CCP-NorCap Seminar

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Dense palladium membranes for hydrogen separation

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Rune Bredesen, Hallgeir Klette and Yngve Larring

Outline:

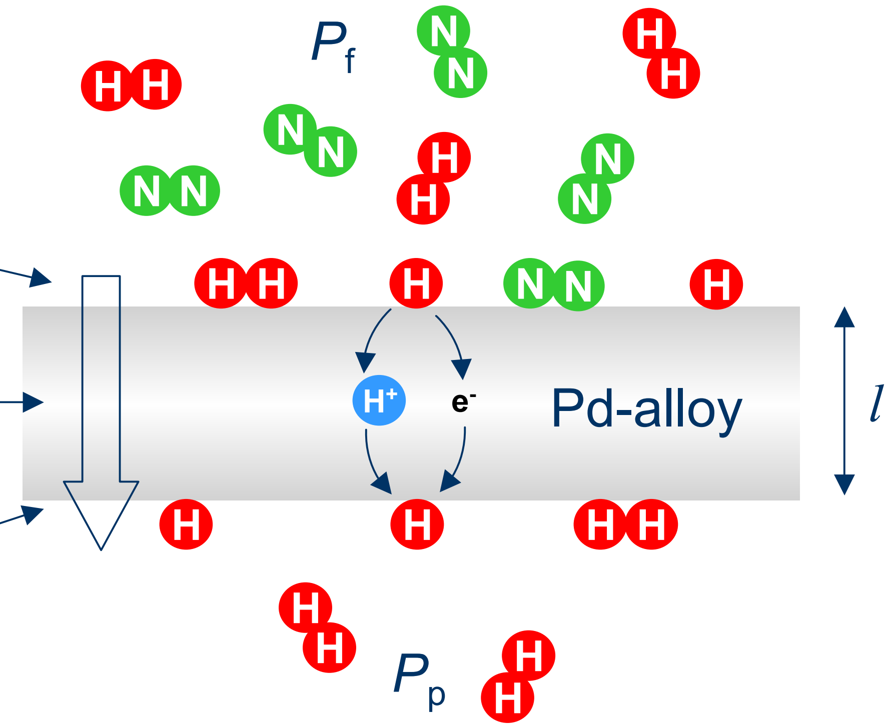
- Introduction
- Preparation at SINTEF
- Membrane modules (generation 1 to 4): design and test results
- Leak testing and inspection
- Concluding summary

Transport mechanism

1. Adsorption/dissociation:
$H_2(g) \rightarrow 2H^+(Pd) + 2e^-$

2. Diffusion:
$$J = \frac{Q^*}{l}(\theta_f - \theta_p)$$

3. Recombination/desorption:
$2H^+(Pd) + 2e^- \rightarrow H_2(g)$



J = flux of hydrogen (mol/ m^2 s)

l = membrane thickness

P_f = partial pressure of hydrogen on feed side

P_p = partial pressure of hydrogen on permeate side

θ_f, θ_p = fractional coverage of hydrogen

n = 0.5 for bulk transport, n $\rightarrow$ 1 for surface kinetic limitation

Q = permeability (mol m/m^2 s (Pa)$^{0.5}$)

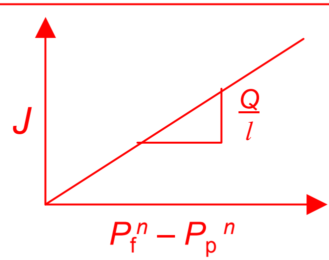
Q/l = permeance (mol/m^2 s (Pa)$^{0.5}$)

If diffusion is the rate limiting step:

$$J = \frac{Q}{l}(P_f^{0.5} - P_p^{0.5})$$

General:

$$J = \frac{Q}{l}(P_f^{n} - P_p^{n})$$



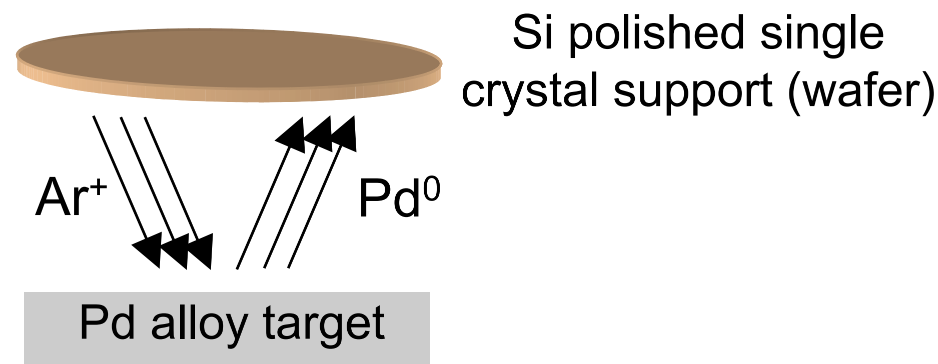
Practical aspects:

- Deactivation/poisoning: other species occupying active surface sites
- Flux limitations due to limited permeance of the support
- Concentration polarisation (observed as flux dependency of feed/purge gas flow rates)
- “Defect free” membranes have “infinite” selectivity to hydrogen. Lower selectivity is due to defects or sealing problems
- Pd alloy segregation

