Long term testing of Pd-membranes under methane steam reforming conditions

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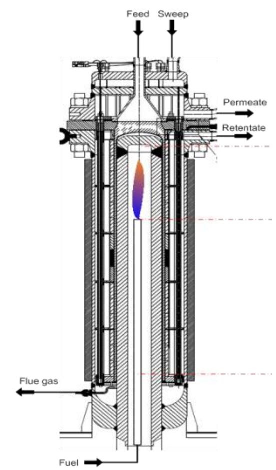
Content

- Introduction
- Aim and approach
- Results of membrane long term testing:
  - Pre test characterization
  - Long term behavior
  - Post test characterization
  - Comparison pre test vs. post test
- Conclusion

Introduction

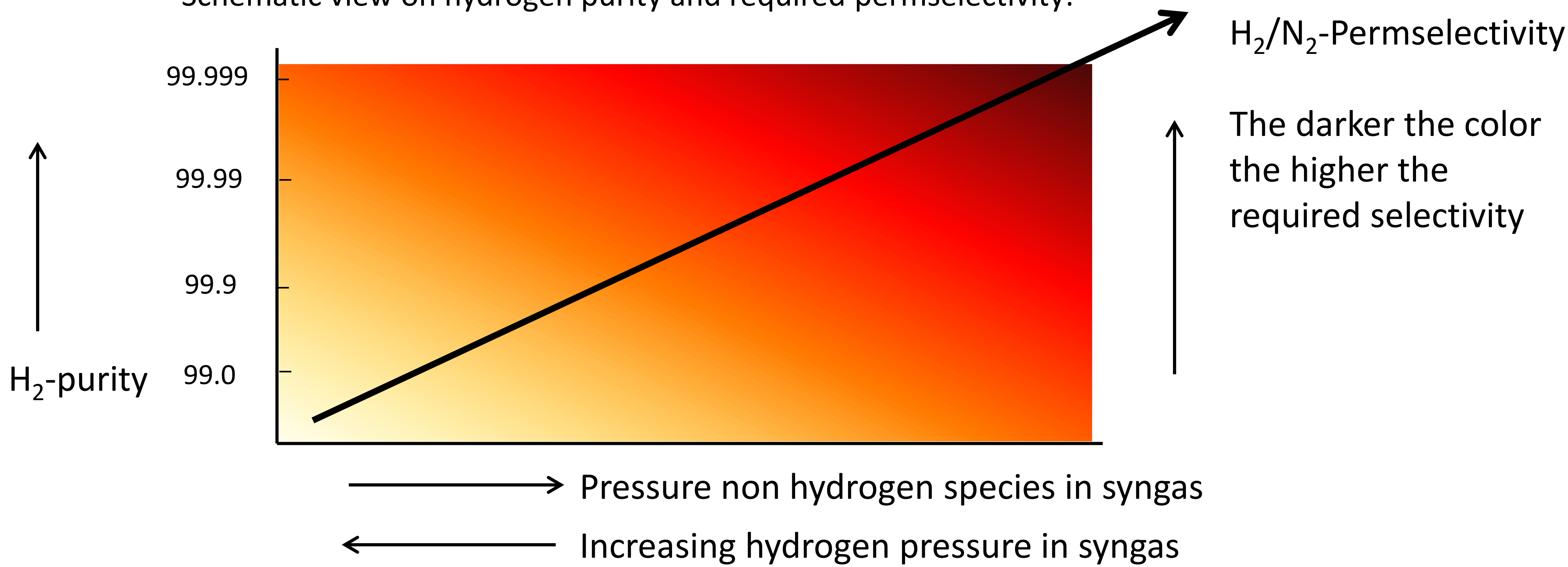
- Development of a steam methane reform membrane reactor at ECN:
  - Application: Hydrogen generation and syngas tuning for methanol synthesis
  - Advantage: Lowering of methane steam reforming temperature:
    - Use of **cheeper alloy steel**
    - **Reduce underfiring**
    - Higher overall **process efficiency**
    - Lower of **CO_2 emissions**
    - Reduced dependence on the **cost of natural gas**
    - Flexibility in using **different heating fluids**



  - Status: Construction and first phase test on integrated multi-tube membrane reactor
    - Hydrogen production capacity of 5 Nm^3/h
  - Important hurdle: Stable high hydrogen selectivity during long term operation

Introduction

- <u>H_2-purity and required H_2/N_2-permselectivity:</u>
  - Schematic view on hydrogen purity and required permselectivity:



