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

F.P.F. van Berkel, M.J. den Exter, H.J. Marsman, J.F. van Wees, J.P. Overbeek, W.G. Haije and Y.C. van Delft

Workshop Scale-up Pd-membrane technology, Petten
20th of November 2014

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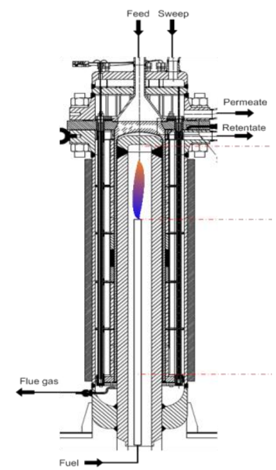
- Aim and approach
- Results of membrane long term testing:
  - Pre test characterization
  - Long term behavior
  - Post test characterization
  - Comparison pre test vs. post test
- Conclusion

Introduction

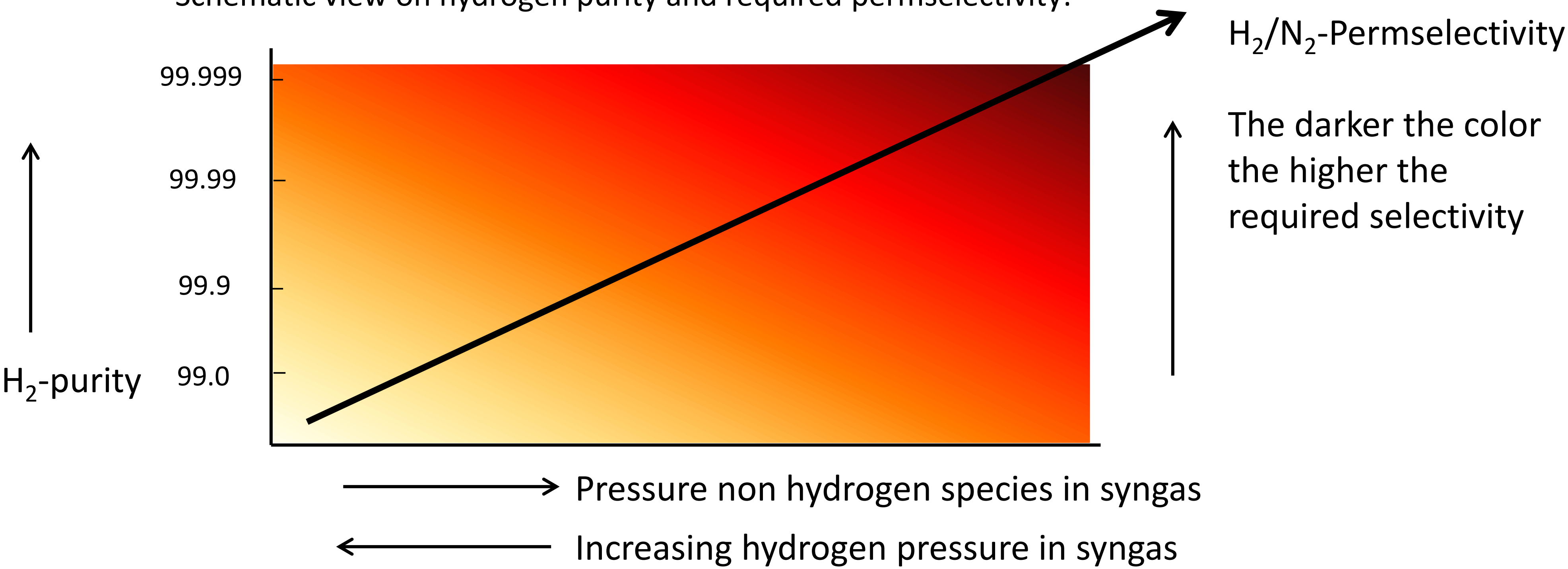
- <u>Development of a steam methane reform membrane reactor at ECN:</u>
  - Application: Hydrogen generation and syngas tuning for methanol synthesis
  - Advantage: Lowering of methane steam reforming temperature:
    - Use of **cheeper alloy steel**
    - **Reduce underfiring**
    - Higher overall **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

