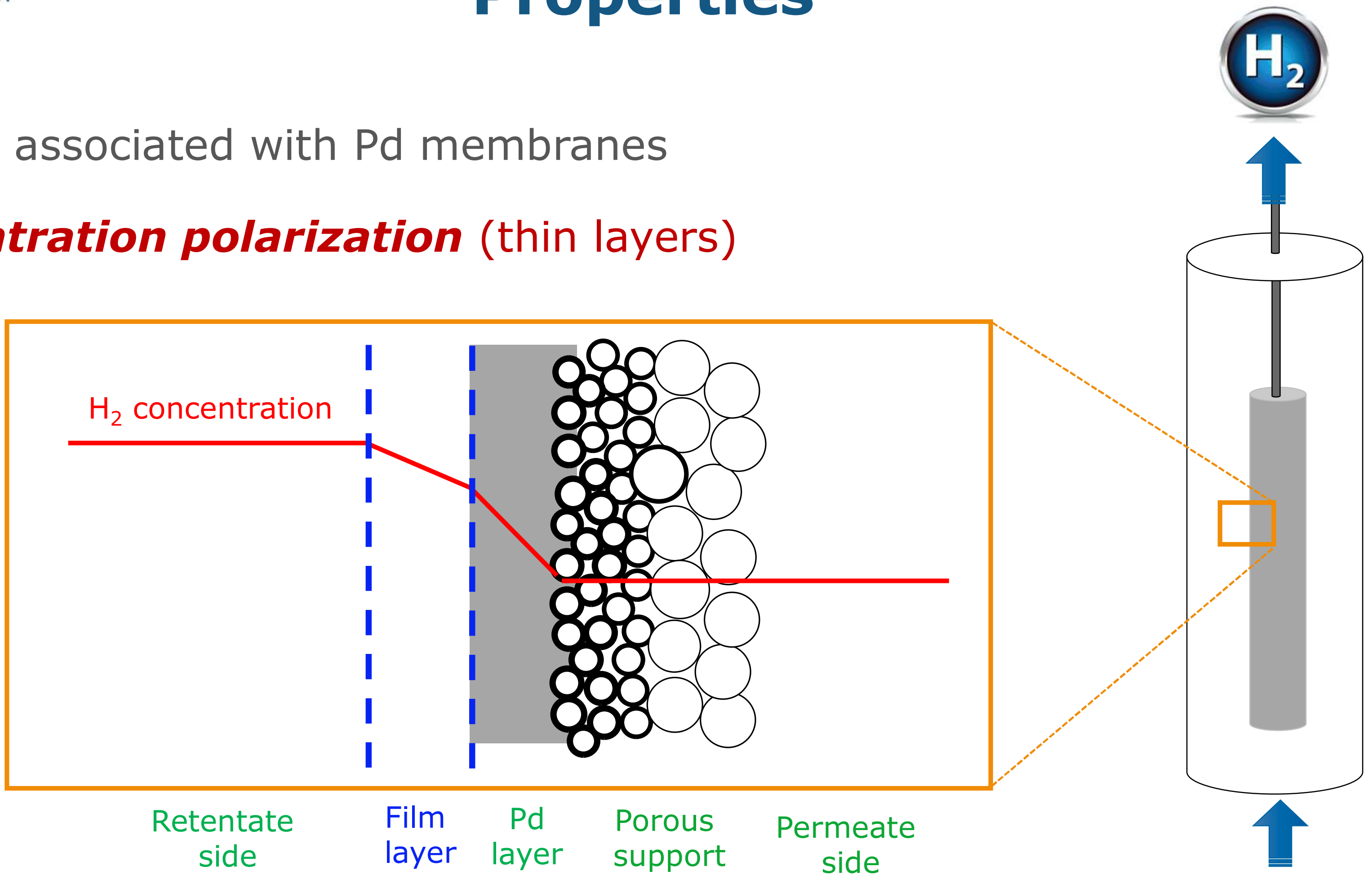
- Problems associated with Pd membranes

Concentration polarization (thin layers)