SINTEF two-step composite membrane preparation

1

Membrane preparation on Si support by magnetron sputtering



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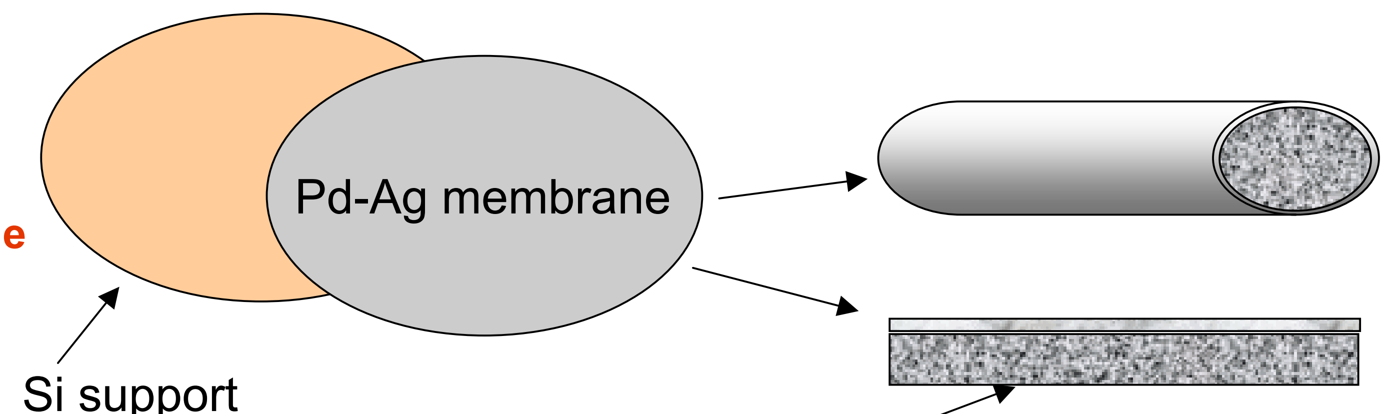
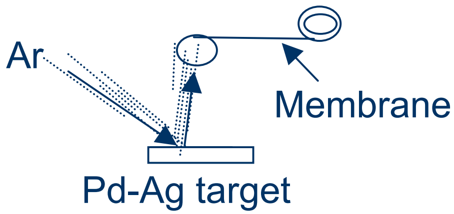
Membrane pull-off from Si support and composite membrane preparation



SINTEF two-step composite membrane preparation

Membrane:

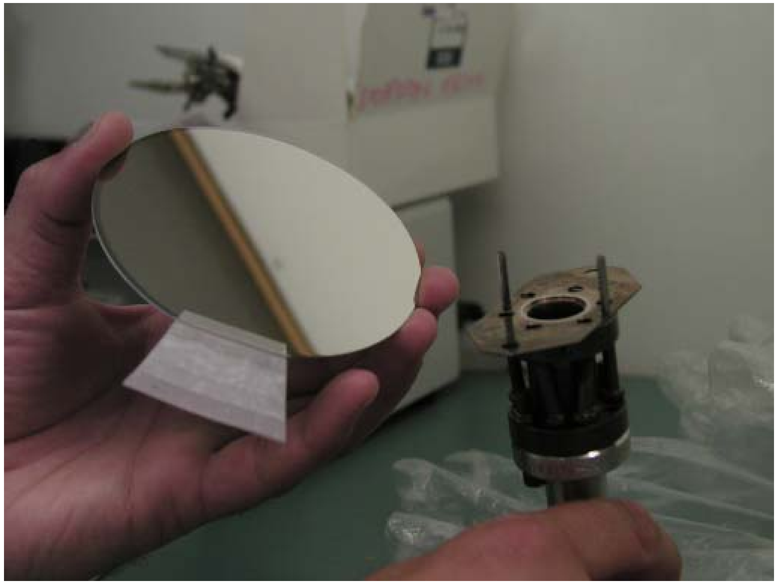
- Homogeneous structure
- No defects formed
- Easy control of composition
- Layered structures possible
- Easy to control thickness
- Continuous process possible



Support:

- Support chosen independently of membrane fabrication process
- High (pore size)/(membrane thickness) ratio possible
- Membrane repair possible