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



Introduction

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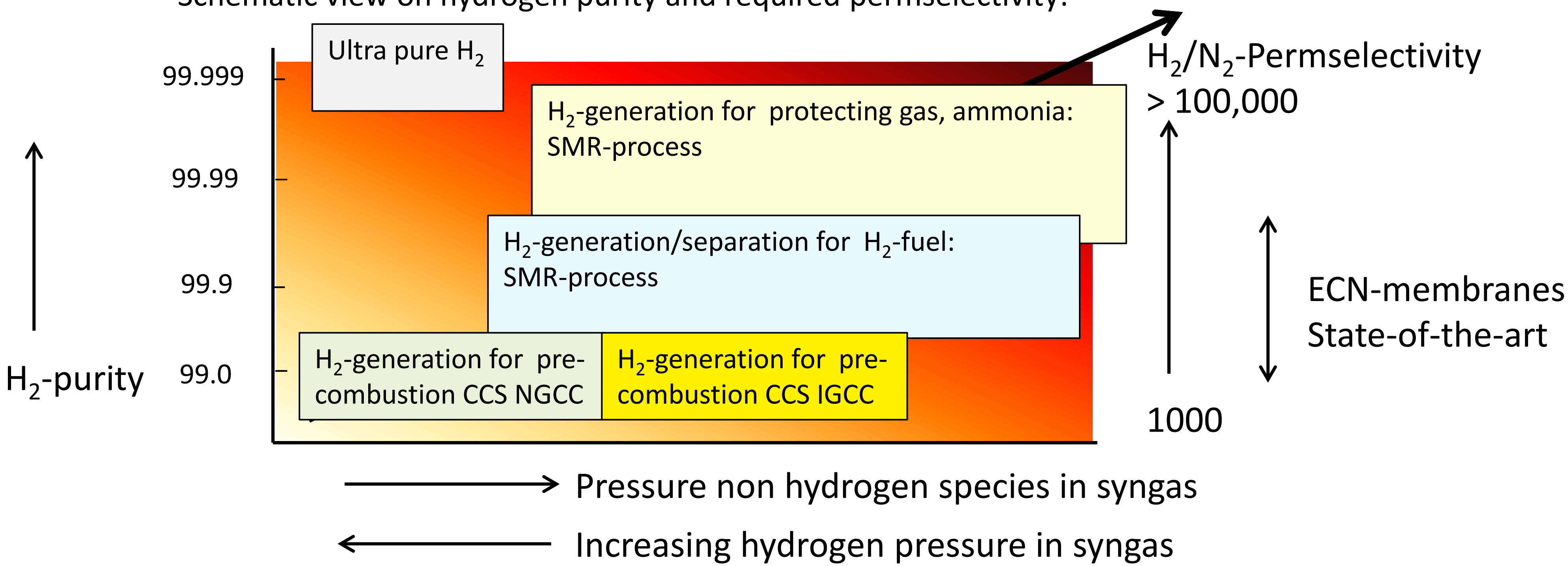


Aim and approach

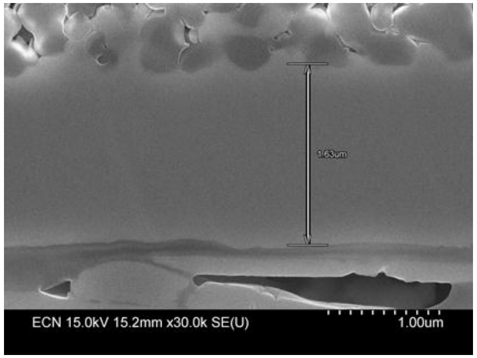
- Aim:
- Long term behavior of membranes under SMR-conditions:
  - Permeance behaviour vs. lifetime
  - Selectivity behaviour vs. life time