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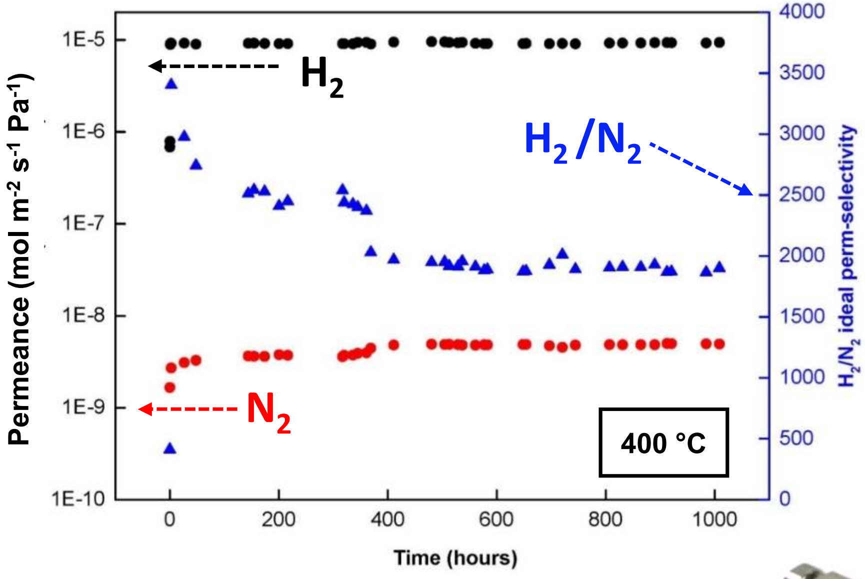
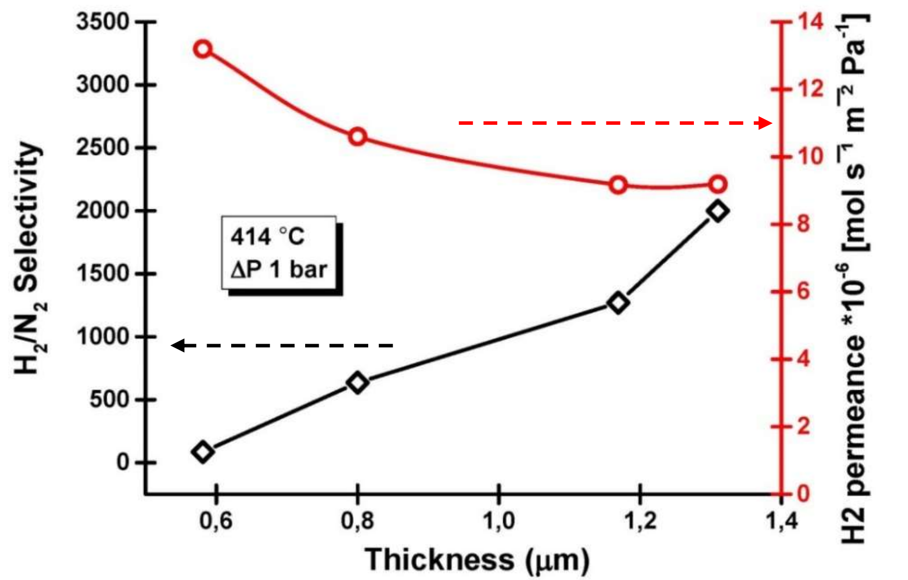
Membrane performance

- Ultra-thin ≤1 μm thick (ceramic support)
- Thin 4-5 μm thick (metallic support)
- Stability test in an empty reactor (metallic support)
- Stability test in FBMR (metallic support)
- Chemical interaction with catalyst

Membrane performance

- Ultra-thin (≤1 μm thick) Pd-Ag membranes (ceramic support)





1.3 μm thick Pd-Ag membrane

J. Melendez et al., J. Membr. Sci 528 (2017) 12-23

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Membrane performance

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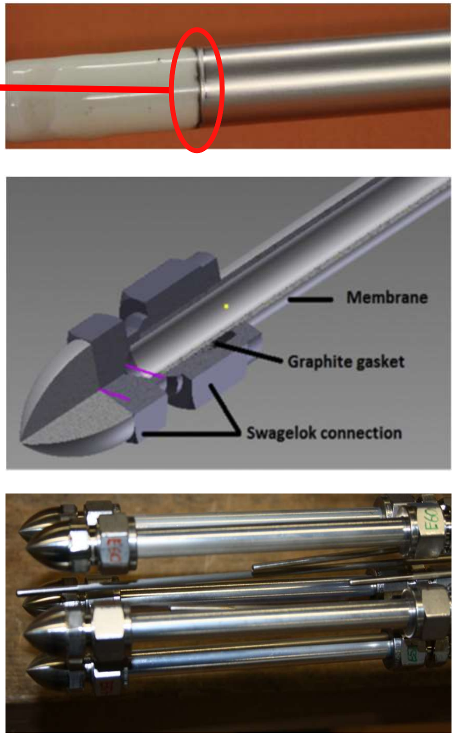
- Thin (4-5 μm thick) Pd-Ag membranes (metallic support)

