MACBETH

Membranes And Catalysts Beyond Economic and Technological Hurdles

Pd membranes

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Winter School
Membrane Reactors in Chemical Industry
January 29th-30th 2024
Eindhoven University of Technology

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement N°869896.

Content

- 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

- 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

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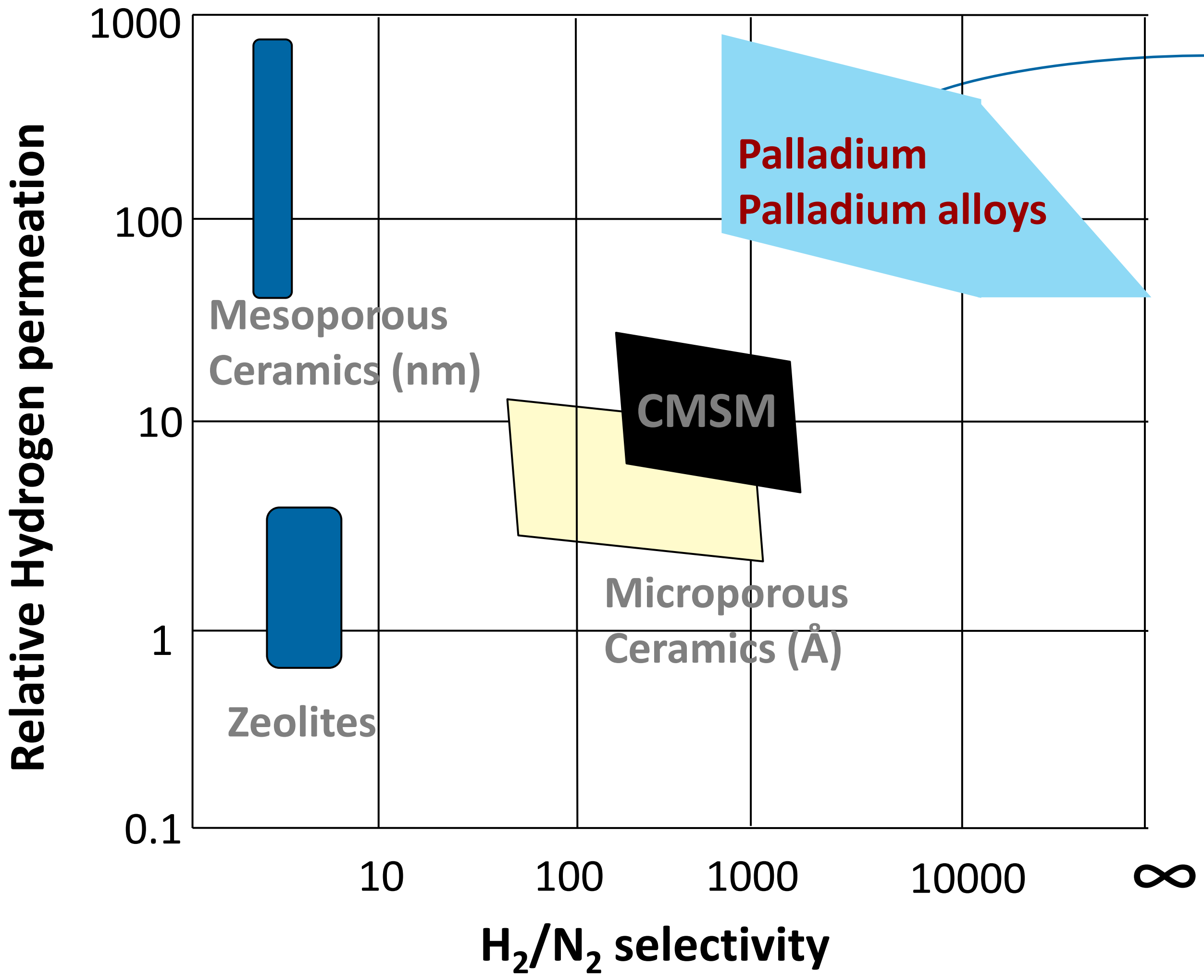
Membranes for H_2 separation



Why Palladium?

Defect free Pd membrane:
∞ selective to H_2

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Why Palladium?

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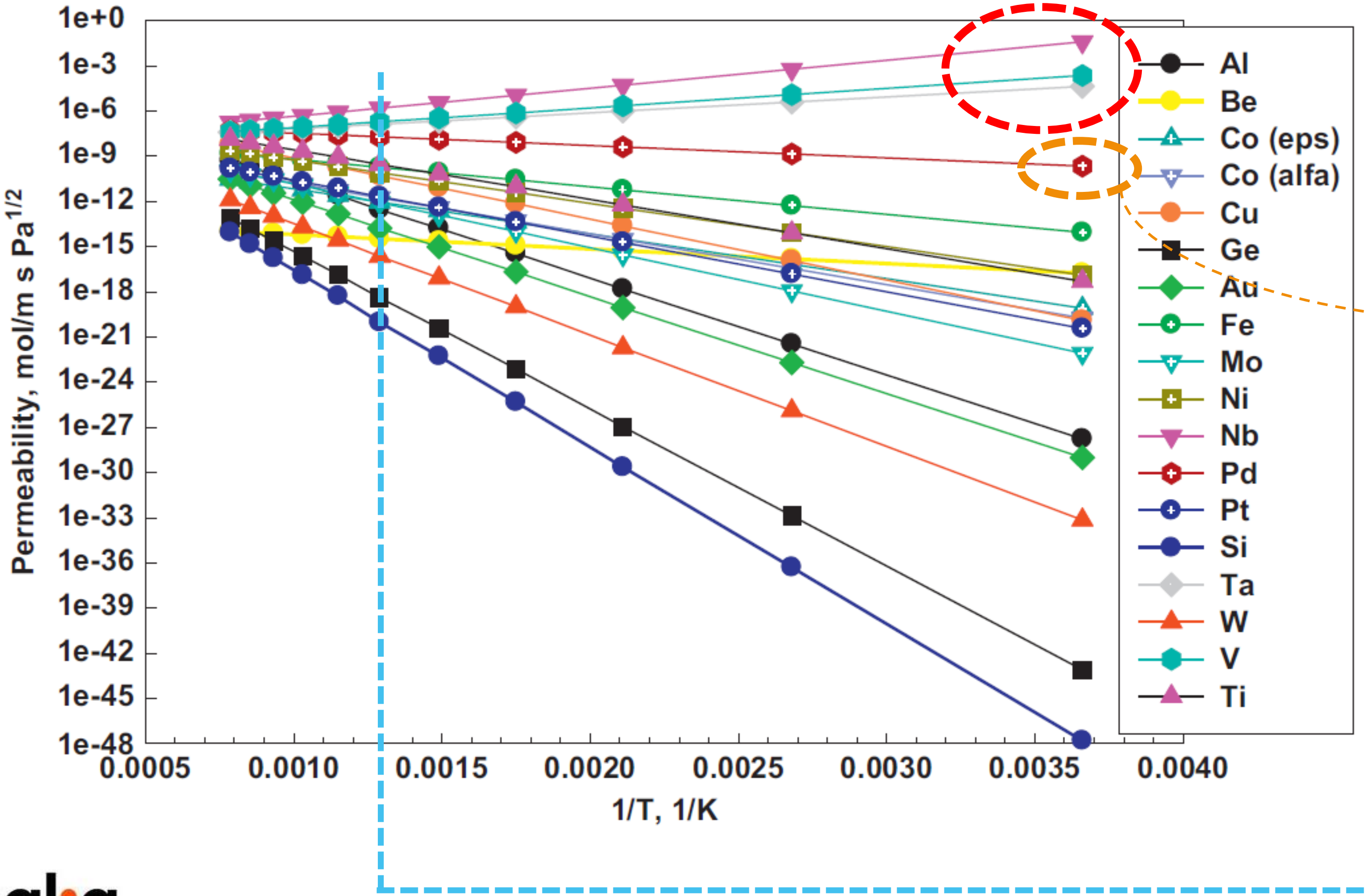
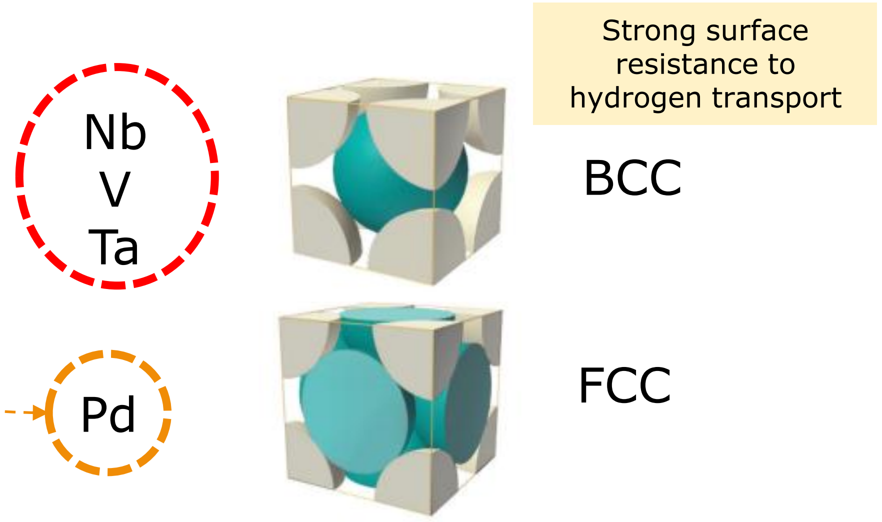
Why Palladium?