- Approach:
  - 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

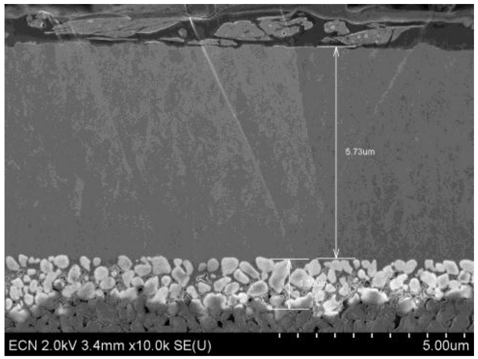
- Al_2O_3 support
- Thin Pd-layer membrane

- 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)



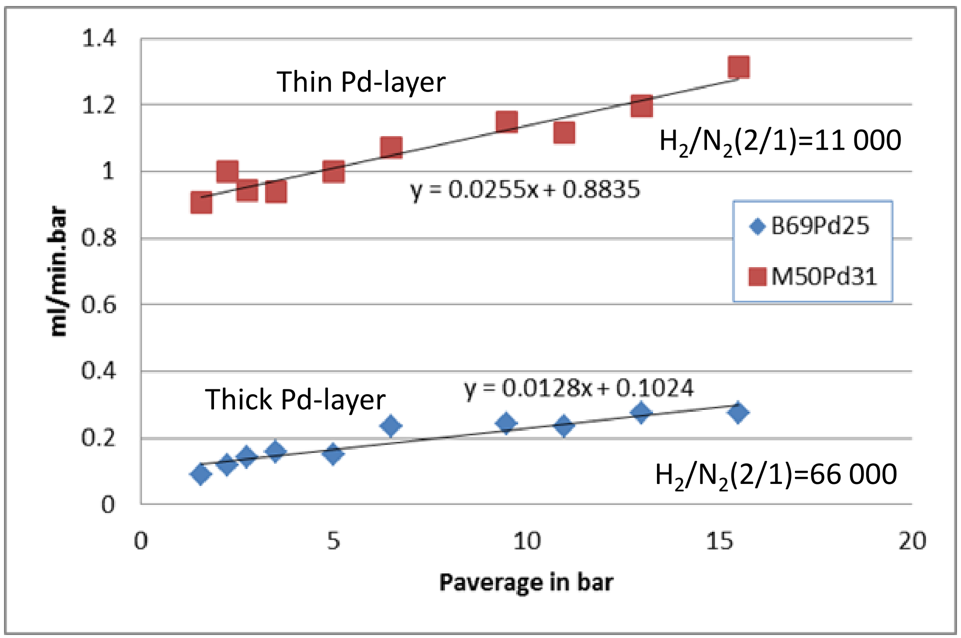
Pre test membrane characterisation

- <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
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)