Introduction

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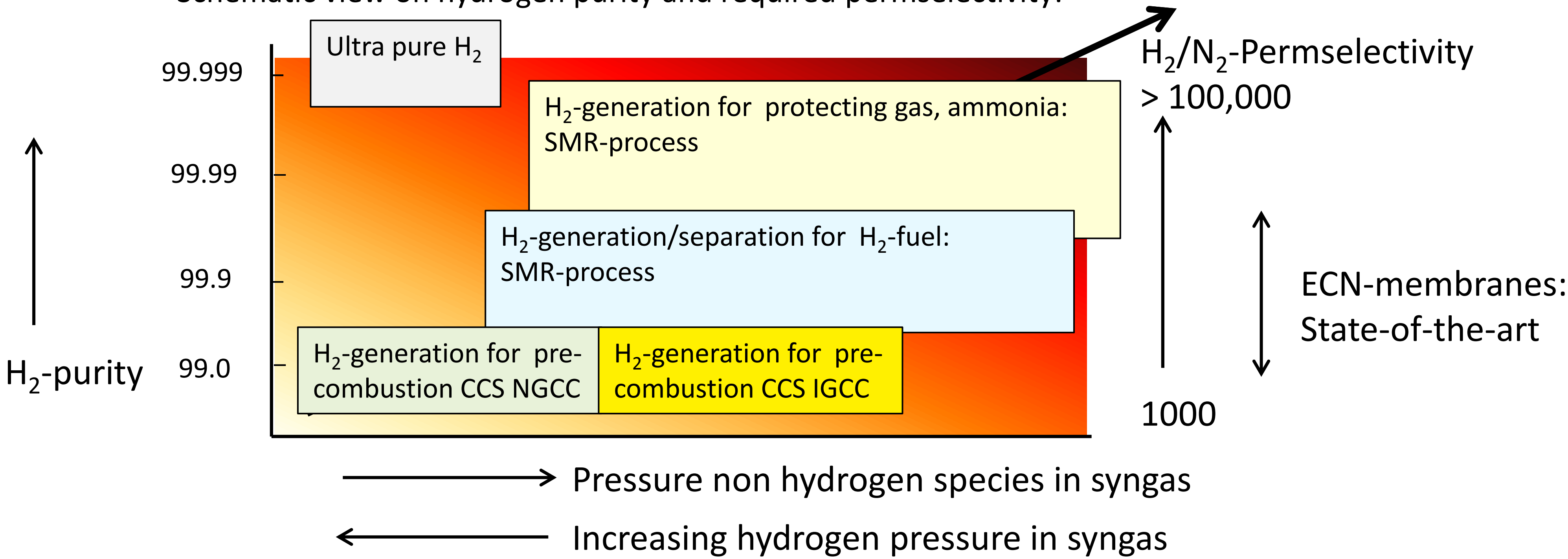


Aim and approach

- <u>Aim:</u>

- Long term behavior of membranes under SMR-conditions:
  - Permeance behaviour vs. lifetime

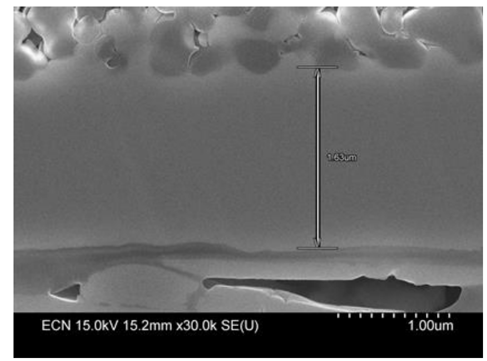
  - Selectivity behaviour vs. life time

- <u>Approach:</u>
  - Comparison thin (1.5-2 μm) and thick (4-5 μm) membrane:
    - Membrane pre-test: leakage characterisation
    - Membrane long term test under SMR-condition
    - Post test leakage characterisation:
      - in-situ (in long term test facility) and ex-situ (Rising water test, He- vs. N_2-leakage)

Membrane properties

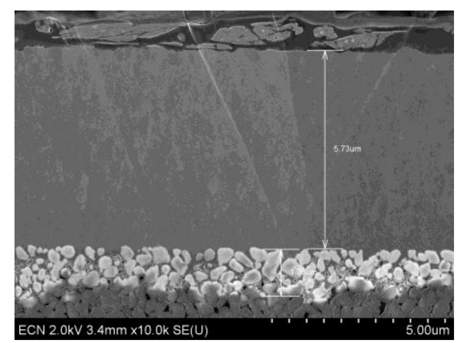
- Al_2O_3 support
- Thin Pd-layer membrane

