Join Workshion on Scale-up of Pd Membrane Technology

Development of Pd based supported membranes

David Alfredo Pacheco Tanaka

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Pd based membranes for hydrogen separation

Pd membranes

Self supported

Supported

- Ceramic
- Metallic

Metallic supports

Advantages | Disadvantages
--- | ---
✓ High mechanical strength  
✓ Easily welded avoiding sealing problems  
✓ Expansion coefficient close to Pd  |  
▪ Rough surface  
▪ Non uniform pore distribution  
▪ Large pores  
▪ Requires a layer between the support and Pd to avoid inter-diffusion  
▪ More expensive than ceramics
Ceramic Support

Commercial asymmetric membranes

Advantages
- Thin Pd membranes can be deposited
- Uniform pore distribution
- Small pore size (5 – 200 nm)
- Smooth surface
- Cheaper than metallic

Disadvantages
- Fragile
- Difficult to joint to metallic parts
- Sealing problems

Alumina
Alumina - Zirconia
Effect of the support on hydrogen permeation of Pd membranes at elevated temperature

α-alumina support

D.A. Pacheco Tanaka..., Chemistry Letters Vol.37, No.9 (2008)
YSZ support


Hydrogen permeation flux versus operating time at 650°C with pressure differences of 100 kPa
Pd –Ag alloy membranes

1.- Improve durability against embrittlement

Palladium membranes suffer from H2 embrittlement due to the $\alpha$-$\beta$ phase transition of PdH at below the critical temperature (293 °C). Often cause fatal fracture of the membrane.

Change in lattice size (Å) of the $\alpha$- and $\beta$-phase in Pd-Ag alloy with Ag content

<table>
<thead>
<tr>
<th>Atom % Ag</th>
<th>$\alpha$- phase</th>
<th>$\beta$-phase</th>
<th>Increase %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.89</td>
<td>4.02</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>3.92</td>
<td>4.00</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>3.94</td>
<td>3.99</td>
<td>1.3</td>
</tr>
<tr>
<td>24</td>
<td>3.99</td>
<td>4.00</td>
<td>0.3</td>
</tr>
<tr>
<td>30</td>
<td>3.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.- Higher H2 permeation
Fabrication methods of Pd membranes

- **CVD**
  - Chemical Vapor Deposition

- **PVD**
  - Physical Vapor Deposition

- Electroless plating
Preparation of H2 membranes by electroless plating

\[ \text{Pd}^{2+} + 2e^- \xleftrightarrow{\text{Pd}} \text{Pd} \]
Preparation of f Pd-Ag membranes


Seeding

Pd acetate in chloroform
Reduce with N2H4

One pot plating

Simultaneous co-deposition of Pd and Ag

Annealing

Control Pd-Ag composition
Pd-Ag Membrane reactor for WGS

“Long term” test
H$_2$/N$_2$ perm selectivity  400°C 2 bar

H$_2$ permeance 3.1 x 10$^{-6}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$
Even after more than 20 heating up and cooling down cycles

30 membranes 19 cm long
Average 1.5 ± 0.7 x 10$^{-10}$ mol m$^{-2}$s$^{-1}$ Pa$^{-1}$
Autothermal reforming of methane

Polished metallic support from Mott with YSZ ceramic layer

[Graph showing permeance of H₂ (mol/s/m²/Pa) over time (hours) at different temperatures: 500 °C, 525 °C, 550 °C, 575 °C, 600 °C.]

Permeance of H₂ (mol/s/m²/Pa)

Selectivity H₂/N₂

Time (hours)
Pd-Ag membranes by PVD magnetron sputtering
by direct deposition on tubular porous supports

CemeCon® CC800/8
Pd-Ag target

40 cm diameter  50 cm height
Direct deposition of Pd-Ag (77-23) by PVD MS

Effect of the support

<table>
<thead>
<tr>
<th>Sample</th>
<th>N2 permeance x 10^{-9} mol m^{-2} s^{-1} Pa^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al_2O_3 100 nm support only</td>
<td>20000-30000</td>
</tr>
<tr>
<td>Pd-Ag (2 μm thick) on support by PVD-MS</td>
<td>1400</td>
</tr>
<tr>
<td>Target of membrane</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Electroless plating</td>
<td>PVD</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>Low cost</td>
<td>Expensive equipment</td>
</tr>
<tr>
<td>Cheap equipment</td>
<td></td>
</tr>
<tr>
<td>Most of Pd used is deposited on the porous substrate</td>
<td>Pd is lost in the chamber</td>
</tr>
<tr>
<td>Difficult to control metal composition in Pd alloy membranes</td>
<td>Better control of multimetal deposition</td>
</tr>
<tr>
<td>Difficult to prepare ultra thin Pd membranes due to the presence of high concentration of stabilizing agents in plating solution</td>
<td>Deposition in clean environment allows preparation of ultra-thin Pd membranes</td>
</tr>
<tr>
<td>Suitable for <strong>micron</strong> Pd membranes</td>
<td>Suitable for <strong>sub-micron</strong> Pd Membranes</td>
</tr>
</tbody>
</table>
Fluidised-bed membrane reactors

Water gas shift (WGS)

Autothema reforming of methane
Composite nano porous membranes packed with Palladium nanoparticles (pore filled membranes)

Nano-sized palladium particles suppress the stress due to lattice expansion by $\alpha \rightarrow \beta$ phase transition.

Composite nano porous membranes packed with Palladium nanoparticle (pore filled membranes)

D.A. Pacheco Tanaka..., Advanced Materials 18, 2006, 630-632
Advantages of pore filled over conventional membranes

- Less Pd is used (a fraction of conventional)
- Mechanically more stable
- Use in fluidized bed reactors
Hydrogen permeation of the YSZ-γAl₂O₃ Pd pore filled membranes

H₂ permeance 500 °C 2.8 x 10⁻⁶ molm⁻²s⁻¹Pa⁻¹
H₂/N₂ selectivity 8000
Membrane Reformers for m-CHP applications

m-CHP micro combined heat and power system

Ethanol steam reforming

ATR reformers for different natural gas compositions
Membrane group at Tecnalia
Many Thanks