Metal	Crystal structure	H_2 permeability at 500 ºC (mol/m·s·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

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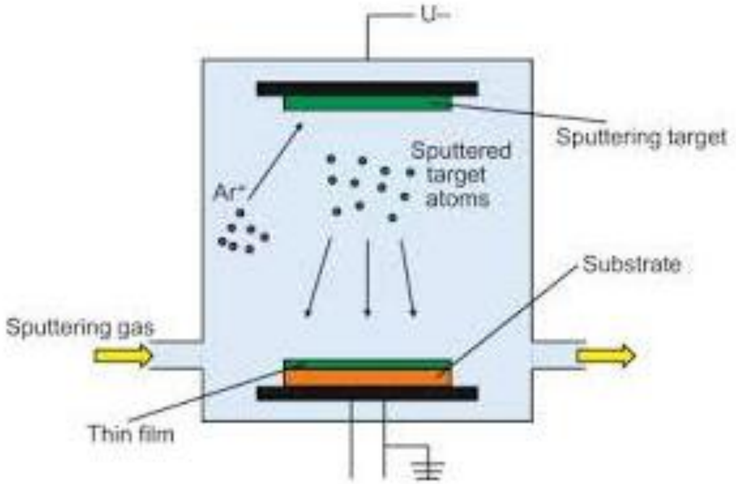
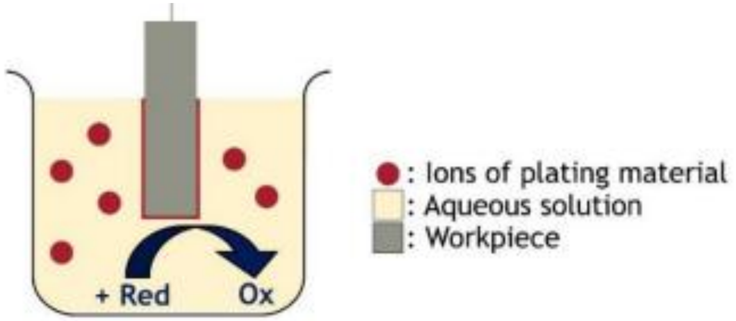
Membrane preparation

- 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

➢ 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

- 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)

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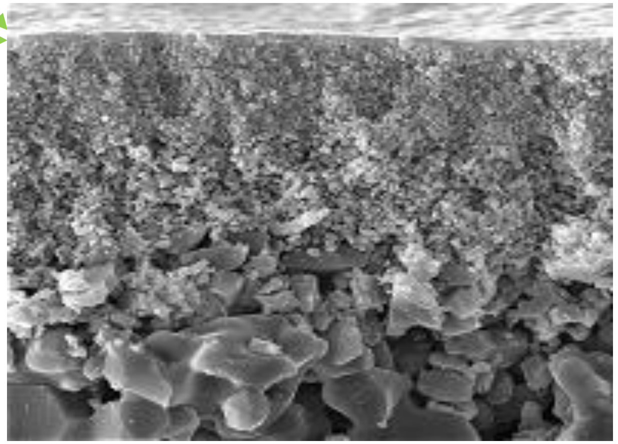
Membrane preparation

- 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

- Importance of the support

  - ✓ Low mass transfer resistance
  - ✓ Small pore size
  - ✓ Smooth surface
  - ✓ Easy to integrate into a reactor
  - ✓ No chemical interaction with Pd-based layer

Asymmetric ceramic support (low mass transfer resistance, small pore size, smooth surface)

Asymmetric metallic support (easy to integrate into a reactor)

No chemical interaction with Pd-based layer:
Ceramic support: α-Al_2O_3, ZrO_2…
Metallic support: interdiffusion barrier

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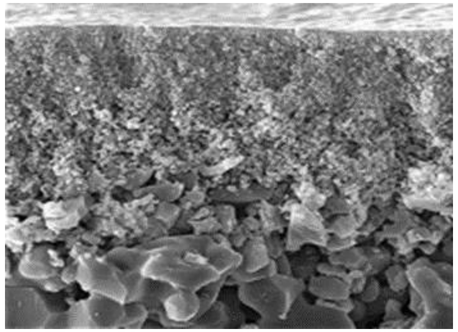
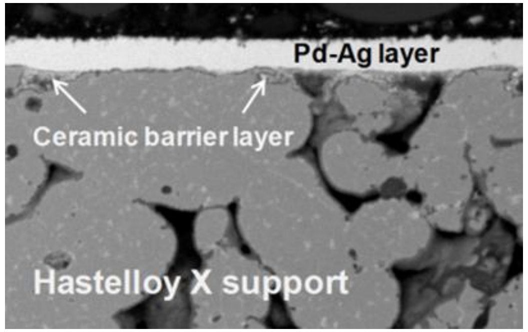
Membrane preparation

- Importance of the support

	Support material (asymmetric)	
	Ceramic	**Metallic**
Pros	• Low resistance 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





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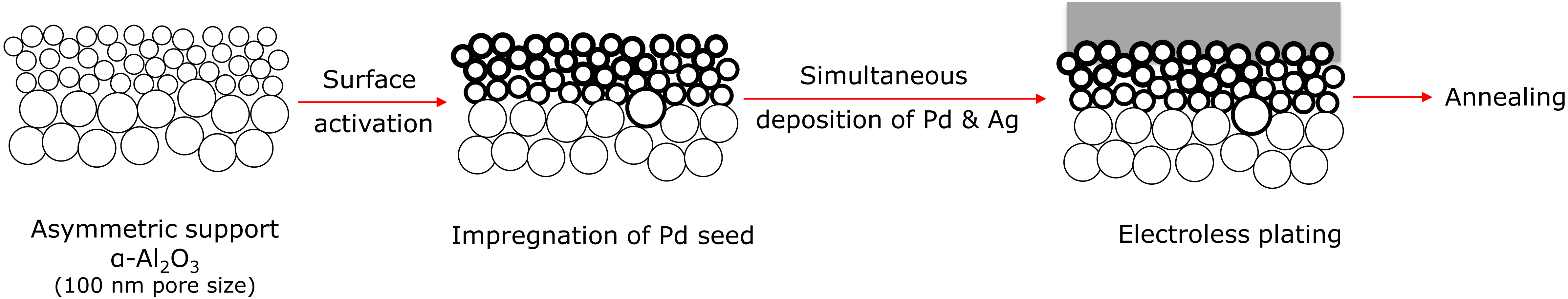
Membrane preparation

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



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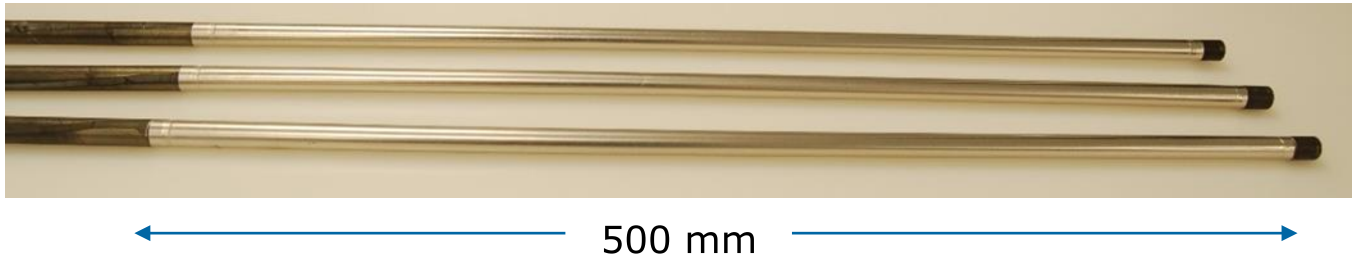
Membrane preparation

- 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)