- Membrane properties:
  - Length is 444 mm; diameter is 14 mm; membrane area is ~0.02 m^2
  - Pd-layer thickness: 1.6 micron
  - Sealing with compression seals (ECN)



- Thick Pd-layer membrane

- Membrane properties(B69Pd25):
  - Length is 364 mm; diameter is 14 mm; membrane area is ~0.015 m^2
  - Pd-layer thickness: 4-5 micron
  - Sealing with compression seals (ECN)



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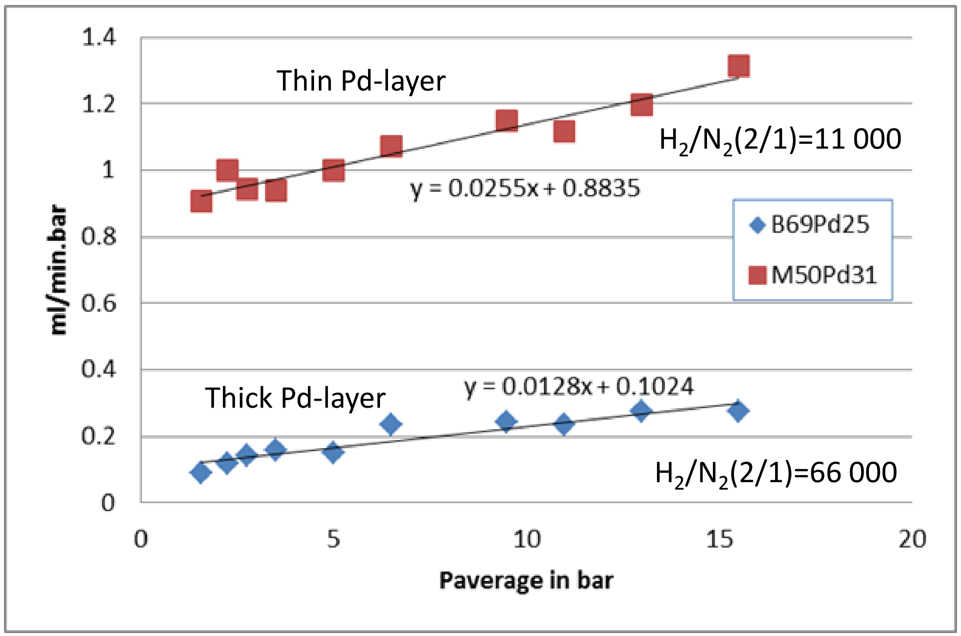
Pre test membrane characterisation

- <u>N_2-leak rate characterisation pre-test:</u>

  Leak rate: $J/dP = a + b*P_{av}$

  Y-axis intersection: Knudsen-flow = a*dP

  Slope: Viscous flow = $b*P_{av}*dP$



Thick Pd-layer results in significant lower Knudsen flow

Slope reduction by a factor 2

Y-axis intersection by a factor of 8

Long term behaviour under SMR condition

- Long term test conditions (H_2-purity and permeance):

Temperature: 450°C

Feed-pressure: 27 bar

Feed composition in vol %		and partial pressure (bar)
CO_2:	4.1	1
CH_4:	18.6	5.1
H_2O:	60.2	16.2
H_2:	17.0	4.6
CO:	0.2	very low…

Permeate pressure: 2 bar

No sweep (pure hydrogen)