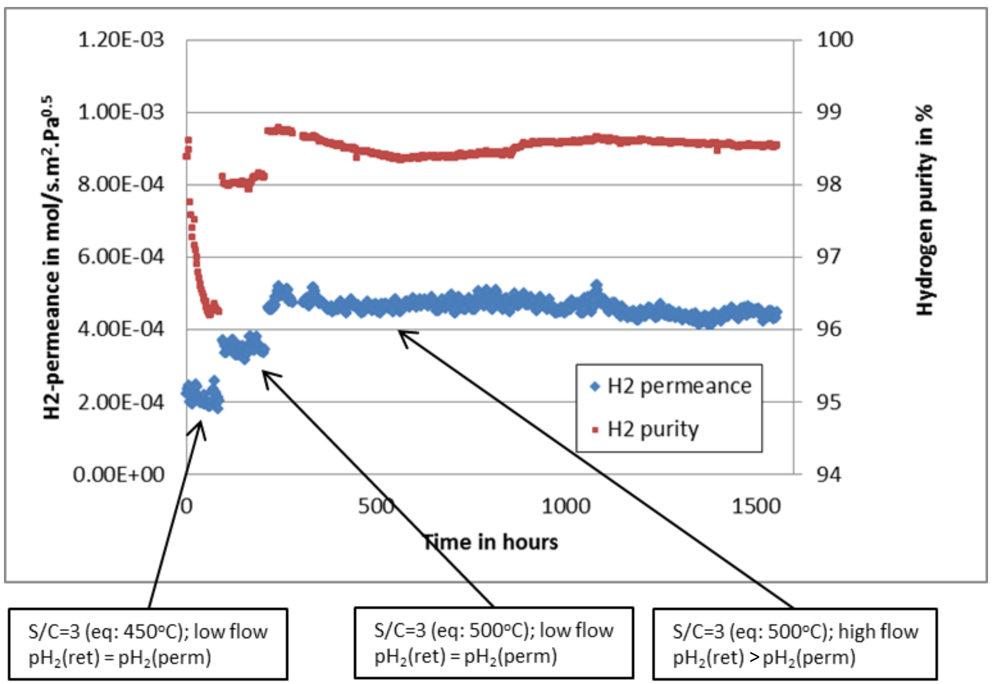
So fairly low driving force

ECN

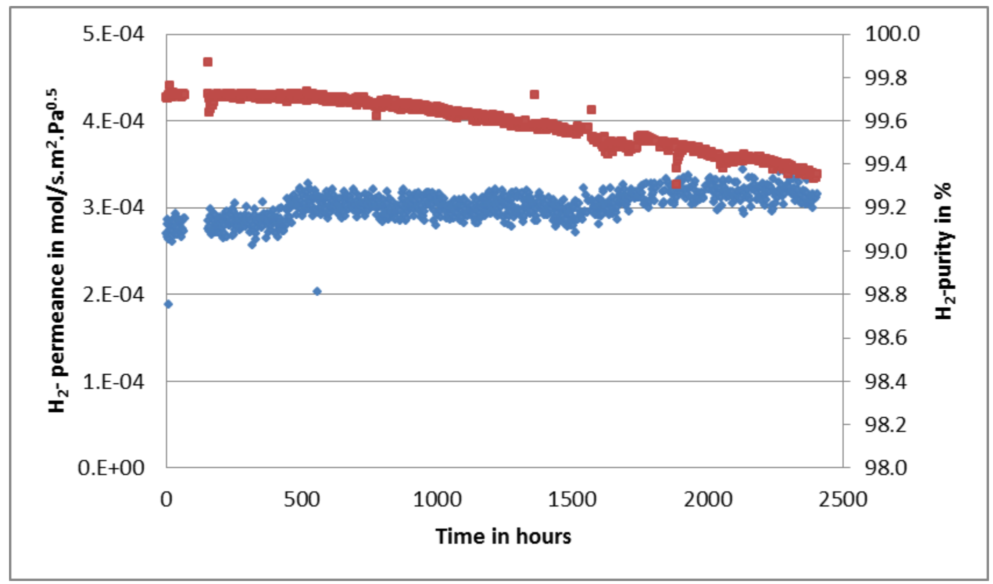
Long term behaviour under SMR condition

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

Thin Pd-layer



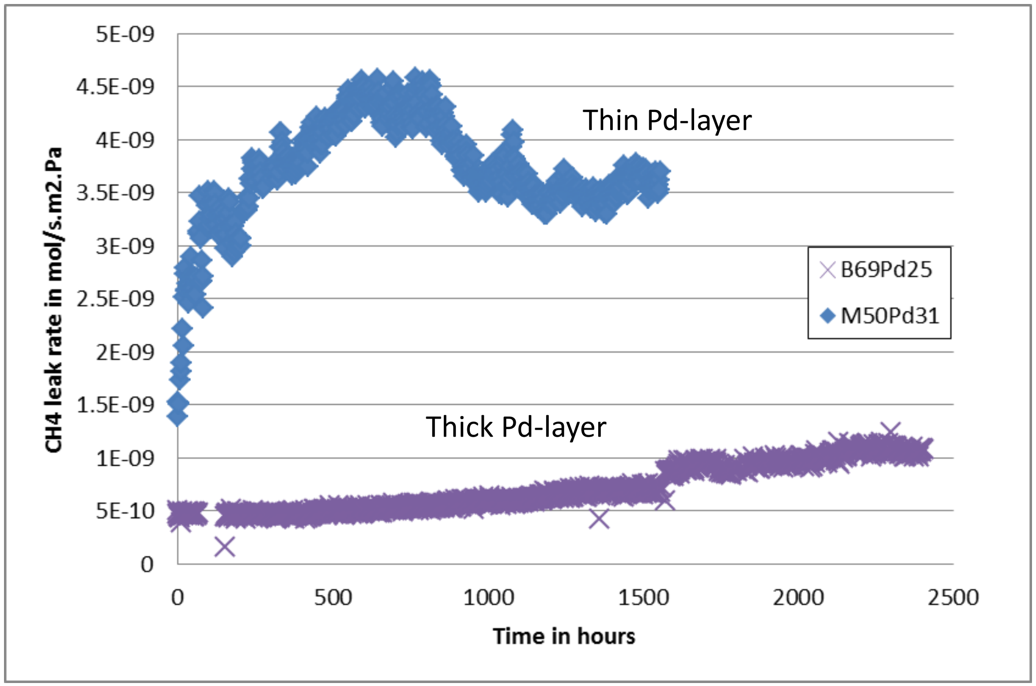
Thick Pd-layer



Long term behaviour under SMR condition

- <u>Membrane performance (CH_4-leak rate or cross-over):</u>