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

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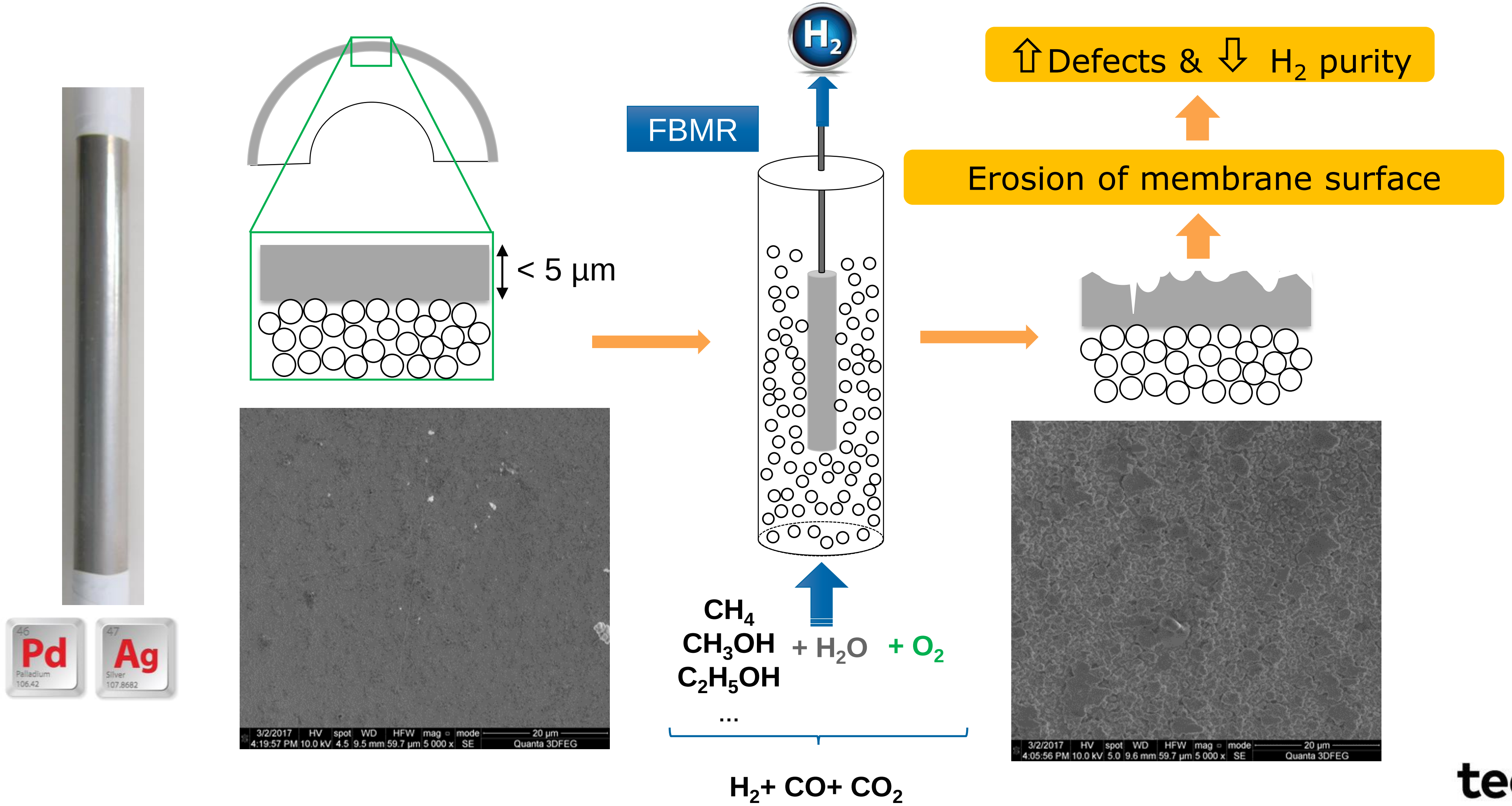
Membrane preparation



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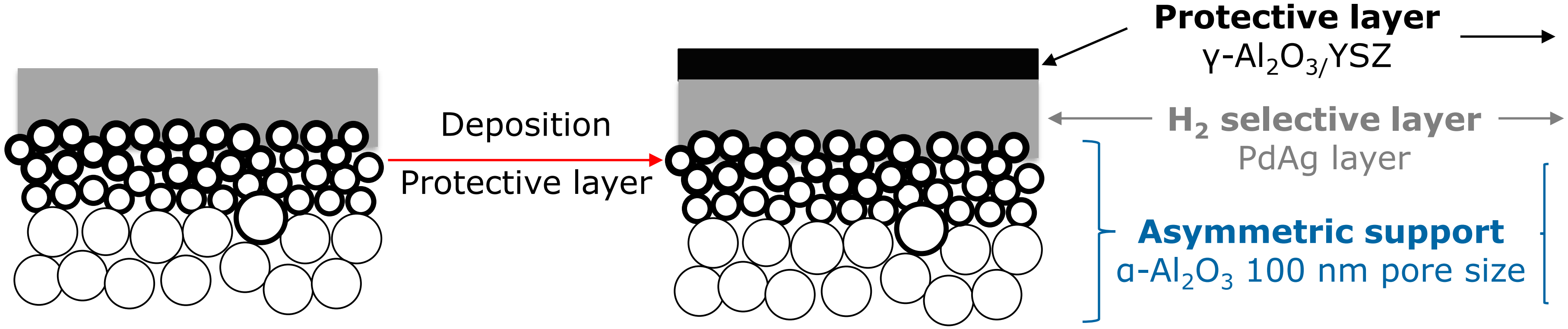
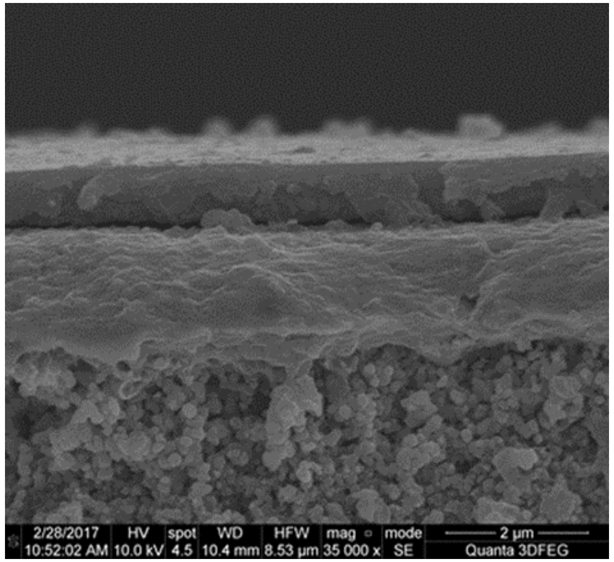
Membrane preparation

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



Conventional Pd-based membrane

Dip-coating



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

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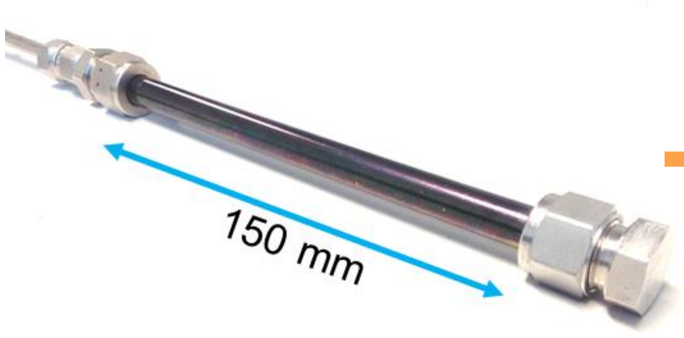
Membrane preparation

- Pd-based double-skinned (DS) membranes

  (for high H_2 permeation, selectivity and **attrition-resistant**)