Ceramic support

Leak zone

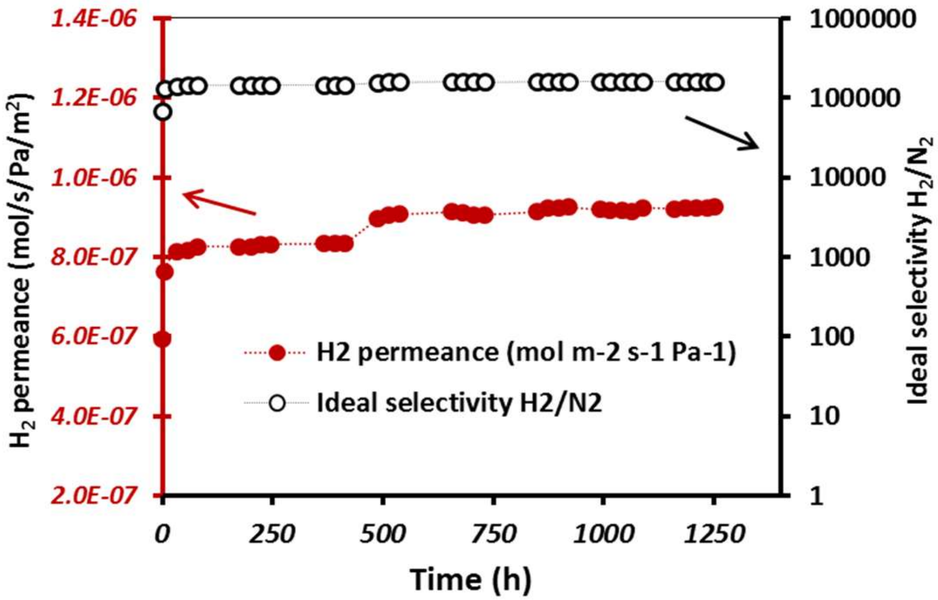


No Leak

No Leak

Metallic support

Long term permeation test at 400 °C



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Membrane performance

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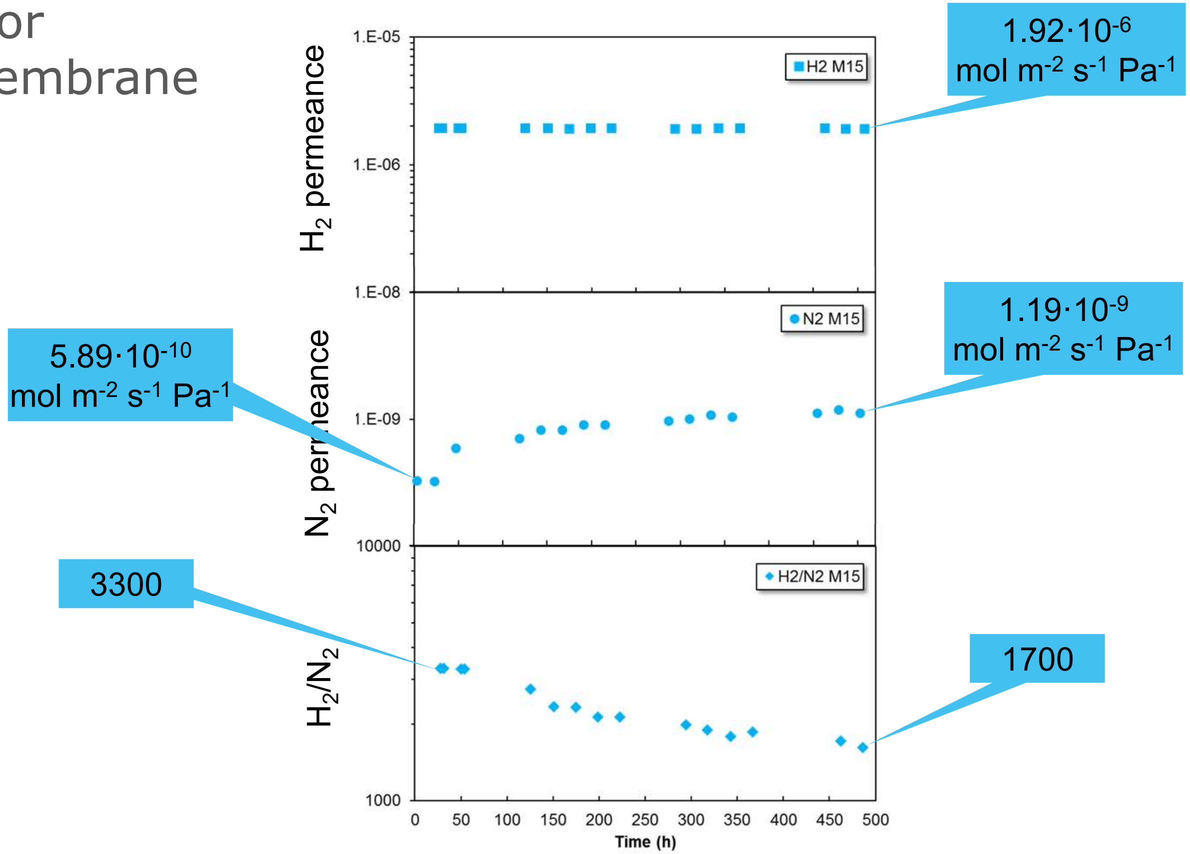
➢ Stability test in an empty reactor
Metallic supported Pd-based membrane