  CH_4-leak rate expressed in permeance



Leak rate behavior pre test vs. post test

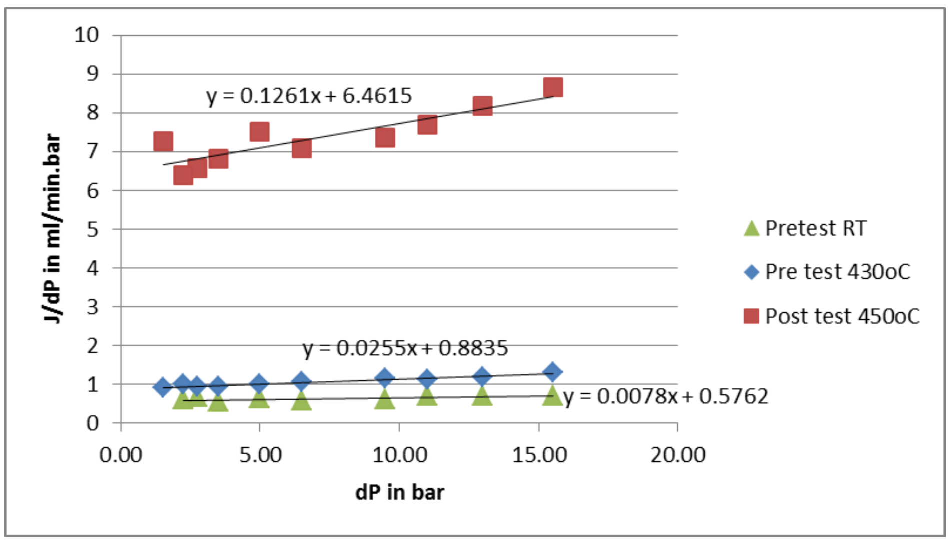
- <u>N_2-leak rate characterisation pretest to posttest:</u>

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

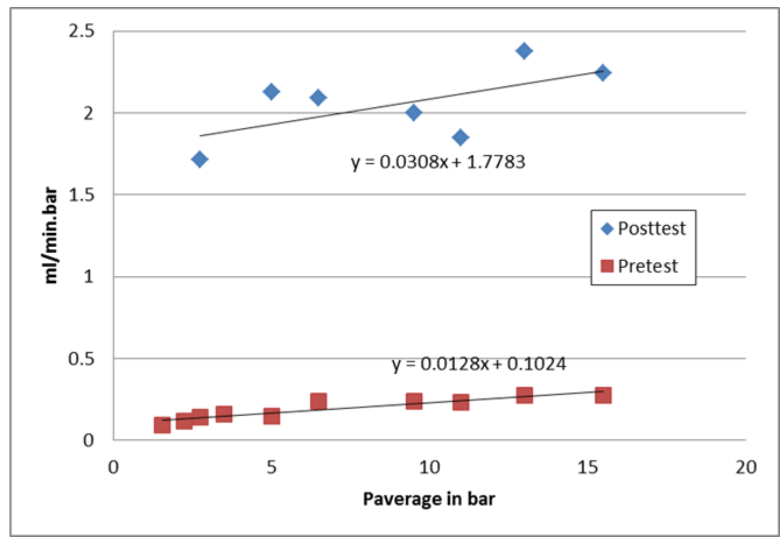
  Y-axis intersection: Knudsen-flow = $\alpha * dP$