Scaling-up membrane production

1 per batch to 8 per batch

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Properties

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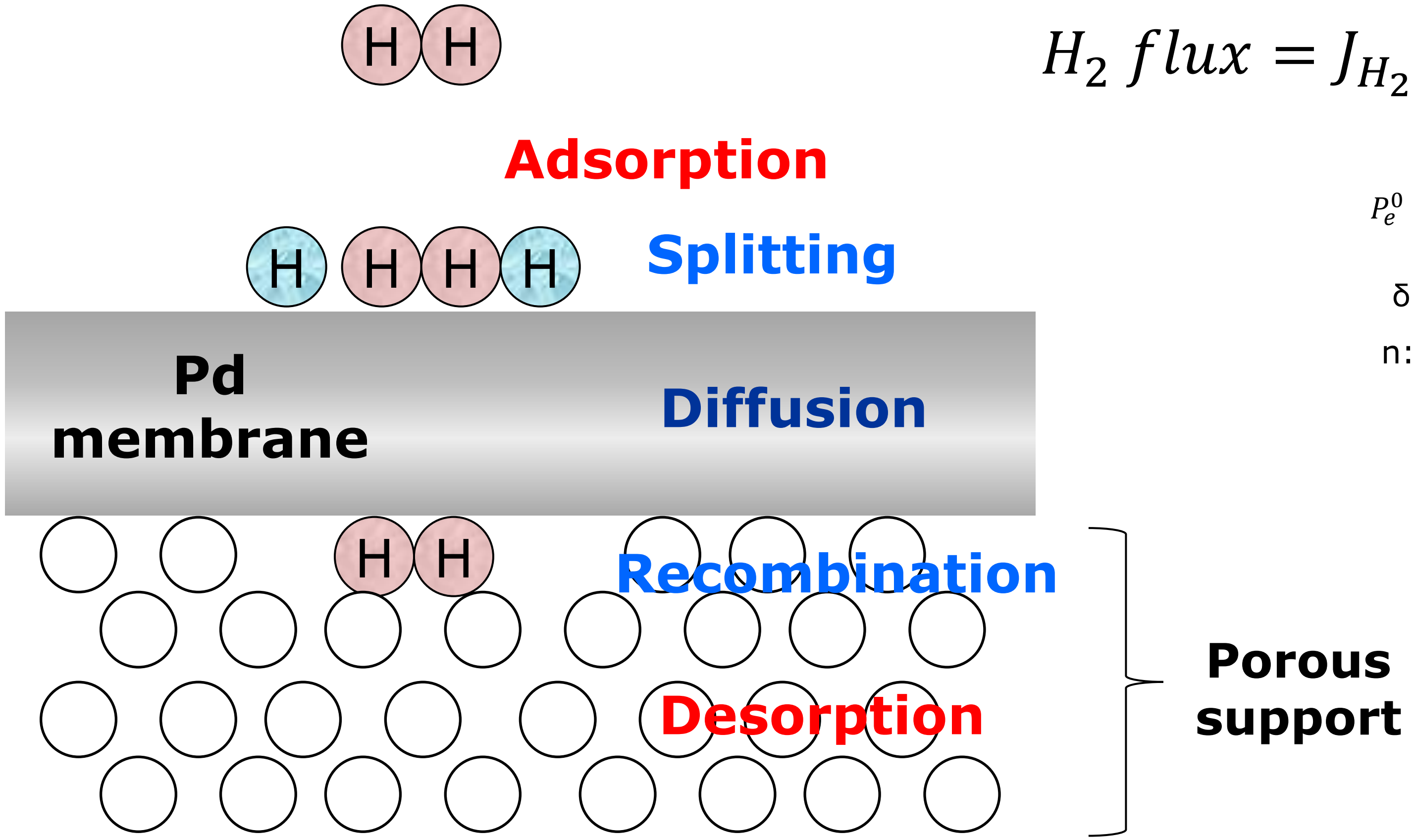
Properties

- 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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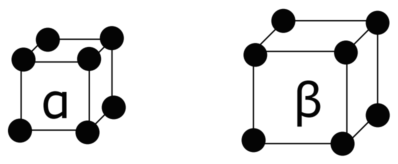
Properties

- 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

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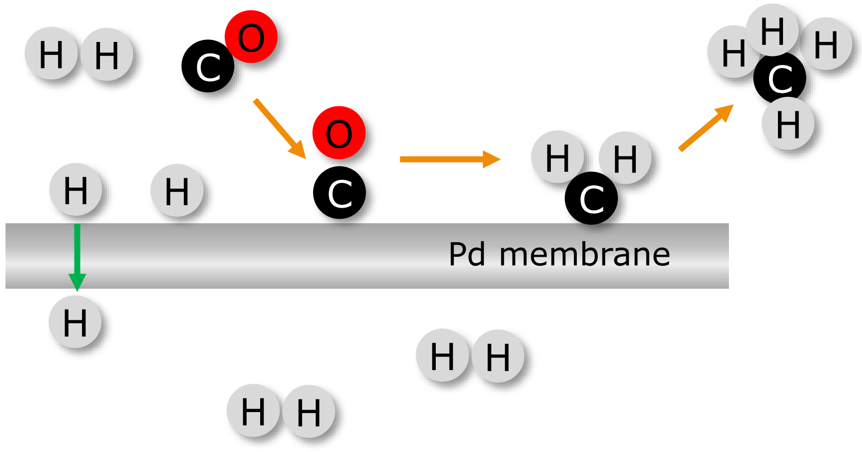
Properties

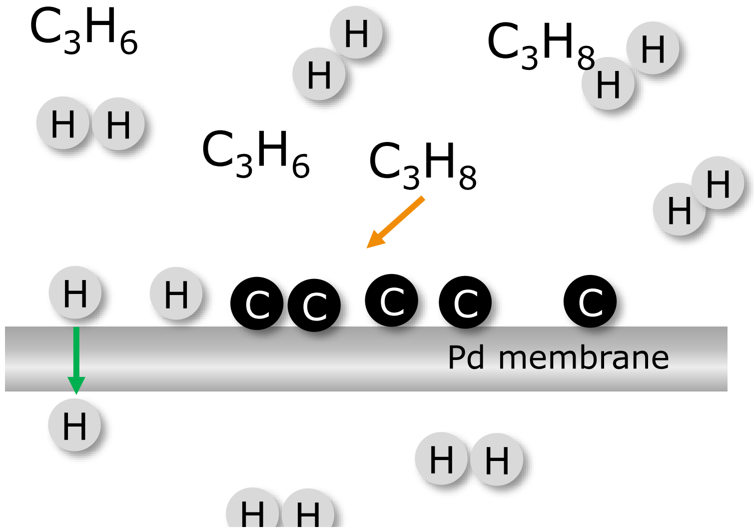
- Problems associated with Pd membranes

CO poisoning
(syngas)

H_2 permeation inhibition

Carbon deposition
(propane dehydrogenation)





↑ **Temp** → ↓ Poisoning

↓ **Temp** ↓ Poisoning

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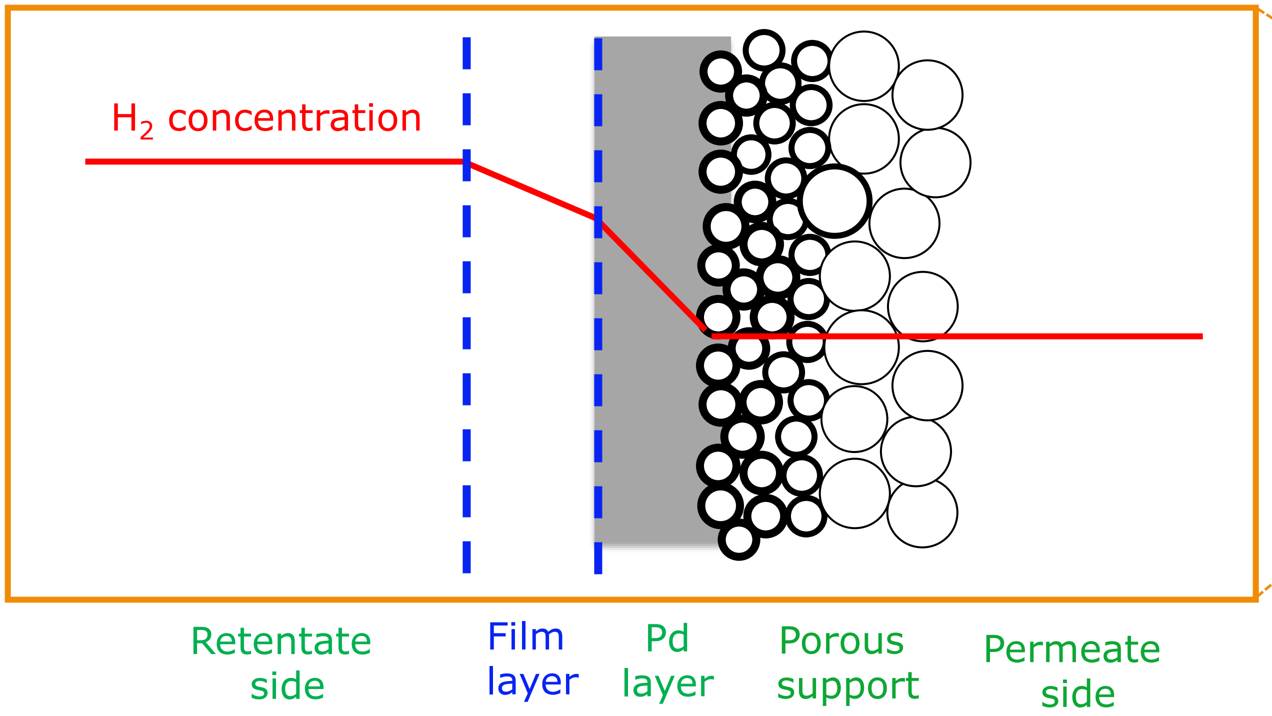
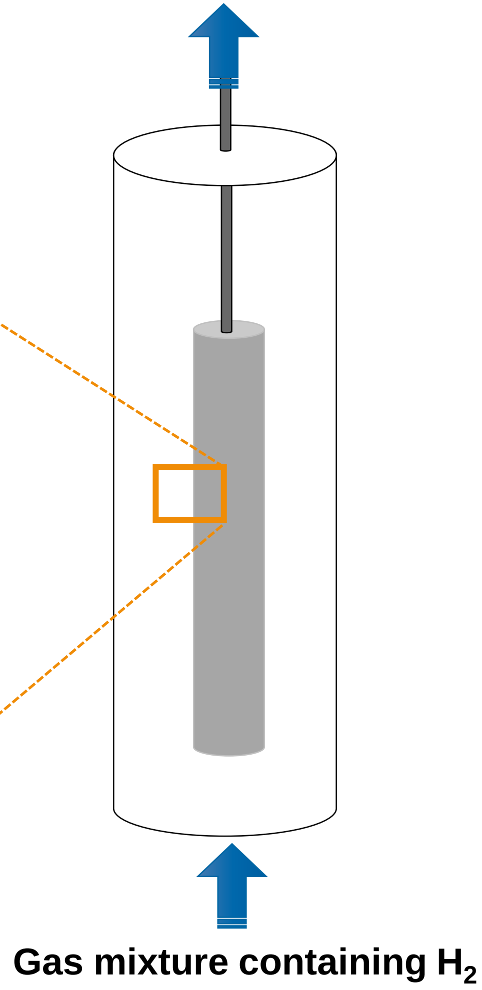
Properties