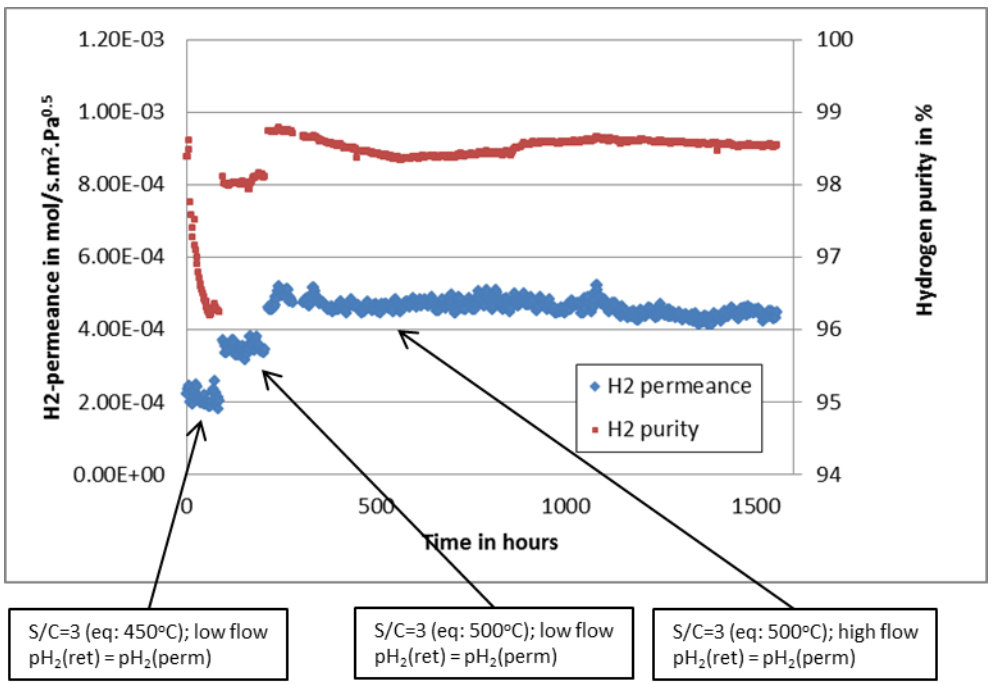
So fairly low driving force

ECN

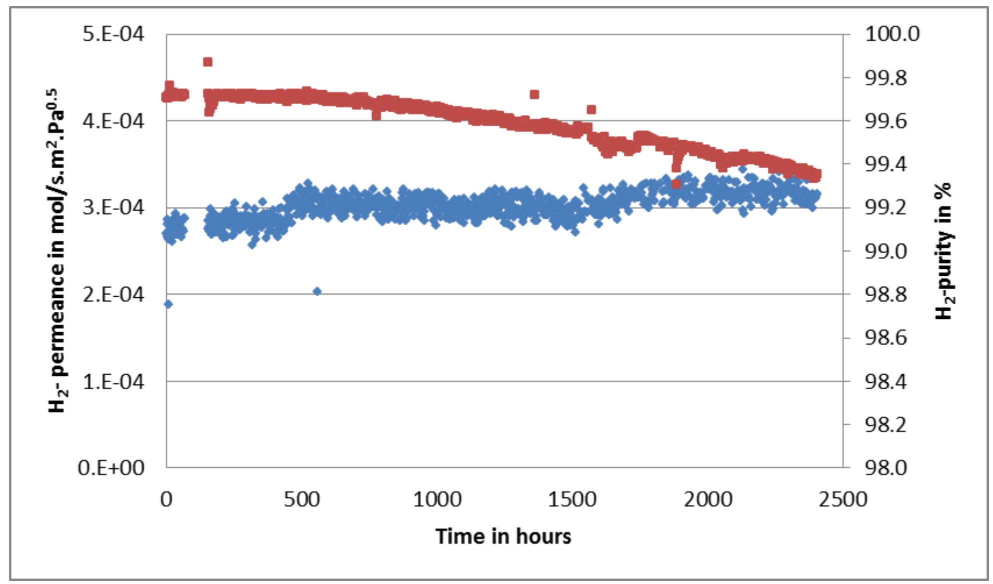
Long term behaviour under SMR condition

- <u>Membrane performance (H_2-purity and permeance):</u>

Thin Pd-layer



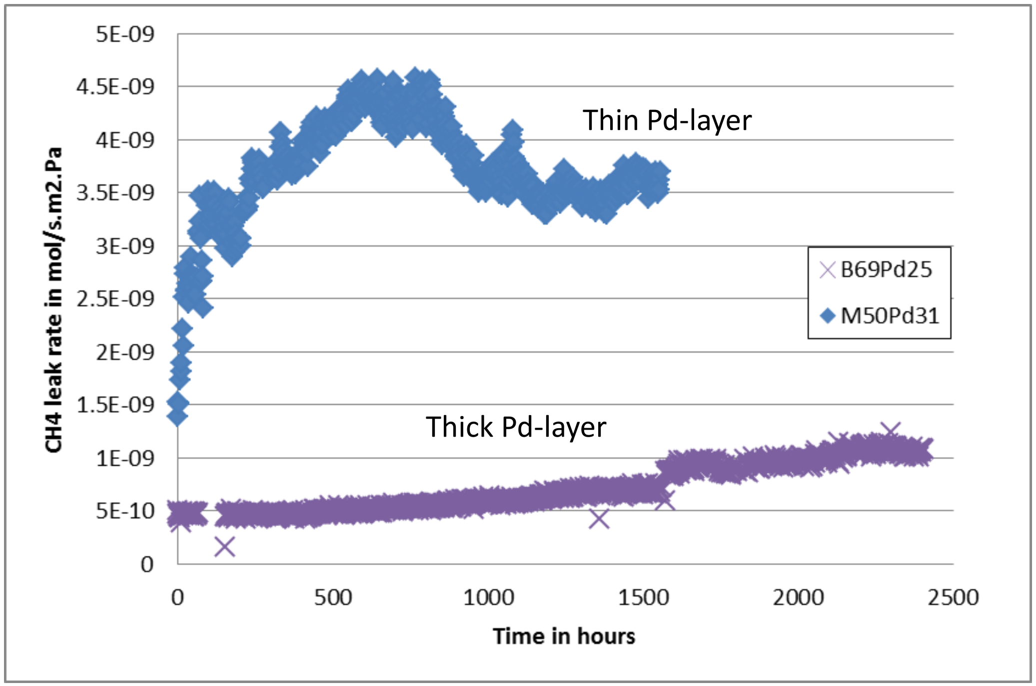
Thick Pd-layer



Long term behaviour under SMR condition