500 °C, ΔP= 1 bar (~ 510 h)

A. Arratibel et.al. J. Membr. Sci. 563 (2018) 419



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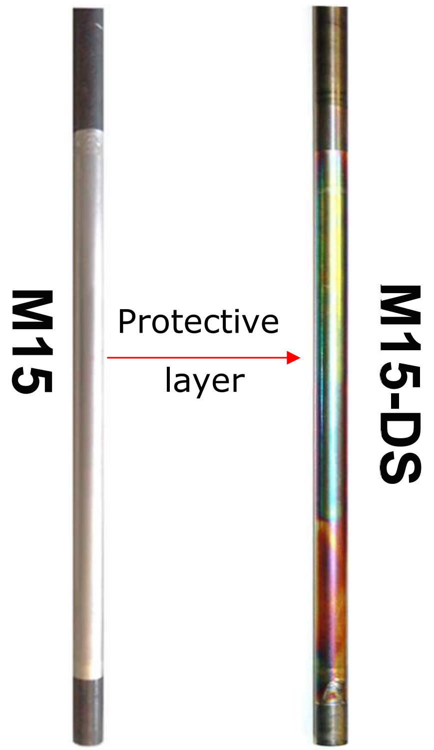
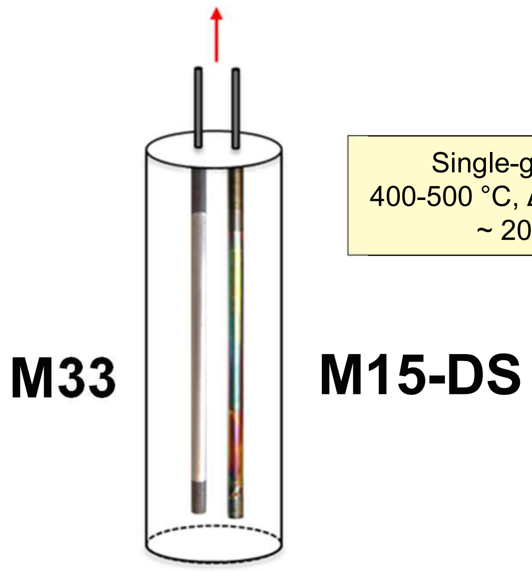
Membrane performance

- Stability test in an empty reactor
  Metallic supported Pd-based membrane





Empty reactor

Single-gas test
400-500 °C, ΔP= 1-4 bar
~ 200 h

Parameter	M15	M15-DS	M33
H_2 permeance* (mol m^{-2} s^{-1} Pa^{-1})	$1.92 \cdot 10^{-6}$	$1.55 \cdot 10^{-6}$	$1.34 \cdot 10^{-6}$
Ideal H_2/N_2 permselectivity	3300	3500000	93300