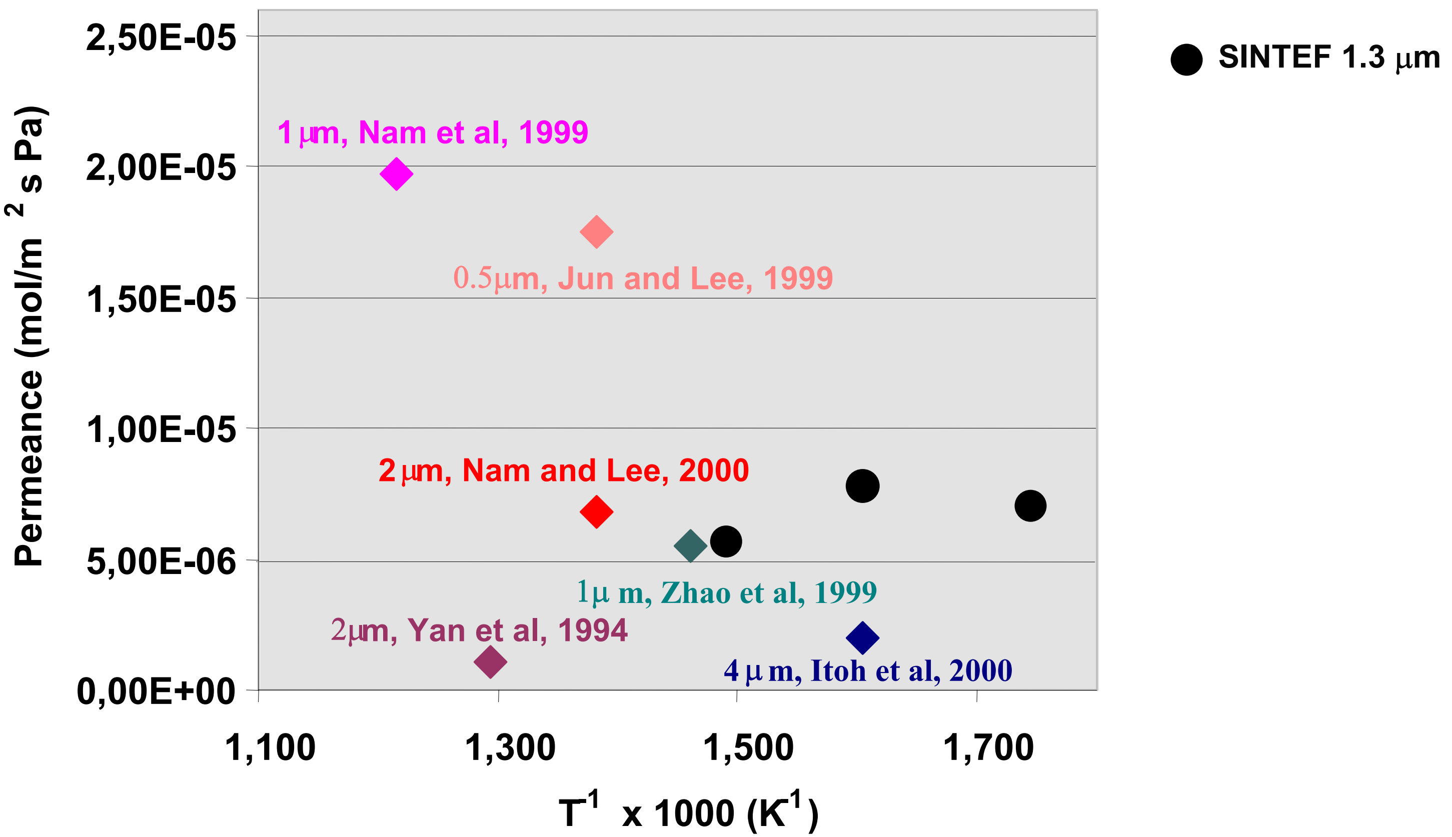
Free-standing Pd-30 Ag membrane:



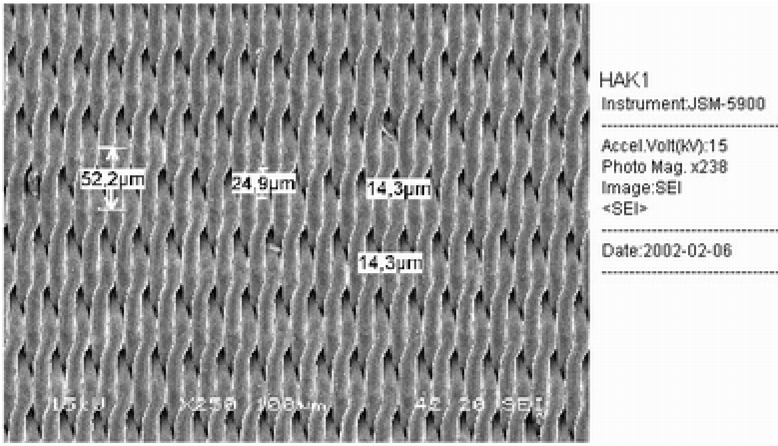
After testing at 300^{o}C

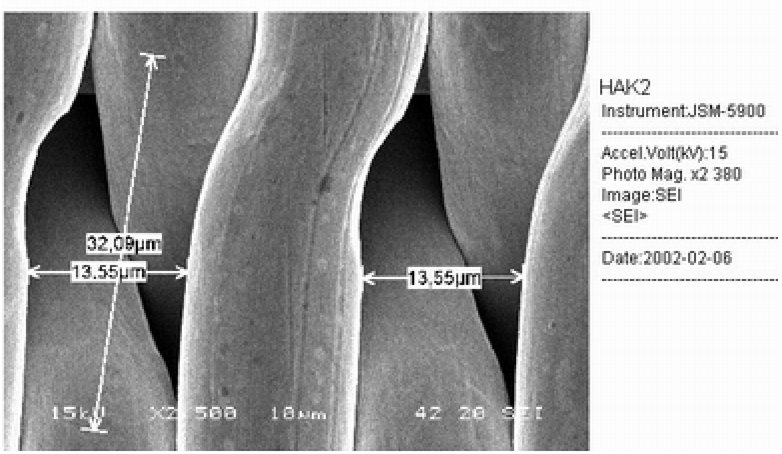
Early example: Pd-30%w Ag membrane on ceramic support

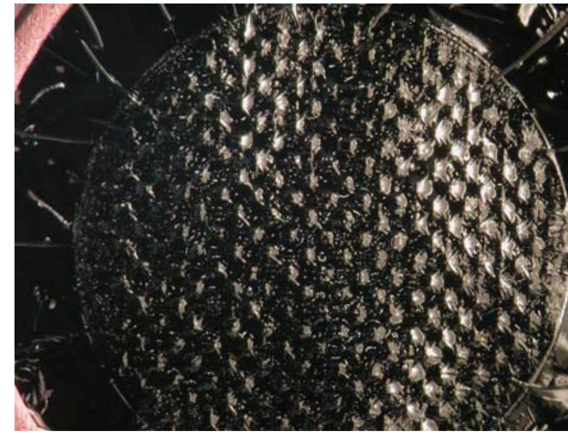
H_2 permeance (n = 1) vs. reciprocal temperature