- Membrane performance (CH_4-leak rate or cross-over):

  CH_4-leak rate expressed in permeance



Leak rate behavior pre test vs. post test

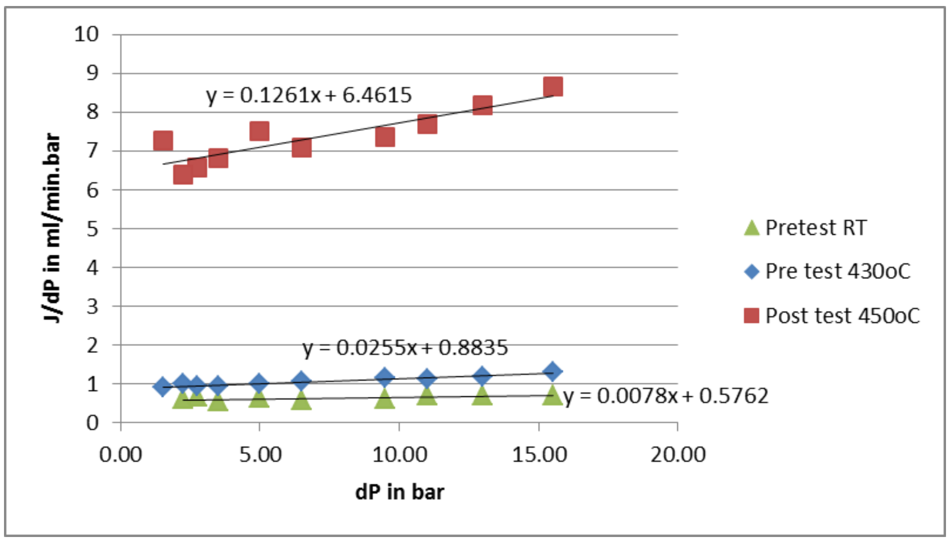
- <u>N_2-leak rate characterisation pretest to posttest:</u>

Leak rate: $J/dP = \alpha + \beta * P_{av}$

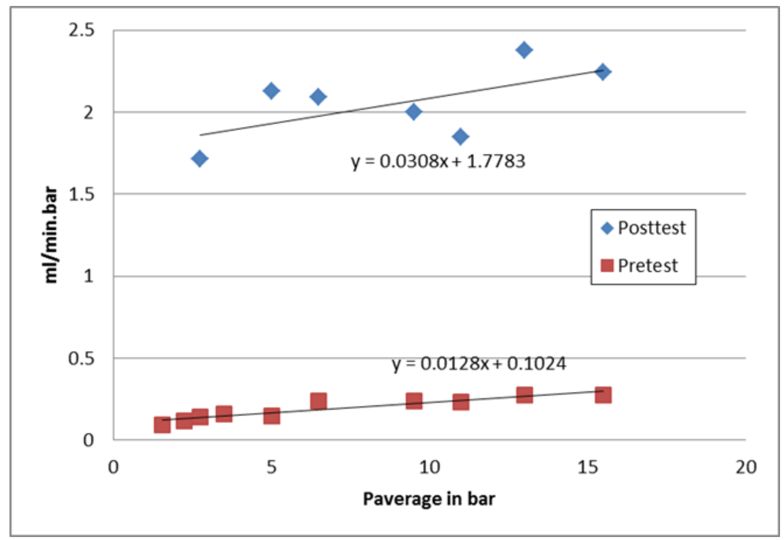
Y-axis intersection: Knudsen-flow = $\alpha * dP$