- 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

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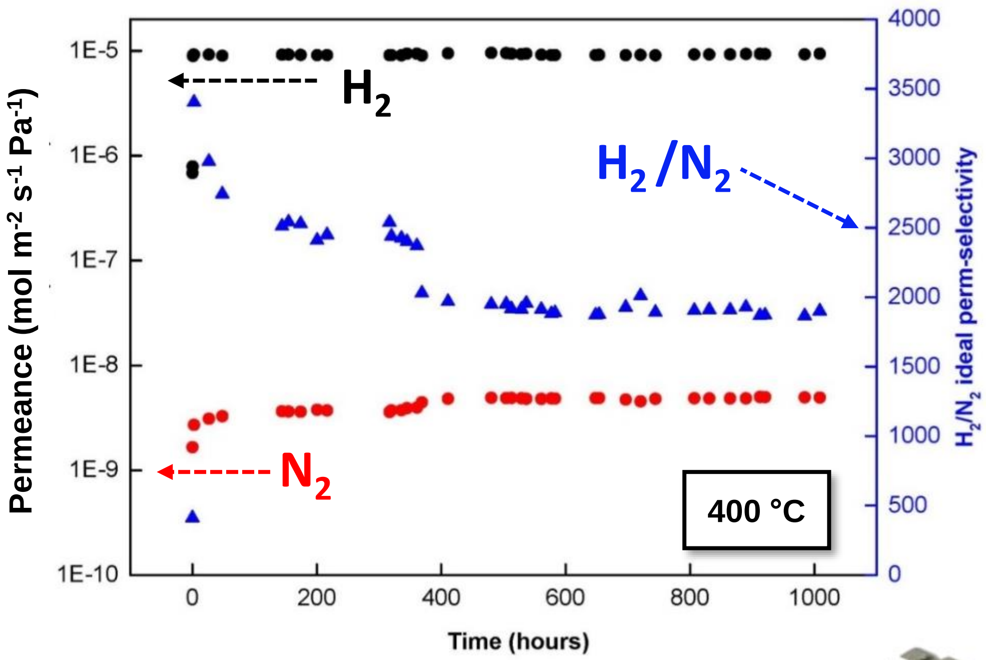
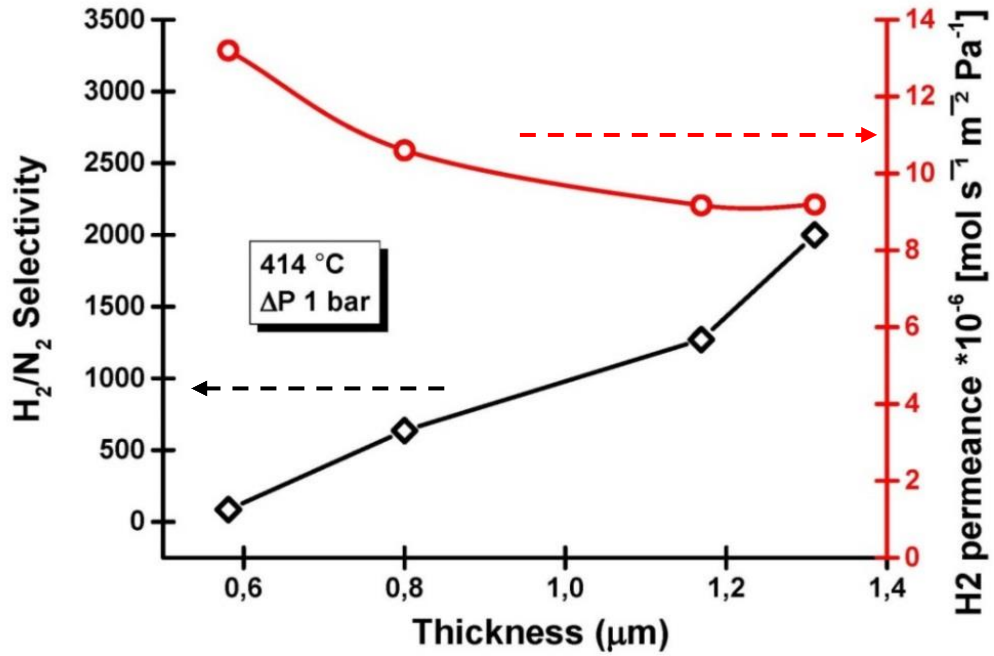
Membrane performance

➢ 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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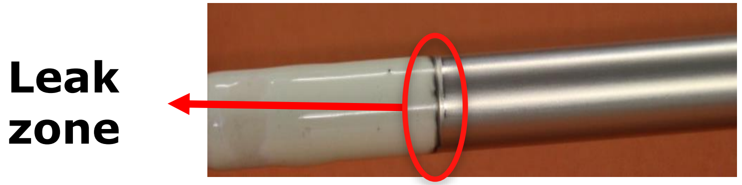
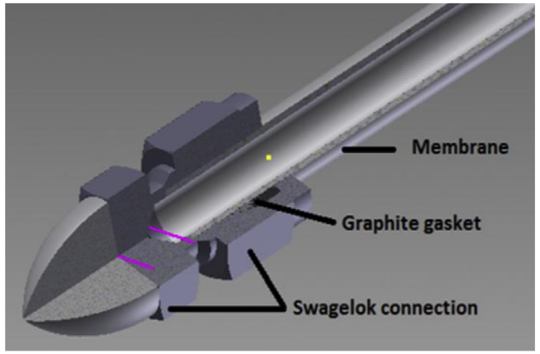
Membrane performance

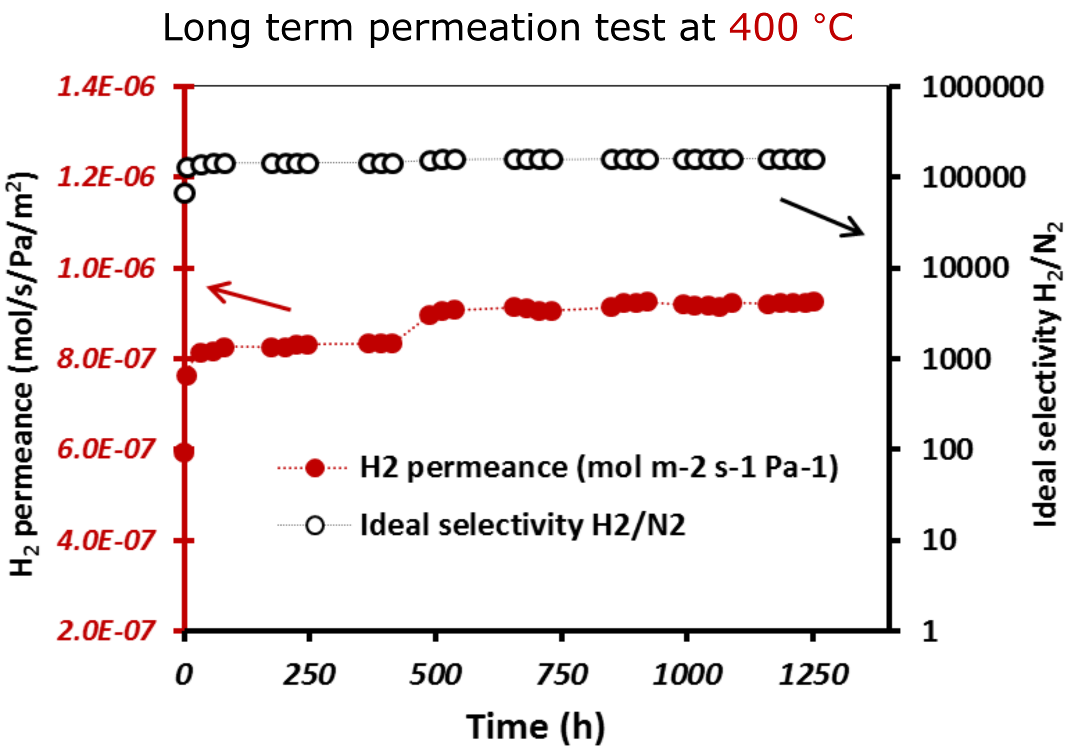
➢ Thin (4-5 µm thick) Pd-Ag membranes (metallic support)