  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

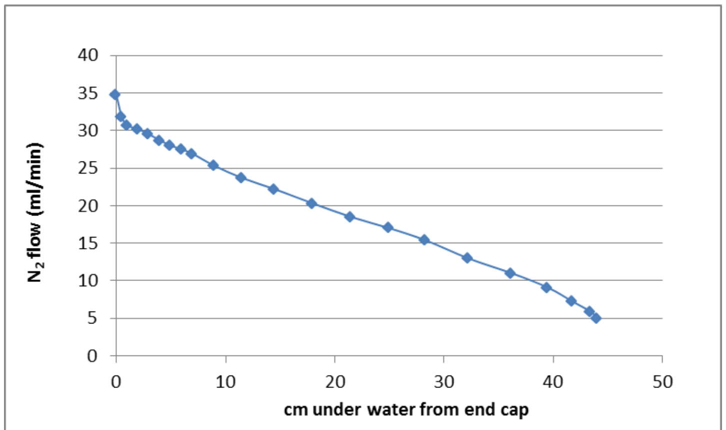
Leak rate (ml.min)	Pressure	He	N_2	
	3 barg	14.5	5.5	Ratio He/N_2 = 2.63

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

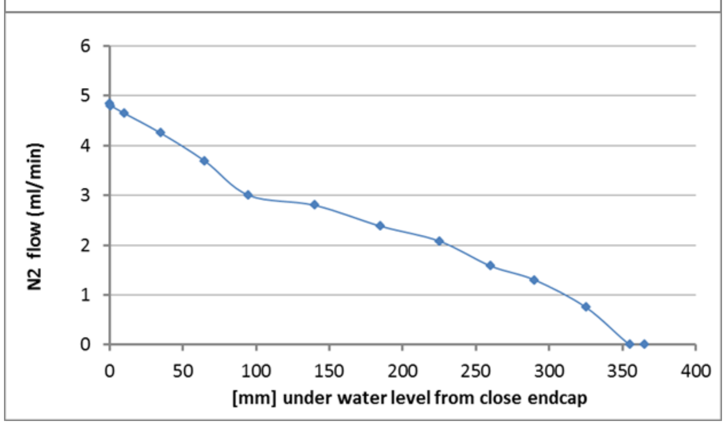
Knudsen diffusion is dominant

Leak rate behavior pre test vs. post test

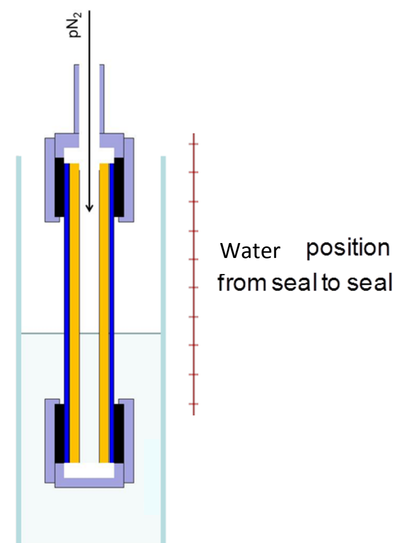
- <u>Post test leak characterisation rising water test:</u>