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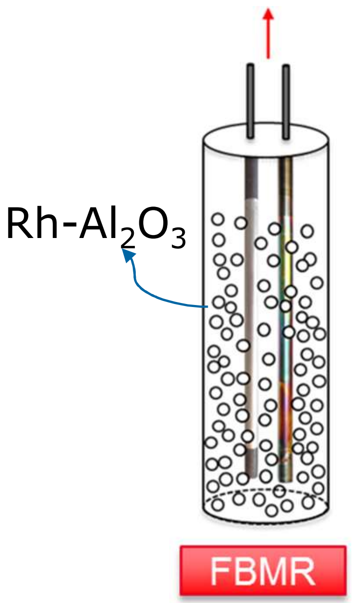
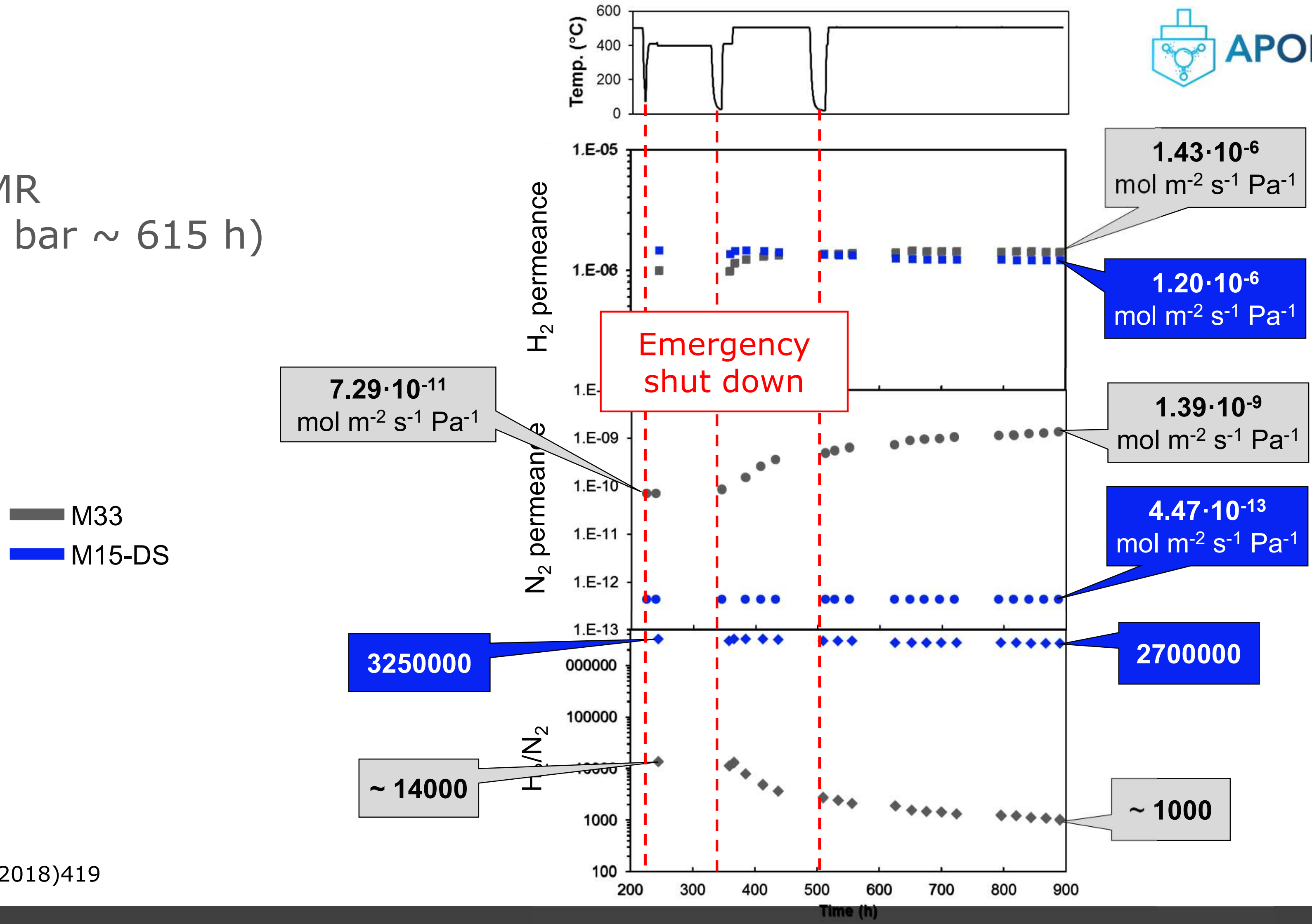
- Stability test in FBMR (400-500 °C, ΔP= 4 bar ~ 615 h)