Ceramic support





Metallic support



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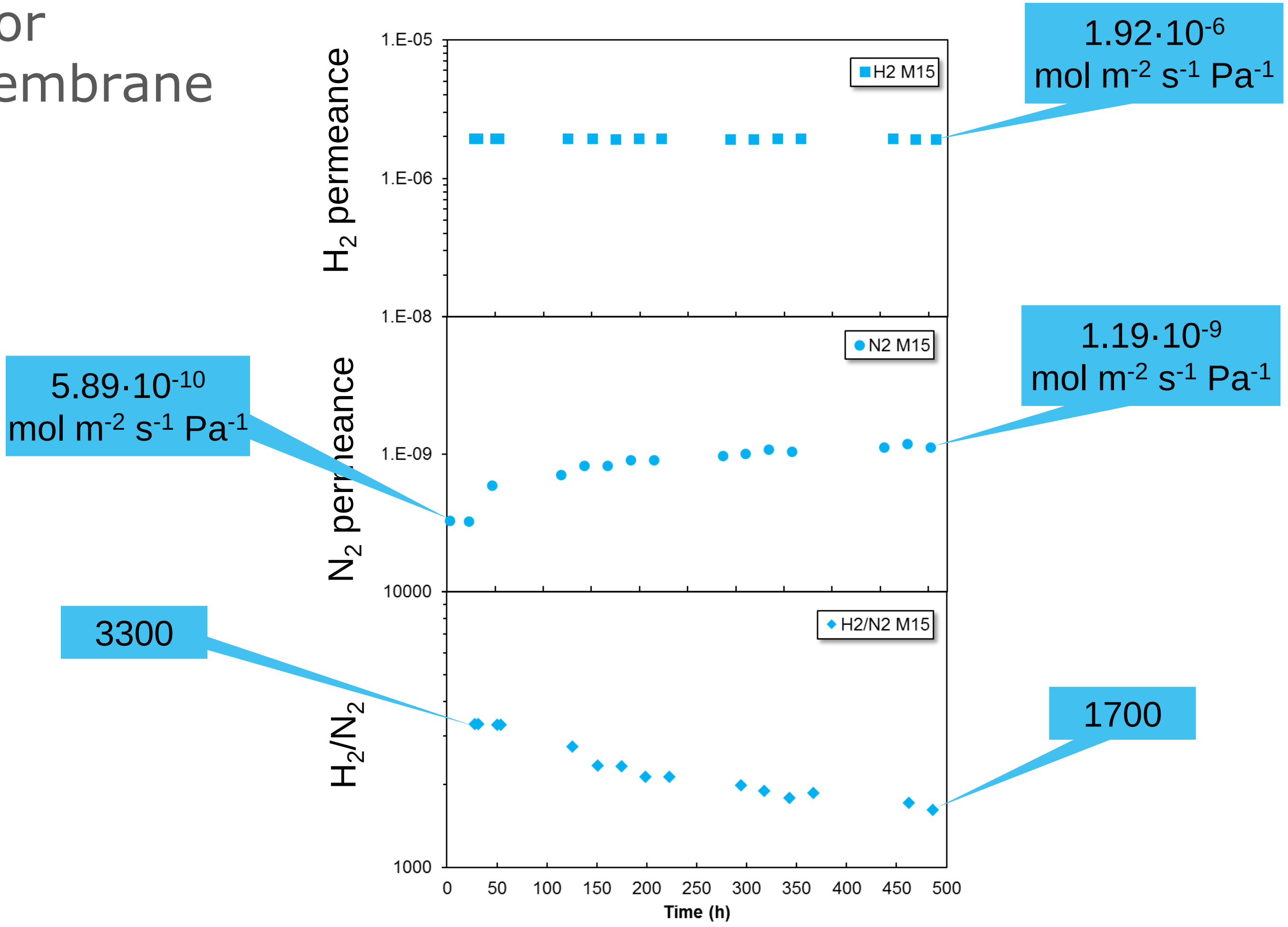
Membrane performance

- 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

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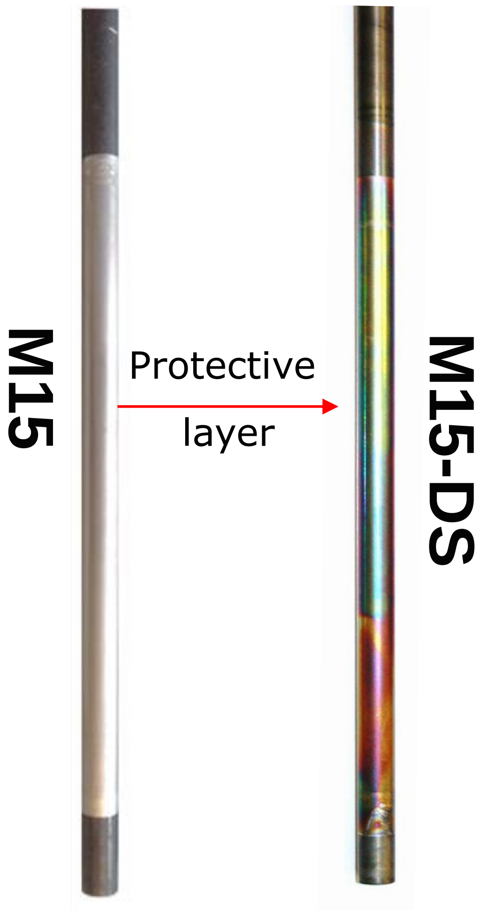