Thin Pd-layer



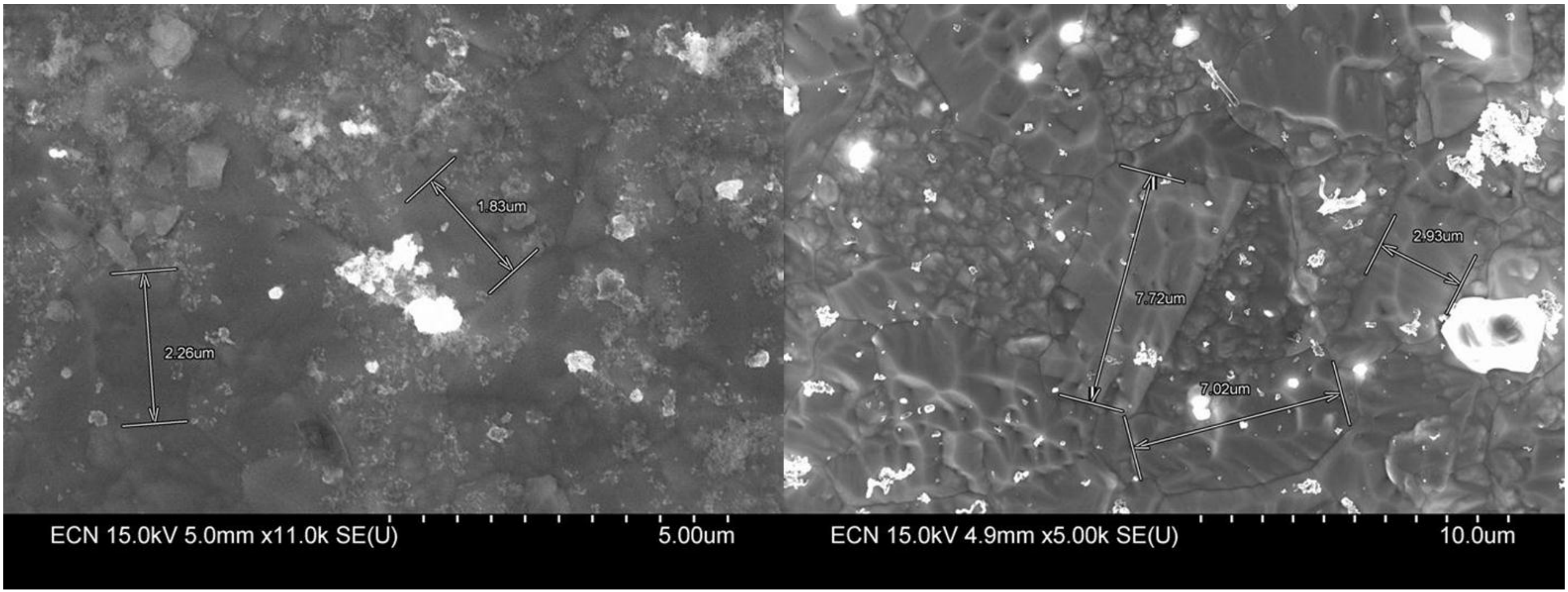
Thick Pd-layer



  – 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)

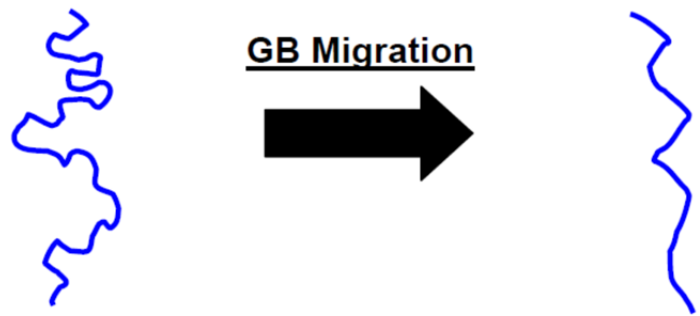
Thick Pd-layer (around 3-7 micron grains)

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

Leak rate behavior pre test vs. post test

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

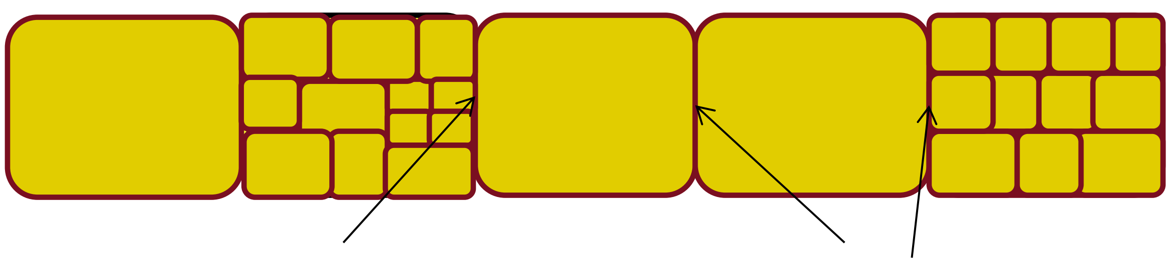
Straightening out of grain boundary from one side to the other