Slope: Viscous flow = $\beta * P_{av} * dP$

Thin Pd-layer



Thick Pd-layer



Mainly increase in Knudsen flow → increase in nano-sized pores

Leak rate behavior pre test vs. post test

- Post test leak characterisation Comparison N_2/He-leak flow :

Thin Pd-layer

Leak rate (ml.min)	Pressure	He	N_2	
	3 barg	84	36	Ratio He/N_2 = 2.36

Thick Pd-layer

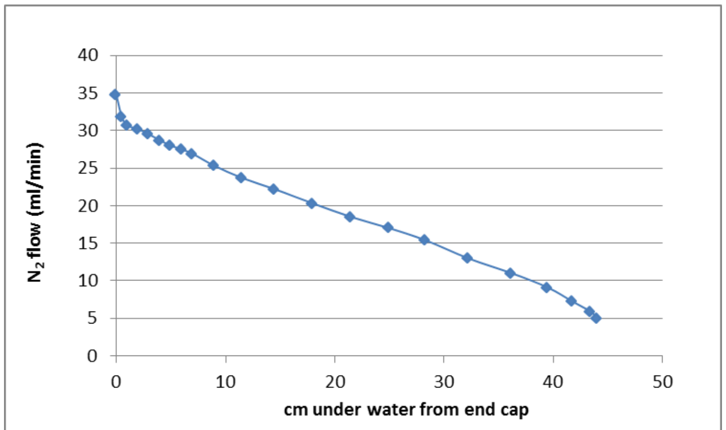
Leak rate (ml.min)	Pressure	He	N_2	
	3 barg	14.5	5.5	Ratio He/N_2 = 2.63

$(MwN_2/MwHe)^{0.5} = 2.65$

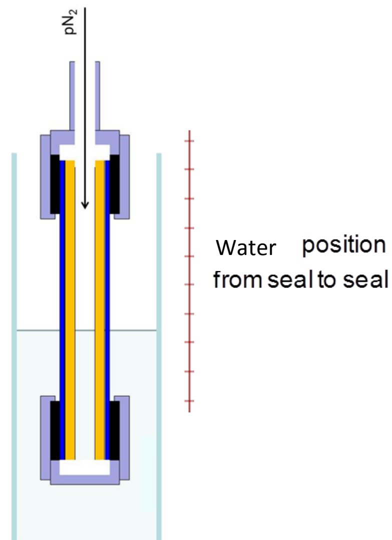
Knudsen diffusion is dominant

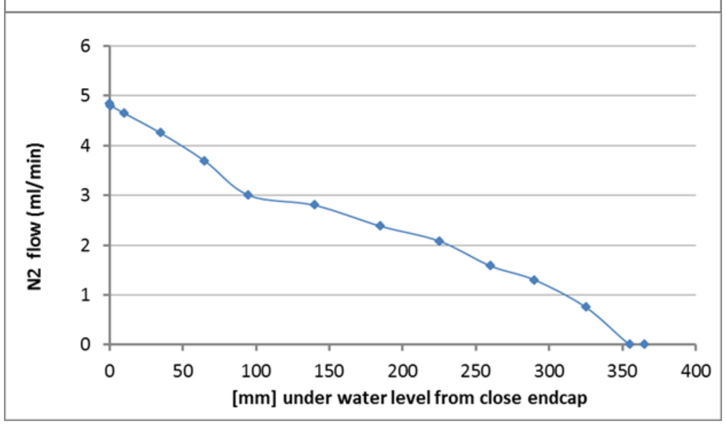
Leak rate behavior pre test vs. post test