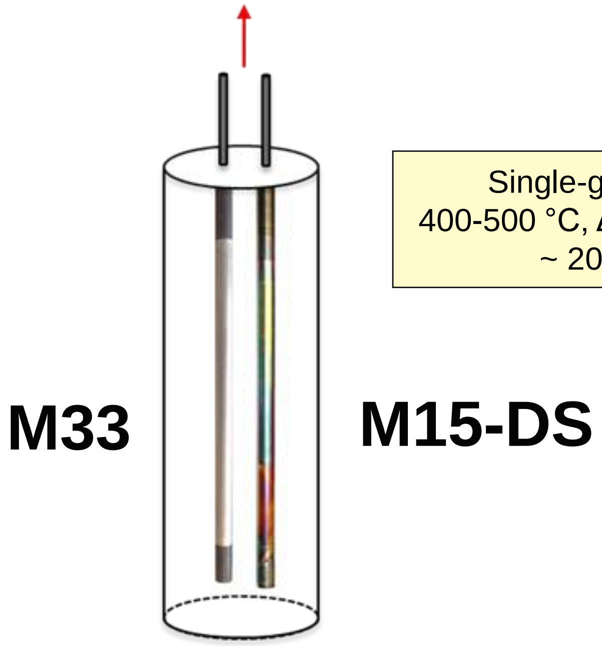

Single-gas test
400-500 °C, ΔP= 1-4 bar
~ 200 h

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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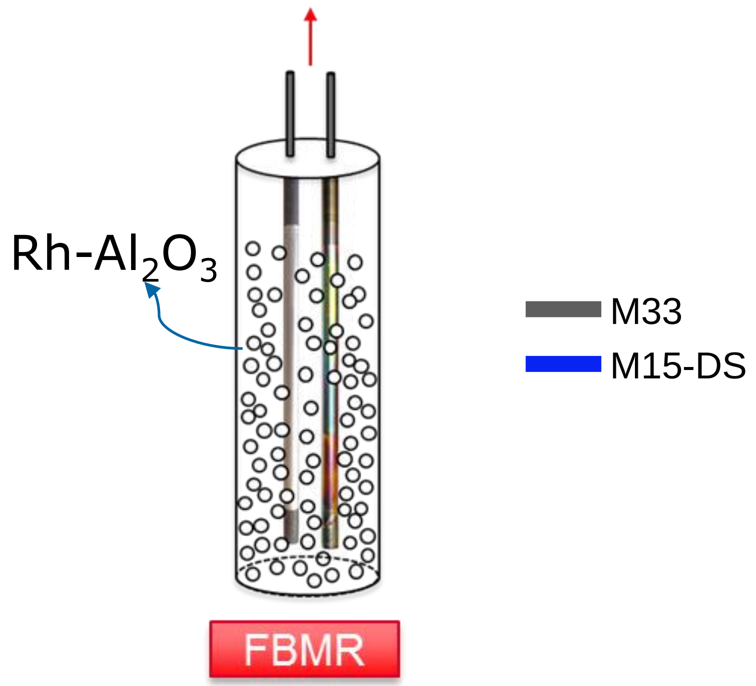
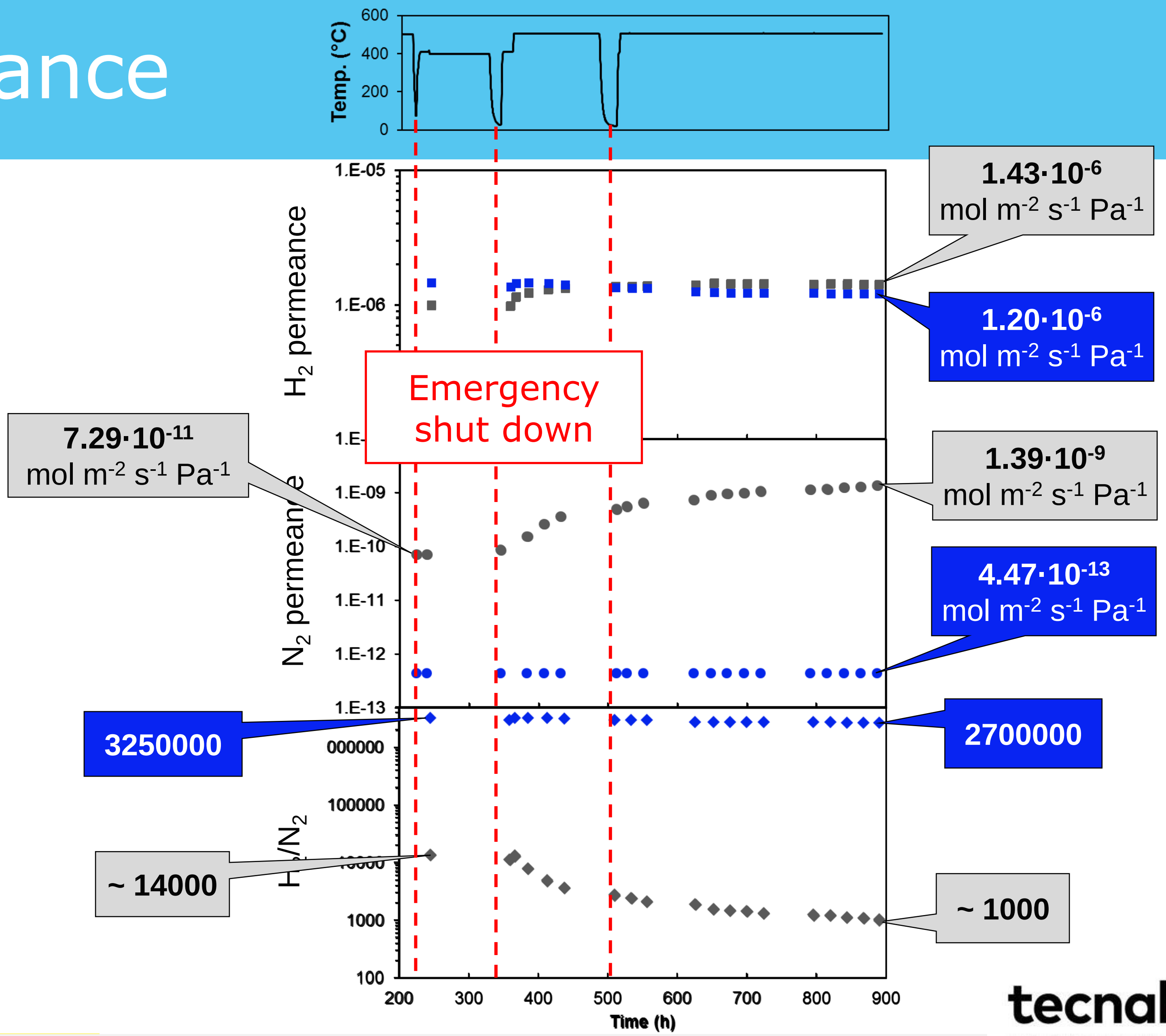
Membrane performance

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





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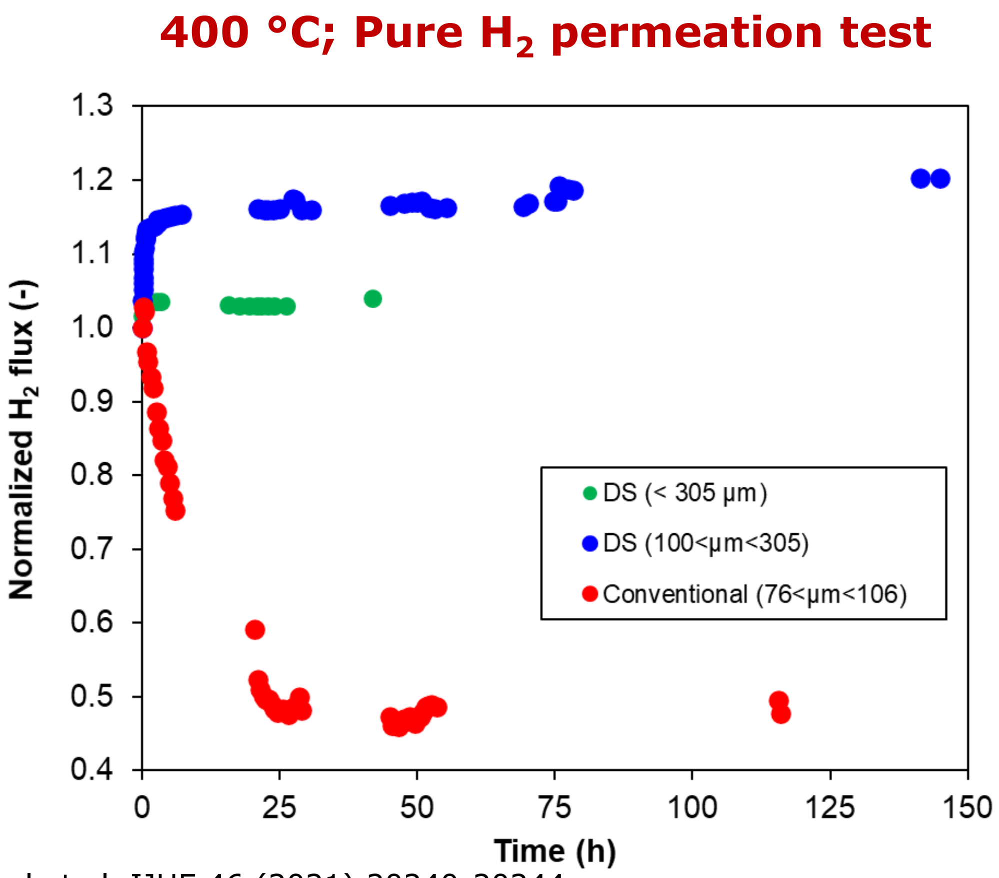
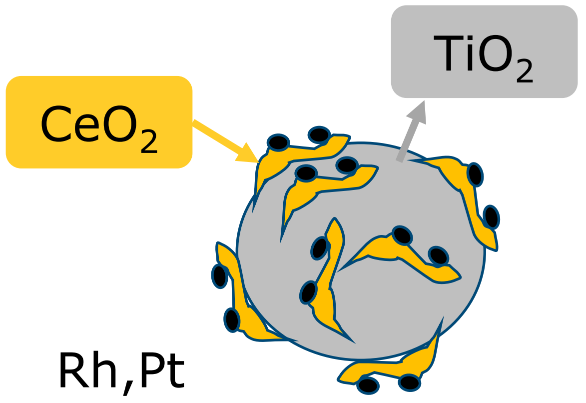
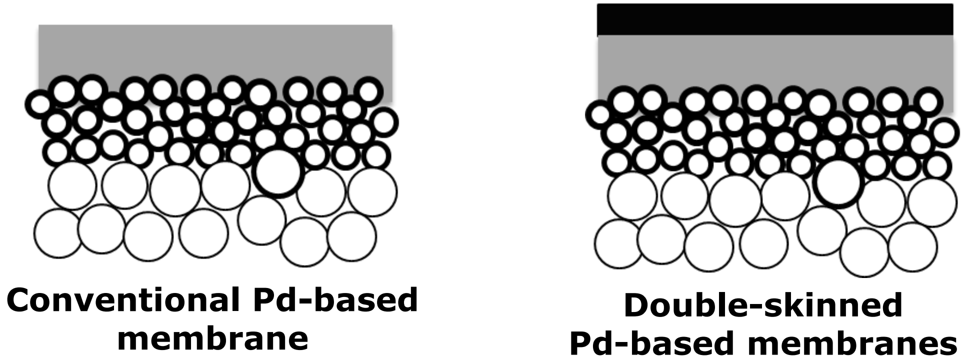
Membrane performance