A. Arratibel et.al. J. Membr. Sci. 563 (2018)419

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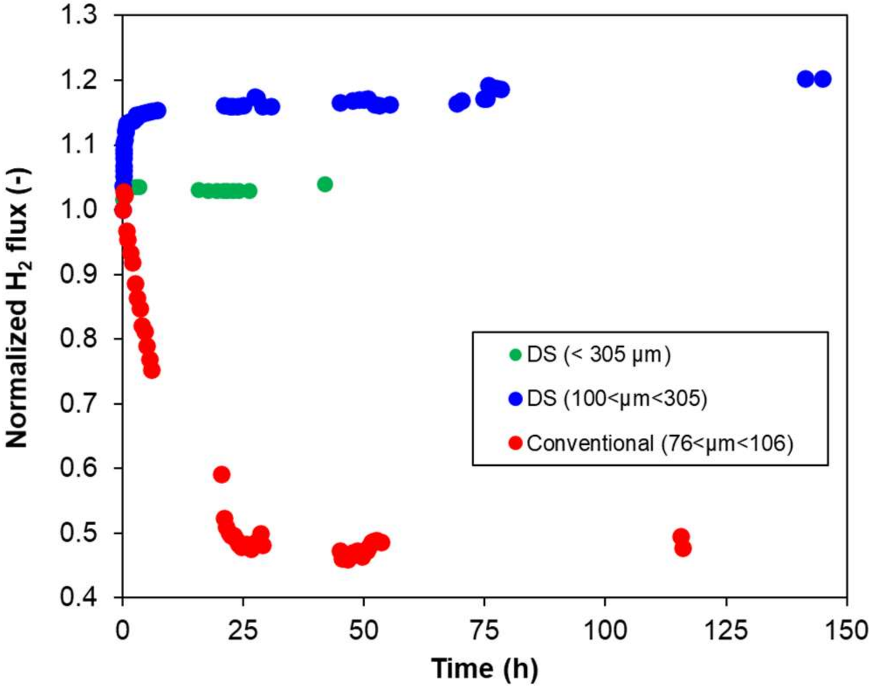
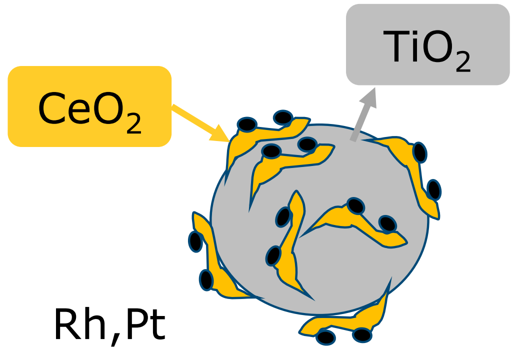
Membrane performance

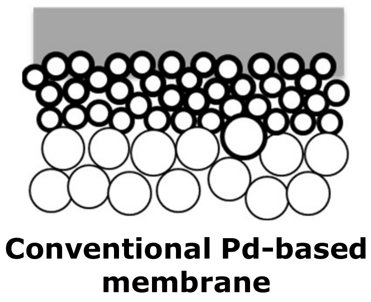
- **Chemical interaction with catalyst**