- <u>Post test leak characterisation rising water test:</u>



Thin Pd-layer



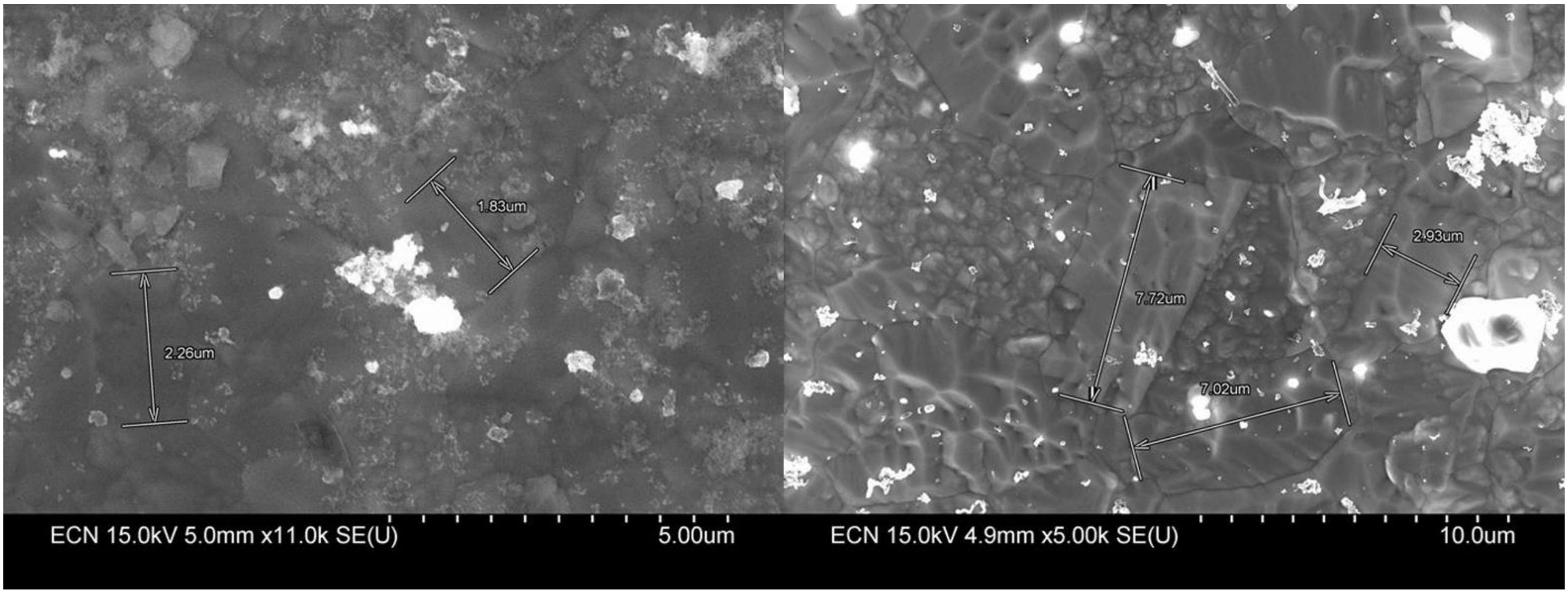


Thick Pd-layer

  – Rising water test: Leak is almost evenly distributed over membrane length

Leak rate behavior pre test vs. post test

- <u>Post test morphology characterisation:</u>



Thin Pd-layer (around 2 micron grains)

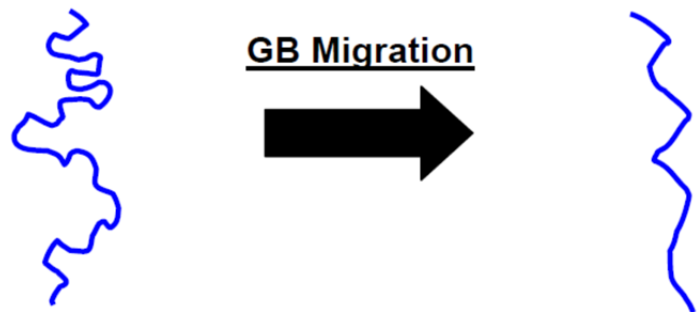
Thick Pd-layer (around 3-7 micron grains)