➢ **Chemical interaction with catalyst**







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

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Applications/EU projects

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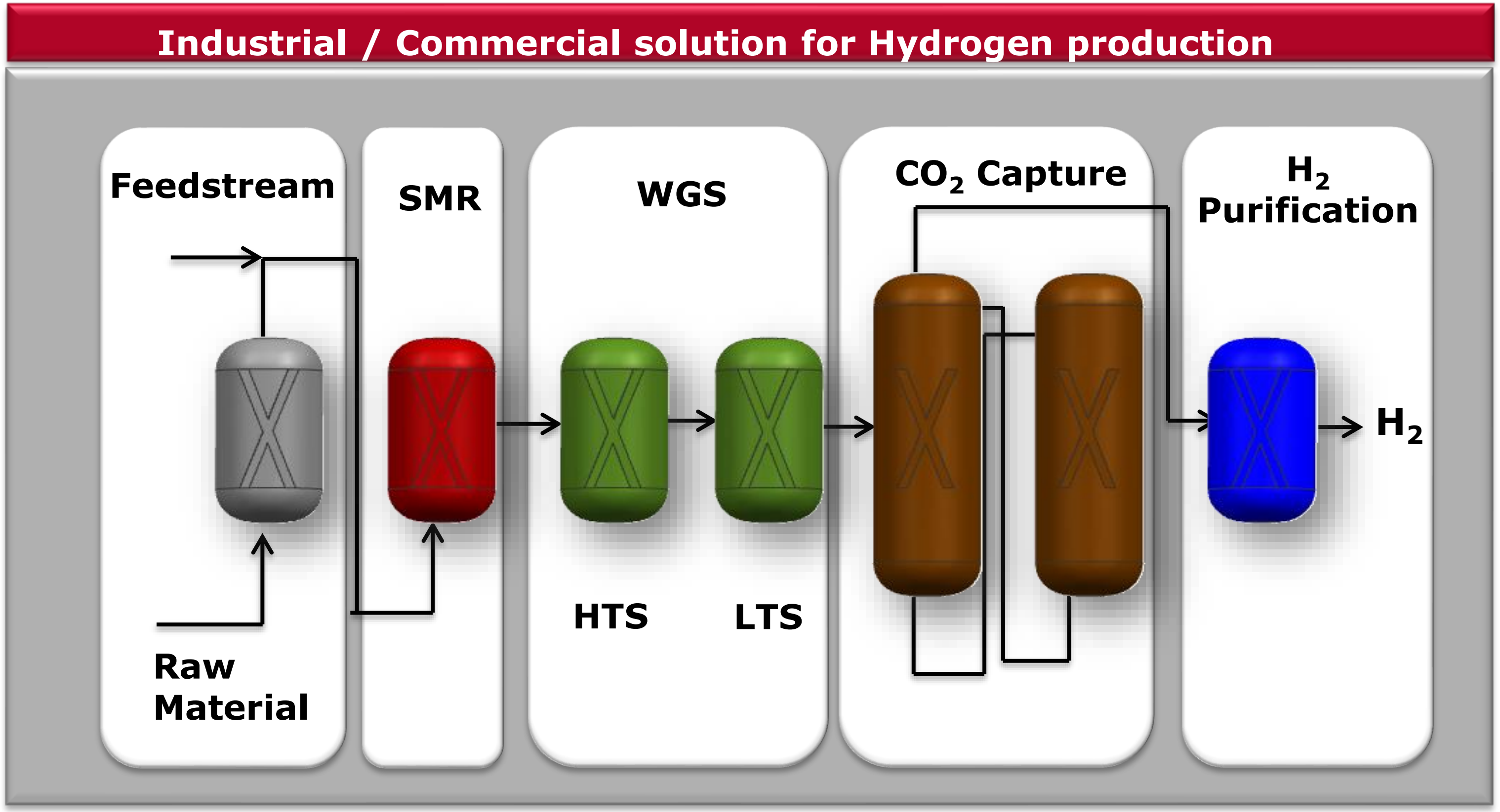
Applications

- Process intensification/ Membrane reactors



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

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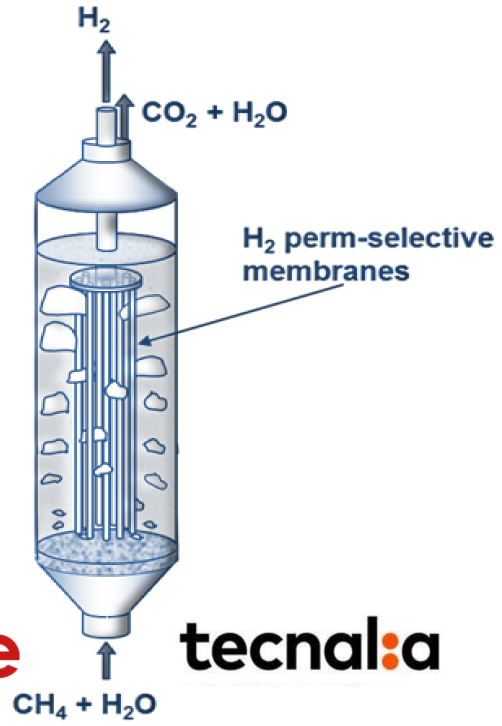
Applications/EU projects

Feedstock	***Membrane reactor***	***Reaction***
Natural gas Biogas (Bio)ethanol		Reforming
Syngas		Water gas shift
Ammonia		Dehydrogenation



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EU Projects

areNH3a | DEMCAMER Catalytic Membrane Reactors | RE4CELL | FERRET | Fluid CELL | MEMBER | BIONICO | MACBETH

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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

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

DEMCAMER Catalytic Membrane Reactors

RE4CELL FERRET BIONICO

FluidCELL

areNH3a

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Applications/EU projects

➢ EU projects on membrane reactors for H_2 production

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[1] Steam reforming of methane (SMR)

[2] Biogas reforming (CH_4 -CO_2)

[3] Propane dehydrogenation (PDH)

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

...

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

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Applications/EU projects

- EU projects on membrane reactors for H_2 production

[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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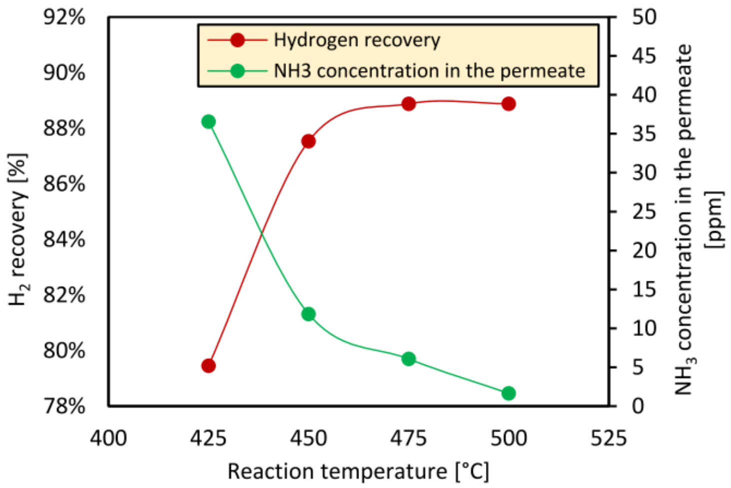
EU projects

areNH3a

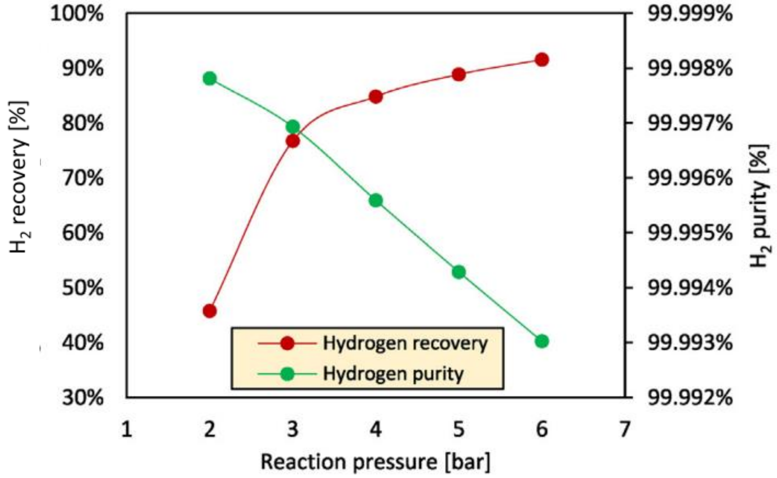
Ammonia decomposition

		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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Thank you for your attention!

MACBETH
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