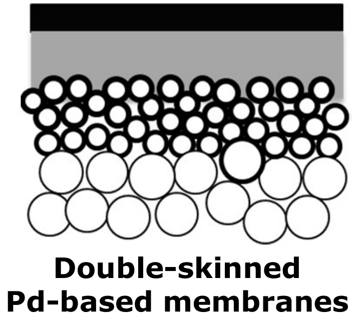
400 °C; Pure H_2 permeation test



A. Arratibel et.al. IJHE 46 (2021) 20240-20244







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Applications/EU projects

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Applications

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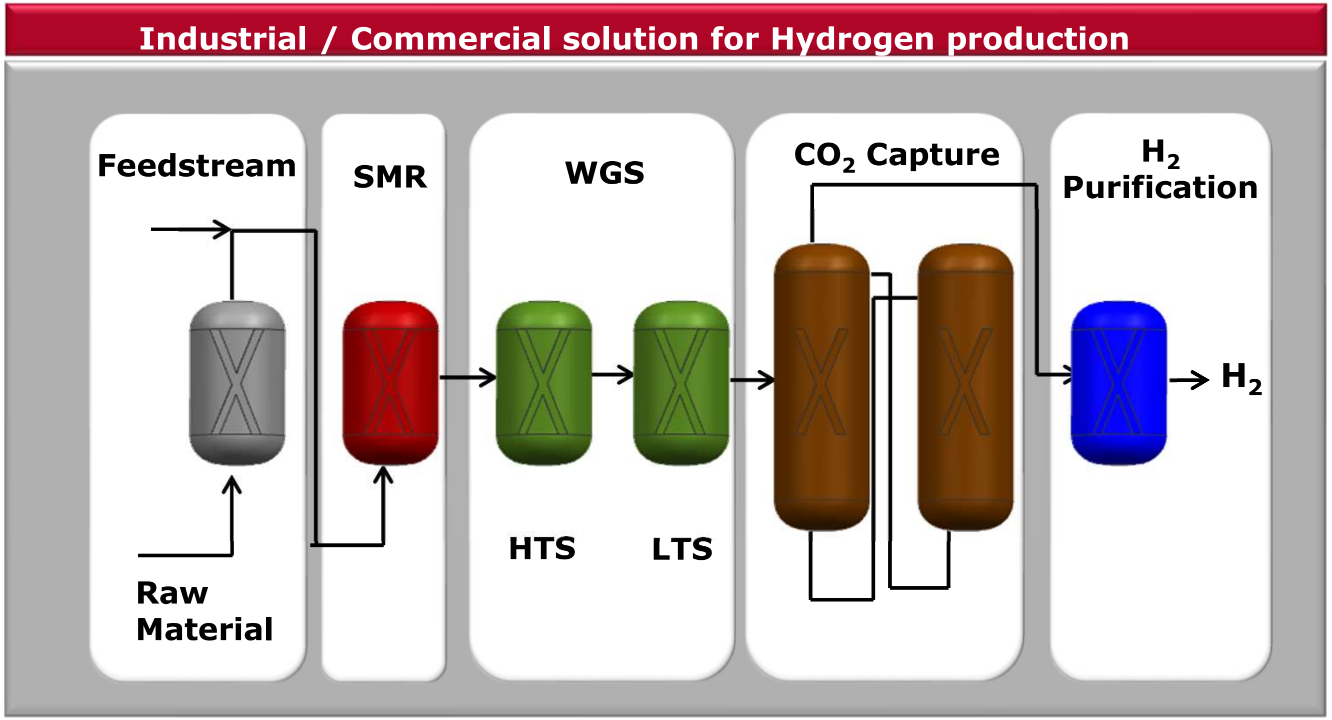
- Process intensification/ Membrane reactors



$$CH_4 + 2\,H_2O \rightleftarrows CO_2 + 4\,H_2$$

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Applications/EU projects

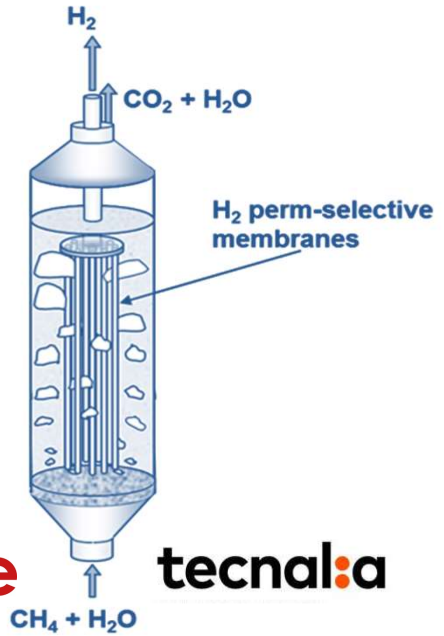
Feedstock

Natural gas
Biogas
(Bio)ethanol

Syngas

Ammonia

Membrane reactor



Reaction

Reforming

Water gas shift

Dehydrogenation

EU Projects

areNH3a | DEMCAMER Catalytic Membrane Reactors | RE4CELL | FERRET | Fluid CELL | MEMBER | BIONICO | MACBETH Membranes And Catalysts Beyond Economic and Technological Hurdles