Initial grain boundary shape

Post test grain boundary shape

Cross sectional schematic impression of morphology



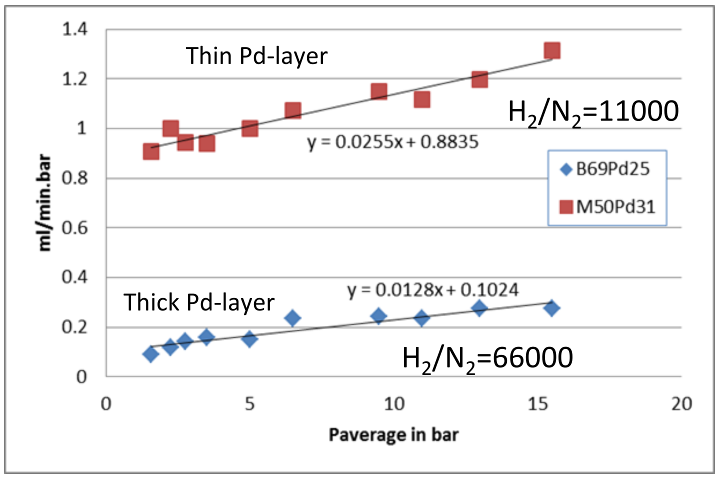
Grain boundary forms a short circuit for gas cross over from one side to the other

ECN

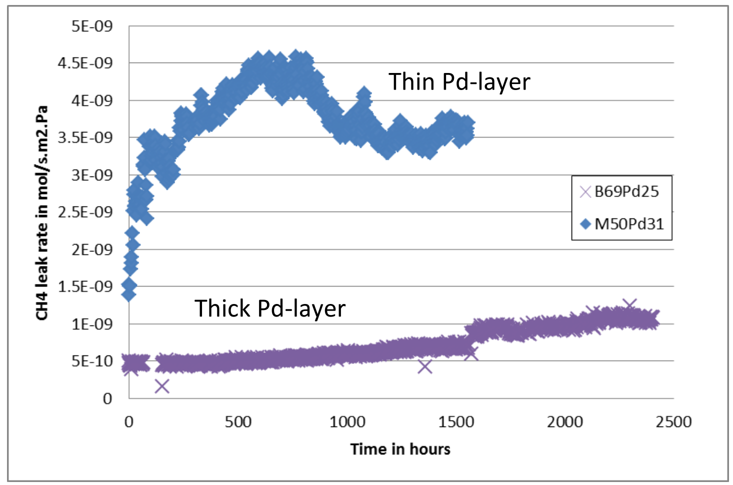
Long term behaviour under SMR condition

- **Overview:**

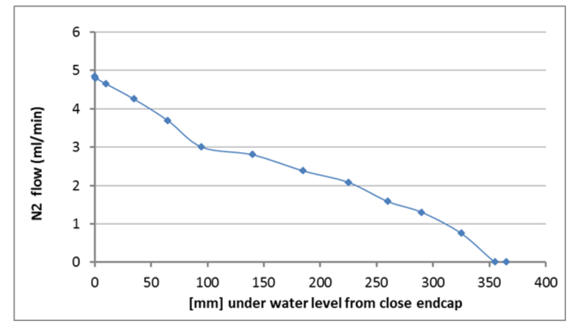
Pre test



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…)

ECN

Acknowledgement

CARENA

ISPT

Sustainability by Innovation in Processing

The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration, under Grant Agreement n° 263007 (acronym CARENA) and from the Dutch Institute of Sustainable Process Technology.