Resulting grain size is in same order as Pd-layer thickness

Leak rate behavior pre test vs. post test

- <u>Possible leakage mechanism:</u>

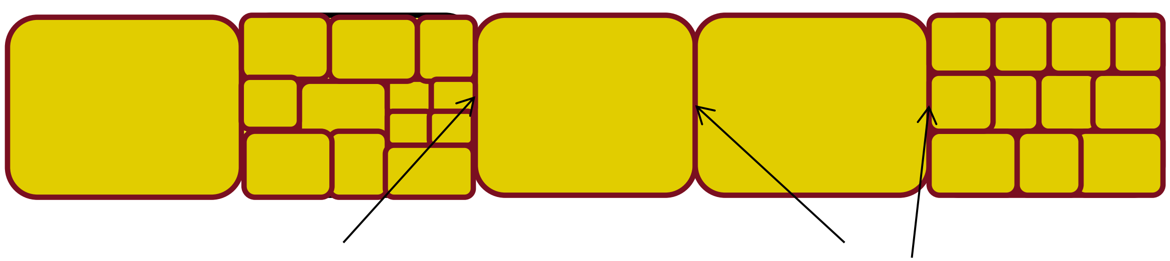
  Straightening out of grain boundary from one side to the other



Initial grain boundary shape

Post test grain boundary shape

Cross sectional schematic impression of morphology

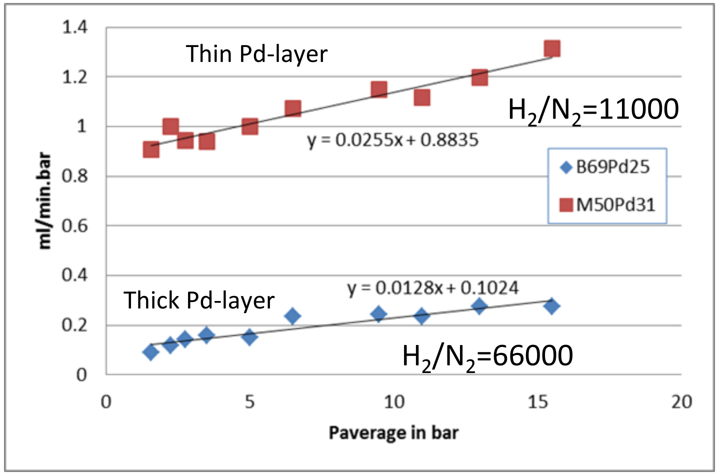


Grain boundary forms a short circuit for gas cross over from one side to the other

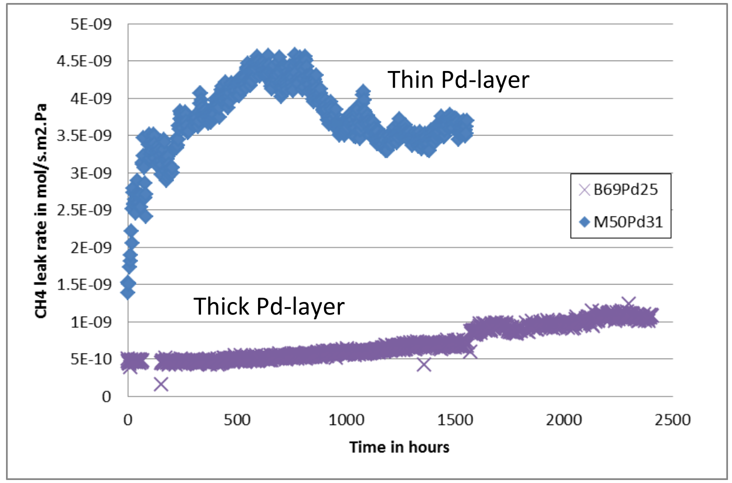
Long term behaviour under SMR condition

- Overview:

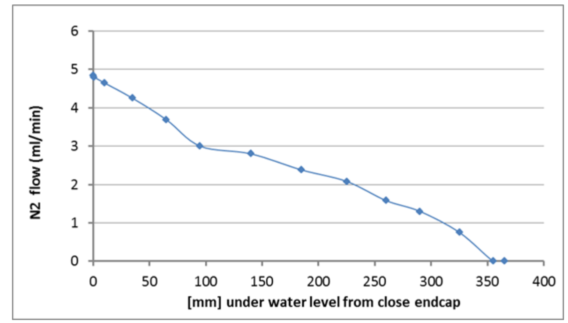
Pre test



Long term test



Post test



Knudsen behavior

- Conclusions:

- Thick Pd-membrane → Initial low leakage level → longer life time
- Increase in leakage due to increase in amount nano-scale defects (Knudsen)
- Main question: origin of Knudsen defects (Layer thickness, plating procedure, support properties, stress state, grain growth…)

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