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Applications/EU projects

- EU projects on membrane reactors for H_2 production

Water gas shift reaction (WGS)

$$CO + H_2O \rightleftarrows \mathbf{H_2} + CO_2$$

Steam reforming of methane (SMR)

$$CH_4 + 2\,H_2O \rightleftarrows CO_2 + \mathbf{4\ H_2}$$

Ethanol steam reforming

$$C_2H_5OH + 3\,H_2O \rightleftarrows 2\,CO_2 + \mathbf{6\ H_2}$$

Ammonia decomposition

$$2\,NH_3 \rightleftarrows N_2 + \mathbf{H_2}$$

SEVENTH FRAMEWORK PROGRAMME
HORIZON 2020
FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING
DEMCAMER Catalytic Membrane Reactors
RE4CELL
FERRET
BIONICO
Fluid CELL
areNH$_3$a

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Applications/EU projects

- EU projects on membrane reactors for H_2 production

MACBETH
Membranes And Catalysts Beyond Economic and Technological Hurdles

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

[1] Steam reforming of methane (SMR)

[2] Biogas reforming (CH_4 -CO_2)

[3] Propane dehydrogenation (PDH)

$$C_3H_8 \rightleftarrows C_3H_6 + \mathbf{H_2}$$

…

$$C_3H_8 \rightleftarrows 3\,C + \mathbf{4\,H_2}$$

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EU projects

➢ EU projects on membrane reactors for H_2 production

MACBETH
Membranes And Catalysts Beyond Economic and Technological Hurdles

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

[1] SMR **(70)**

[2] CH_4 -CO_2 **(125)**

[3] PDH **(20)**

215 membranes of 40-45 cm long manufactured for 5 demoplants

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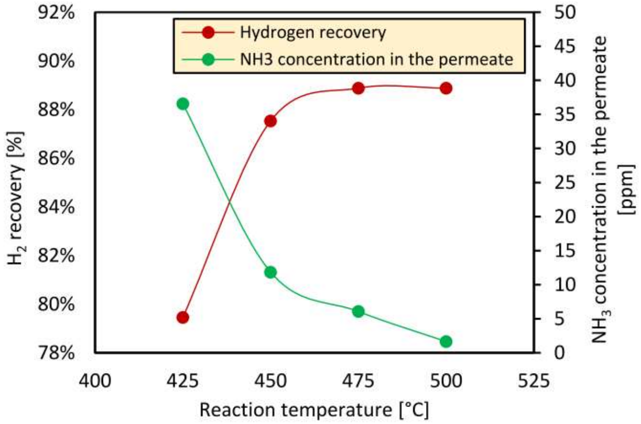
EU projects

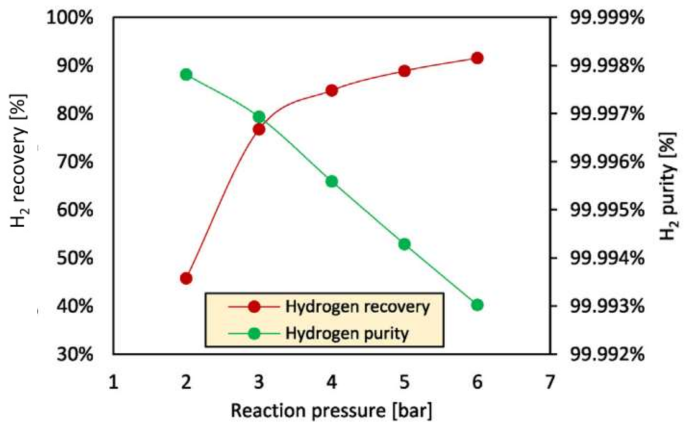
➢ Ammonia decomposition

		450 ºC & 1 barg			
Membrane code	Thickness Selective layer (µm)	H_2 permeance (mol s^{-1} m^{-2} Pa^{-1})	**N_2 permeance (mol s^{-1} m^{-2} Pa^{-1})**	Pressure exponent (-)	Ideal H_2/N_2
A-2	~ 1	$2.22 \cdot 10^{-6}$	**$4.26 \cdot 10^{-10}$**	0.80	5210
A-3	~ 6-8	$1.15 \cdot 10^{-6}$	**$1.66 \cdot 10^{-11}$**	0.72	68960

500 ºC; 4 bar(a); Ff= 0.5 L_N/min NH_3	
H_2 recovery (%)	NH_3 concentration in the permeate (ppm)
93.2	47 (±2.1)
84.8	<0.75



A-3; 5 barg; 0.5 L_N/min NH_3



A-3; 500 ºC; 0.5 L_N/min NH_3

V. Cechetto et al., IJHE 47 (2022) 21220-21230

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BASED ON ONBOARD AMMONIA CRACKING
THROUGH NOVEL MEMBRANE REACTORS

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Winter School
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