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


Workshop Scale-up Pd-membrane technology, Petten
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• 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 cheaper alloy steel
    - Reduce underfiring
    - Higher overall process efficiency
    - Lower of CO₂ 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 Nm³/h
  - **Important hurdle:** Stable high hydrogen selectivity during long term operation
Introduction

- **H₂-purity and required H₂/N₂-permselectivity:**
  
  Schematic view on hydrogen purity and required permselectivity:

  The darker the color the higher the required selectivity

  
  - Pressure non hydrogen species in syngas
  - Increasing hydrogen pressure in syngas
Introduction

- **H₂-purity and required H₂/N₂-permselectivity:**
  - Schematic view on hydrogen purity and required permselectivity:

  - **H₂-purity**
    - 99.999
    - 99.99
    - 99.9
    - 99.0

  - **H₂/N₂-Permselectivity**
    - > 100,000
    - > 100,000

  - **H₂-generation for protecting gas, ammonia:**
    - SMR-process

  - **H₂-generation/separation for H₂-fuel:**
    - SMR-process

  - **H₂-generation for pre-combustion CCS NGCC**

  - **H₂-generation for pre-combustion CCS IGCC**

- **Increasing hydrogen pressure in syngas**

- **Pressure non hydrogen species in syngas**

- **ECN-membranes:**
  - State-of-the-art

- **Ultra pure H₂**
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. N₂-leakage)
Membrane properties

- **Al$_2$O$_3$ 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**

- **N₂-leak rate characterisation pre-test:**
  
  Leak rate: \( \frac{J}{dP} = a + b \cdot P_{av} \)
  
  Y-axis intersection: Knudsen-flow = \( a \cdot dP \)
  
  Slope: Viscous flow = \( b \cdot P_{av} \cdot dP \)

![Graph showing leak rate vs. P average for thin and thick Pd-layer](image)

- 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 (H₂-purity and permeance):

  Temperature: 450°C

  Feed-pressure: 27 bar

  Feed composition in vol % and partial pressure:
  
  - CO₂: 4.1
  - CH₄: 18.6
  - H₂O: 60.2
  - H₂: 17.0
  - CO: 0.2

  Permeate pressure: 2 bar
  No sweep (pure hydrogen)
  So fairly low driving force
Long term behaviour under SMR condition

- Membrane performance ($H_2$-purity and permeance):

### Thin Pd-layer

- $H_2$-permeance in mol/m$^2$*Pa*time
- $H_2$ purity in %

### Thick Pd-layer

- $H_2$-permeance in mol/m$^2$*Pa*time
- $H_2$ purity in %

S/C=3 (eq: 450°C); low flow $pH_2$(ret) $>$ $pH_2$(perm)

S/C=3 (eq: 500°C); low flow $pH_2$(ret) $=$ $pH_2$(perm)

S/C=3 (eq: 500°C); high flow $pH_2$(ret) $<$ $pH_2$(perm)
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

- **N₂-leak rate characterisation pretest to posttest:**
  - Leak rate: \( J/dP = \alpha + \beta \cdot P_{av} \)
  - Y-axis intersection: Knudsen-flow = \( \alpha \cdot dP \)
  - Slope: Viscous flow = \( \beta \cdot P_{av} \cdot dP \)

**Thin Pd-layer**

\[
y = 0.1261x + 6.4615
\]

**Thick Pd-layer**

\[
y = 0.0255x + 0.8835
\]

Mainly increase in Knudsen flow \( \rightarrow \) increase in nano-sized pores
**Post test leak characterisation Comparison \( \text{N}_2/\text{He}-\text{leak flow} \):**

<table>
<thead>
<tr>
<th>Thin Pd-layer</th>
<th>Pressure (barg)</th>
<th>( \text{He} ) (ml.min)</th>
<th>( \text{N}_2 ) (ml.min)</th>
<th>Ratio ( \text{He}/\text{N}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>84</td>
<td>36</td>
<td>2.36</td>
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</table>

<table>
<thead>
<tr>
<th>Thick Pd-layer</th>
<th>Pressure (barg)</th>
<th>( \text{He} ) (ml.min)</th>
<th>( \text{N}_2 ) (ml.min)</th>
<th>Ratio ( \text{He}/\text{N}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>14.5</td>
<td>5.5</td>
<td>2.63</td>
</tr>
</tbody>
</table>

\((\text{Mw}_\text{N}_2/\text{Mw}_\text{He})^{0.5}\) = 2.65

Knudsen diffusion is dominant
Leak rate behavior pre test vs. post test

- Post test leak characterisation rising water test:

  - Rising water test: Leak is almost evenly distributed over membrane length
Leak rate behavior pre test vs. post test

- **Post test morphology characterisation:**

  - 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

- **Possible leakage mechanism:**
  Straightening out of grain boundary from one side to the other

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...)

Thick Pd-layer

Thin Pd-layer

H₂/N₂=66000

y = 0.0128x + 0.1024

Thick Pd-layer

y = 0.0255x + 0.8835

H₂/N₂=11000

\[ \text{H}_2/\text{N}_2 = 66000 \]

\[ \text{H}_2/\text{N}_2 = 11000 \]
Acknowledgement

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