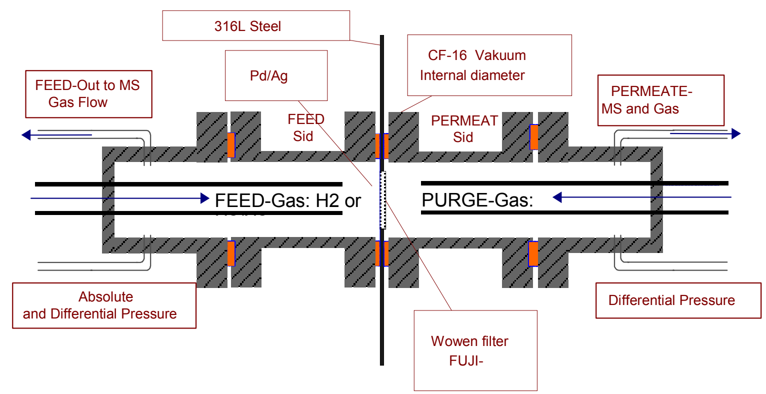
Pd-30 Ag membrane on flat support







The Pd/Ag flat membrane after the test

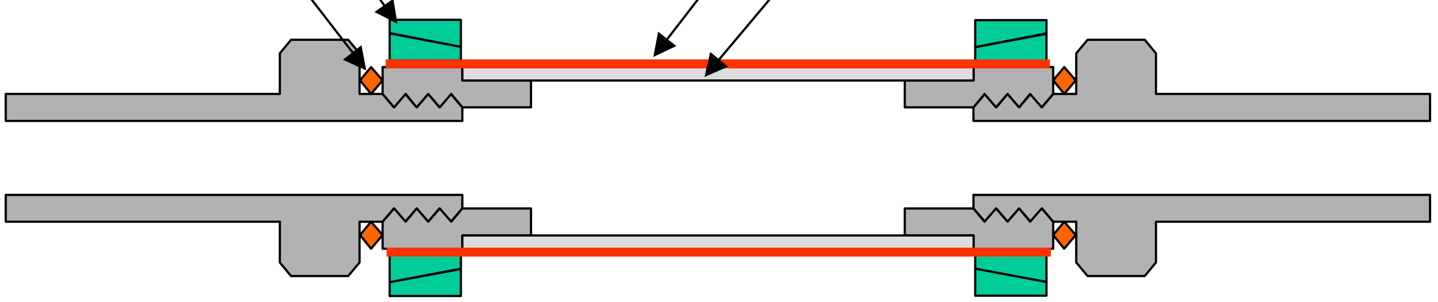


SEM micrographs of the fine mesh layer of the Fuji Filter support

Permeance: $6.8 \cdot 10^{-6}$ mol/(m^2sPa) at 300 °C

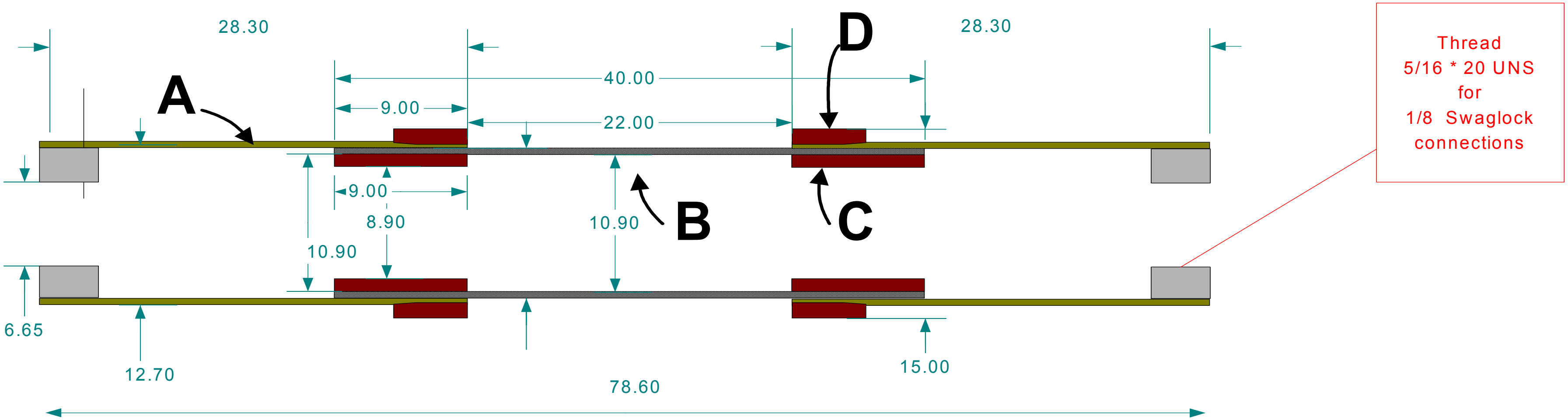
'driving force normalised': $4.6 \cdot 10^{-3}$ mol/(m^2sPa$^{0.5}$)

SINTEF 1st generation CCP-GRACE module:



Tubular Pd/Ag membrane on stainless steel support
Tube diameter: 12 mm
Active length: about 20 mm

SINTEF 2nd generation CCP-GRACE module:



The Pd-filter assembly consist of the following parts

A: Connection tubes

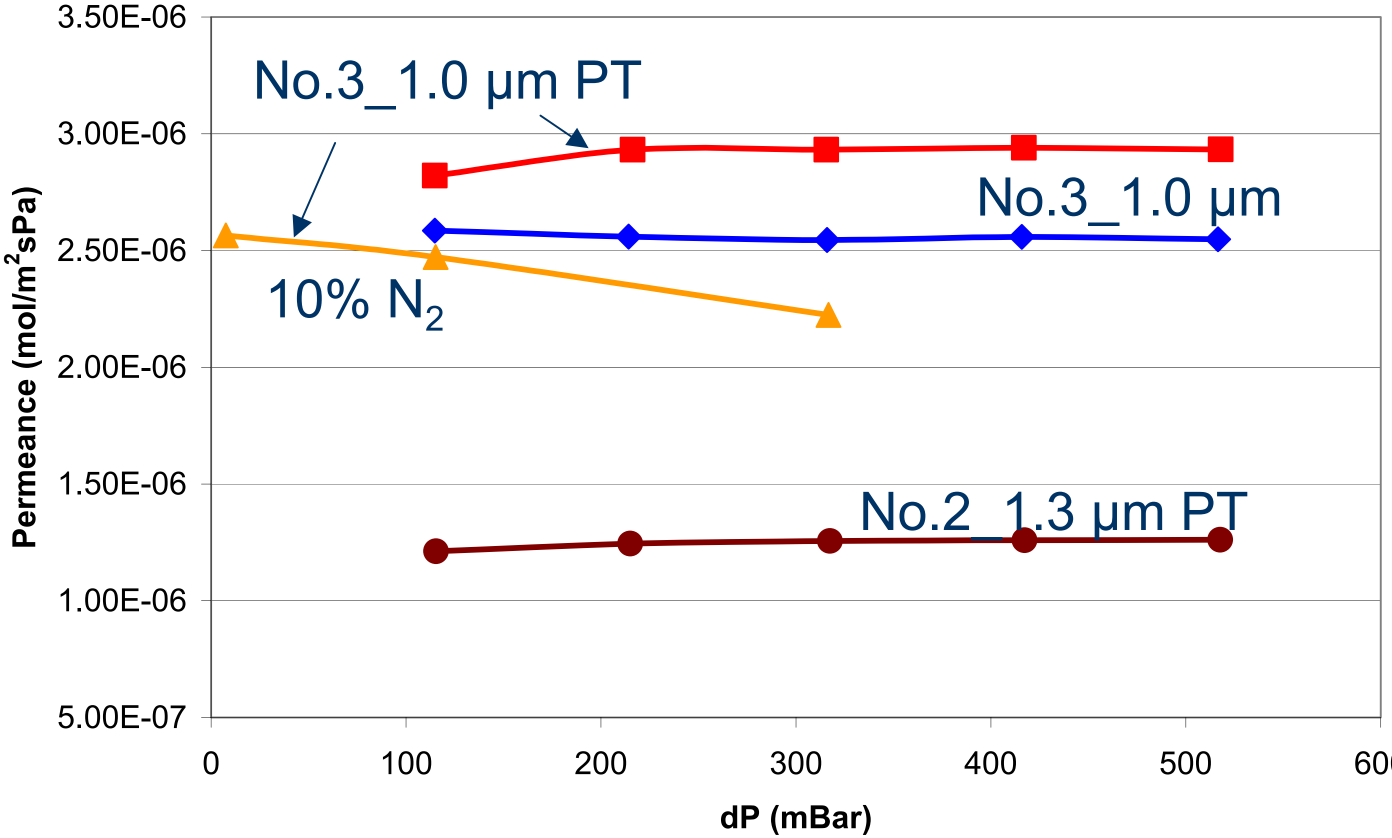
B: The Pall-Accusep, 2 mircon grade filter

C: The inner ring

D: The outer ring (also called the clamp ring)

Compression tool for the attachment of the fixation rings. One prototype of the second generation tubular membranes is shown

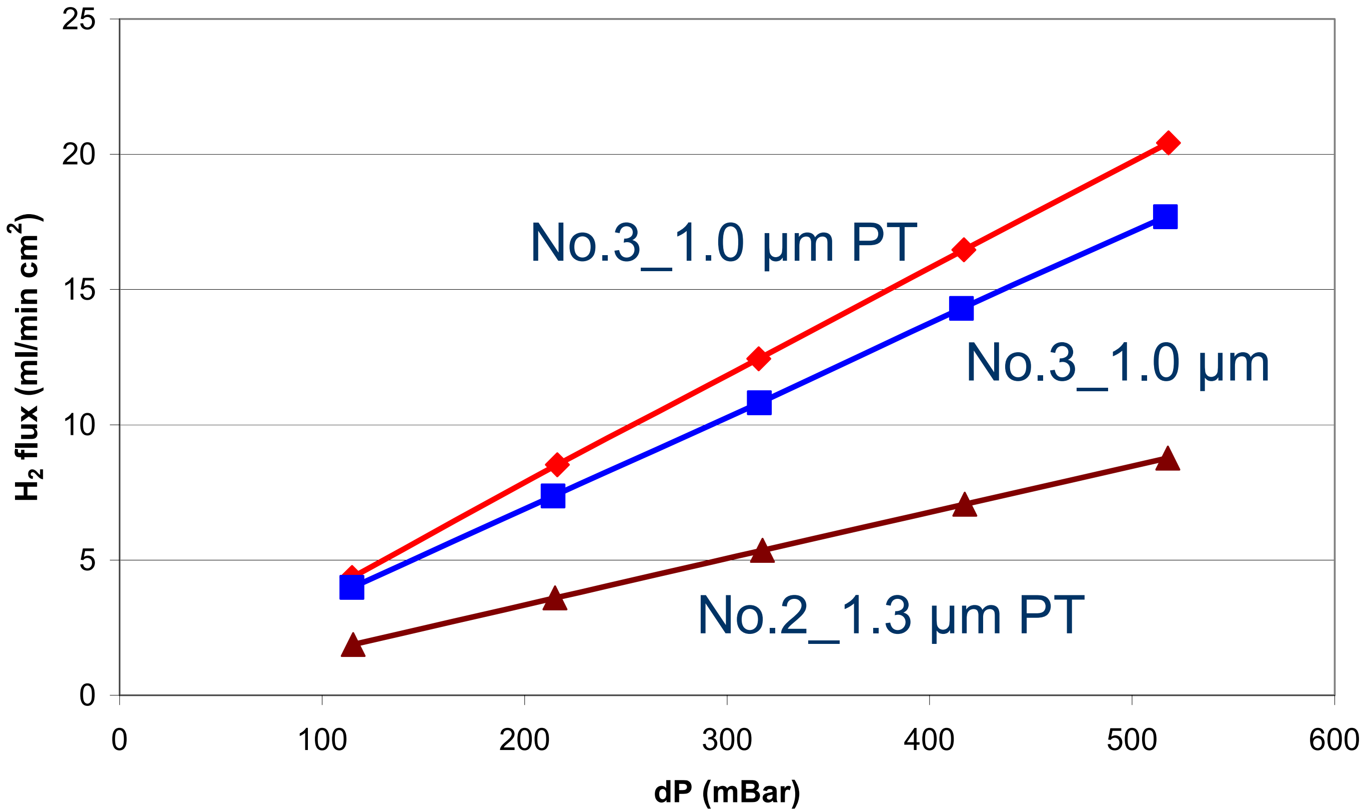
SINTEF 2nd generation CCP-GRACE module:



Permeance vs. differential pressure

Feed side; 180ml/min H_2. Permeate side; no sweep gas. ΔP; variable

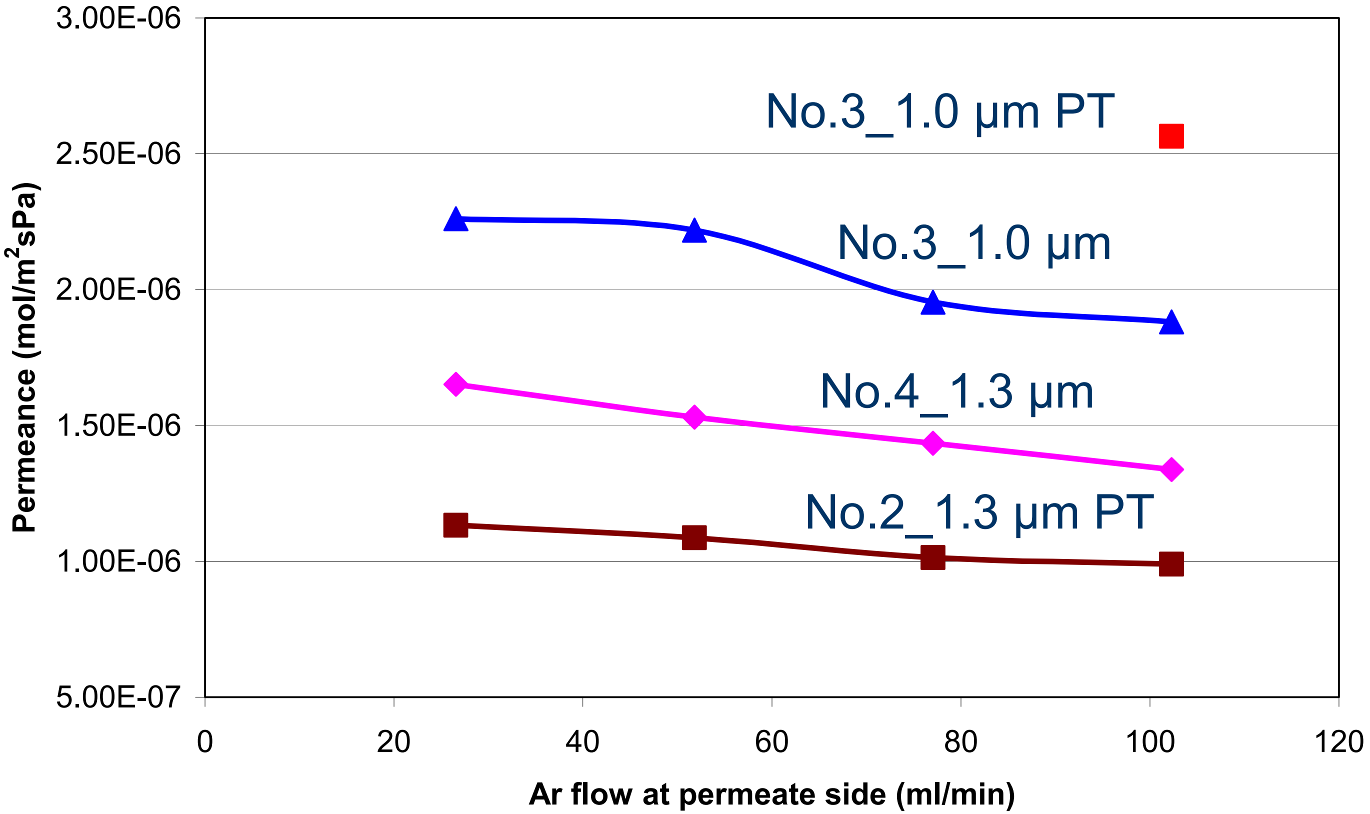
SINTEF 2nd generation CCP-GRACE module:



H_2 flux vs. differential pressure

Feed side; 180ml/min H_2. Permeate side; no sweep gas. ΔP; variable

SINTEF 2nd generation CCP-GRACE module:



Permeance vs. flow of sweep gas

Feed side constant; 180ml/min H_2 and 20ml/min N_2. Perm side; variable. ΔP; ~8mBar

SINTEF 3rd and 4th generation CCP-GRACE module:

Work towards higher pressure and catalyst on film side:

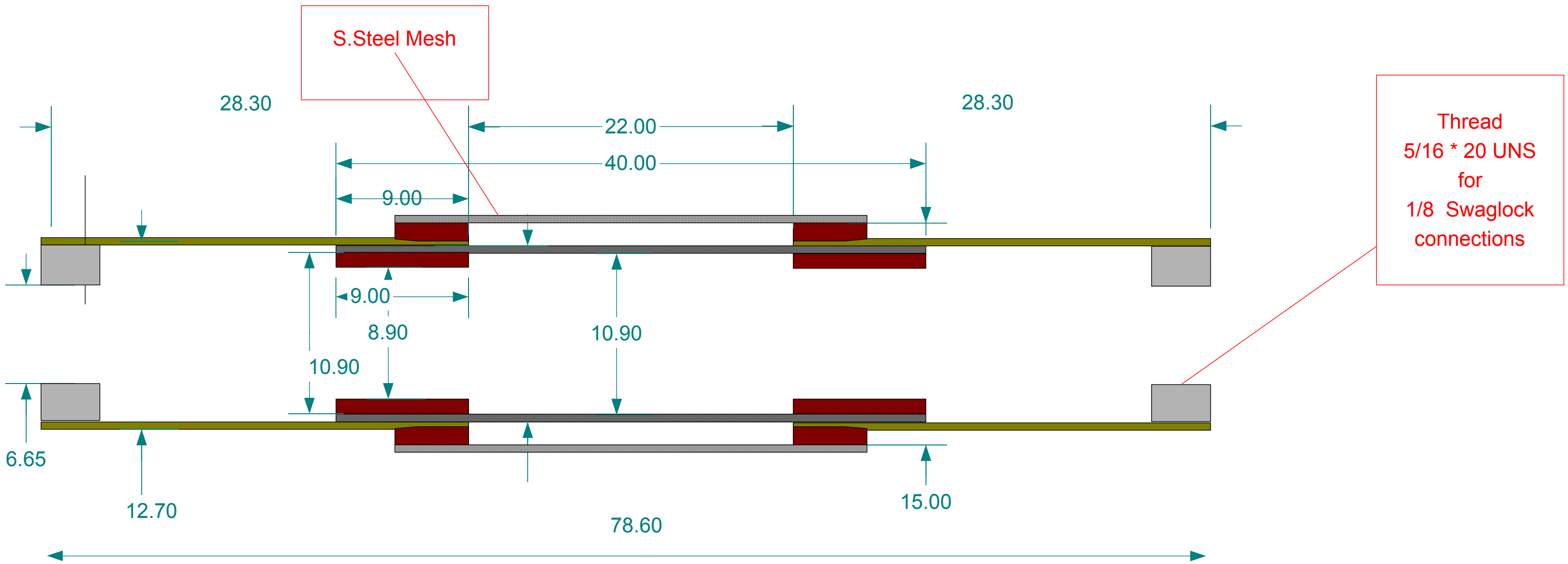
3rd generation:

- Maximum pressure 4 bar
- External protective filter to separate membrane surface and catalyst particles

4th generation:

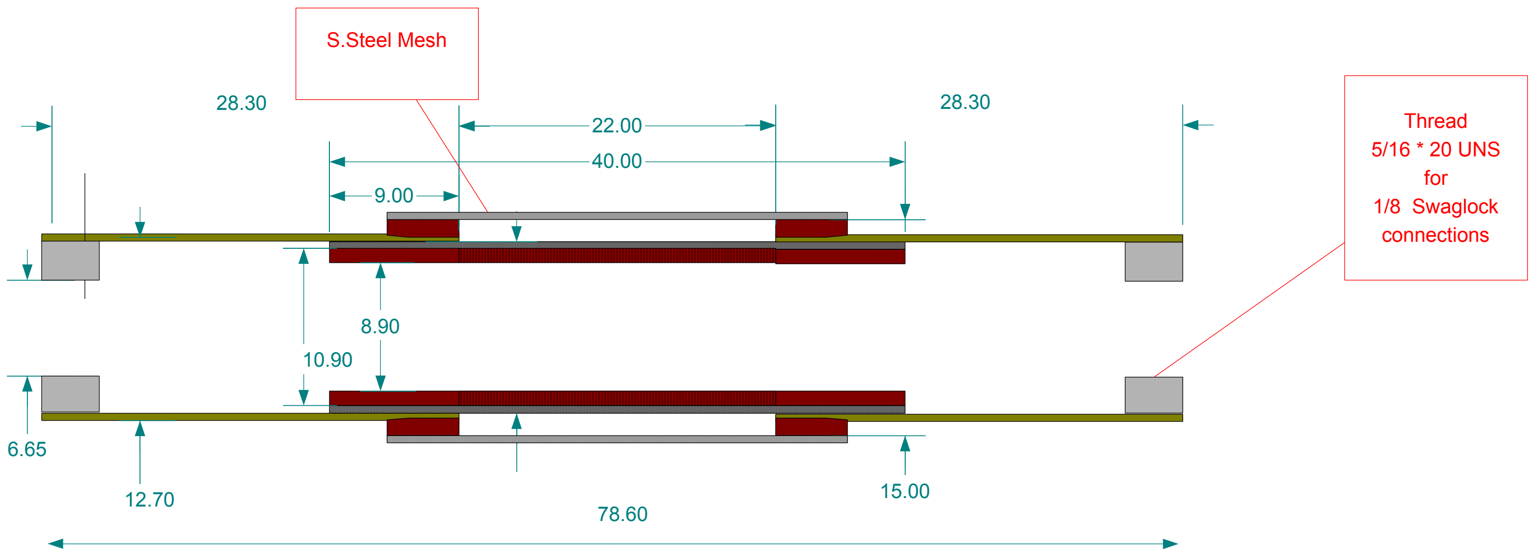
- Maximum pressure 15 bar
- Internal support tube to give pressure tolerance
- External protective filter to separate membrane surface and catalyst particles

SINTEF 3rd generation CCP-GRACE module:



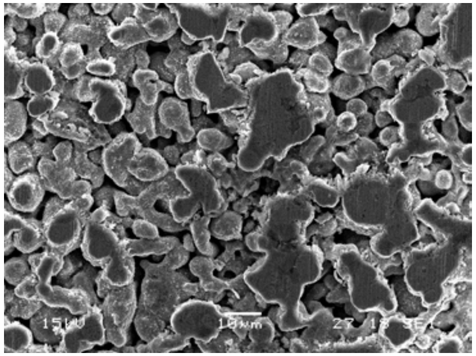
A steel net around the membrane to protect it against the catalyst particles

SINTEF 4th generation CCP-GRACE module:



The fourth generation tubular Pd/Ag membrane with steel insert to withstand high pressure

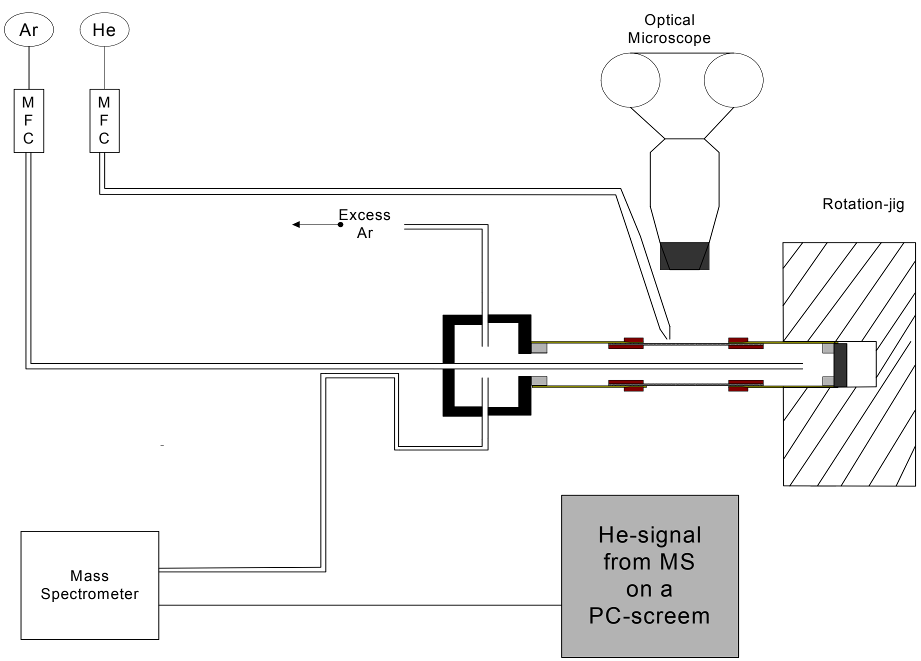
Porous support after polishing and its internal reinforcement tube

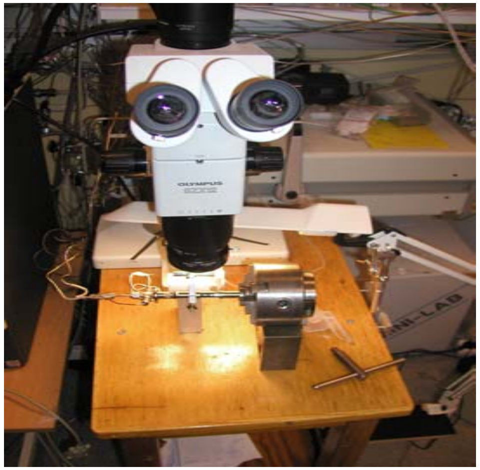


Porous support surface after mechanical abrasion with SiC-polishing paper

A method for locating and sealing leaks on a Pd-membrane

- By the use of a MS, we can detect very low concentrations of He in an Ar-flow almost in real-time.
- By purging with Ar on the inside the membrane and spraying with He outside, the He gas will pass through any leaks, and be transported to the leak-detector by the Ar-flow.
- Either by rotating the filter or movement of the He-needle, leaks are easily detected.





The set-up, with MFC, MS,microscope, He needle and the membrane unit inserted into a rotating jig. The He signal is visualised on a PC-screen

Concluding summary:

- Four generations of tubular Pd-alloy membranes on stainless steel supports have been developed in the GRACE project
- Testing of the tubular Pd-alloy membranes suggest a permeance of $3 \cdot 10^{-6}$ mol/(m^2 s Pa) in pure hydrogen at 300 °C
- External protective screen to separate membrane surface and catalyst particle
- Design transmembrane pressure up to 15 bar
- Also studied:
  - Methods for defect inspection and repair
  - Overlapping film is gas tight
- The combined high selectivity and permeance of Pd-alloy membranes is very cost effective

Challenges in future development

- Improving and verifying long term stability of thin supported membranes
- Up-scaling of thin membrane production technology on adequate supports
- Development of larger membrane module technology
- Identification of cost driving factors

International Conference on Inorganic Membranes

ICIM-4, Gatlinburg 1996

ICIM-5, Nagoya 1998

ICIM-6, Montpellier 2000

ICIM-7, Dalian 2002

ICIM-8, Cincinnati 2004

July 18-24, www.icims.org

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ICIM-9, Oslo, June 2006