Ultra-thin supported inorganic membranes

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Structure of this talk

Description/definitions inorganic membranes

Long-term performance goals

Micro-structural optimization <500 nm thickness

Examples

Conclusions and perspectives
Example of designed and real structures

- Micro-porous or dense membrane (10 nm...1 µm)
- Meso-porous intermediate (100 nm...5 µm)
- Macro-porous support (1 µm...2 mm)
- Macro-porous carrier (0.5...2 mm)
Four different length scales

2 mm thick multilayer structure for H₂, CO₂, air, water separation

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1. **g-Permeance** \( k/\Delta p > 10^{-5} \text{ mol/(m}^2\text{·s·Pa)}; \alpha > 100 \\
2. **Degradation** \(<50\% \text{ over } >10,000 \text{ hrs} \\
3. **Production yield** \( >90\% \); **reproducibility** \(<10\% \\
4. **Membrane surface density** \( >100 \text{ m}^2/\text{m}^3 \\
5. **Cost price** \(<$500/\text{m}^2. \\
   - Structural components: earth-abundant elements \\
   - Thin layer manufacturing time/step to <1’
# Options for H₂-permeable membranes

<table>
<thead>
<tr>
<th>Material:</th>
<th>Sol-gel SiO₂</th>
<th>Pd-alloy</th>
<th>MIE (H⁺,e⁻)</th>
<th>Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Stability</td>
<td>Poor?</td>
<td>Poor?</td>
<td>Good</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
General approach

Find very thin selective (1 nm...1 μm) film
- Identify mechanism for selective transport

Find very strong, smooth, permeable multi-layer
- No surface defects, (<1 nm...<1 μm) roughness
- Design: analysis/measurement transport
- Intermediate layers as thin as possible
- Carrier as thick/strong as possible

Deposit film defect-free on multi-layer

Make sure it can be dirt-cheap
- But do no work with dirt!
Why multi-layer defect control

Deviation from quasi-homogeneous structure

Connected pore defects:
• ↓ selectivity

Surface defects:
• ~ in the next layer

All defects:
• ↓ life time
• ↓ reproducibility
• Hinder basic research

Contamination

Process bubbles
Approach to defect control

All layers: high $\rho$ packing particles similar $\mathcal{D}_s$

Dispersion, colloidal stabilization:
- $\mathcal{D}_s$-selective purification
- US removal micro-bubbles

Deposition:
- Colloidal filtration, casting
- Film, dip, spin deposition

Dense in-situ/secondary growth
- Template-free/epitaxial

Support permeance $\gg$ membrane
Dispersion of:
- *homogenous* particles

Stabilization by:
- *Charge, steric*

Rheology by:
- *Hydro polymers*

Deposition by:
- *Support modification*

At 1 nm…10 μm length scale
AA3 $\alpha$-$\text{Al}_2\text{O}_3$ carriers ($\varnothing_s = 3 \, \mu\text{m}$)

Aqueous $\text{HNO}_3$; $p_H = 2.0$

33 wt\% AA3

*Chilled* US 60 W for 10 min

20 $\mu$m # nylon screen

Colloidal casting 43 mm $\varnothing$

1300°C for 10 hrs

“Floaters” require:

- Polyacrylate wetting agent
Improving support layers ($\phi_p = 80$ nm)

- $\alpha$-Alumina Powder
- Colloidal stabilizer (HNO$_3$, APMA)
- Ultrasonic dispersion
- Ultrasonic Ti Finger
- Cooling Beaker
- Purification by screening
- $\alpha$-Al$_2$O$_3$ compact formation
- Water is drained
- Filtration Manifold
- Nitrocellulose Membrane
- Porous Glass Support
- To Vacuum
- Optically smooth support
- Sintering of Green Body
- $\alpha$-Al$_2$O$_3$ compact formation
- Water is drained

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Homogeneous meso-porous intermediate

Water-clear dispersions (narrow PSD; \( \varnothing < 20 \) nm)
Modification with hydro-phylllic polymer chains:
- Dip-coating rheology
- Drying lubrication
- Support \( \varnothing_p \), and affinity
Homogeneous 50 nm thick SSZ zirconia

SSZ $\varnothing_p = \sim 2 \text{ nm}, \ X = 50 \text{ nm}$ on porous $\alpha$-$\text{Al}_2\text{O}_3$

- With industrial partner:
  - sono-chemical synthesis 3 nm SSZ particles
- Polymer-assisted film coating
Recent example amorphous silica

Standard sol-gel $\text{SiO}_2$
- $f_{H_2} = 3 \times 10^{-8}$ [SI], $\alpha > 100$
- $f$ lowered by \textit{infusion} first layer?
  - Enhanced suction
- Good for \textit{stability}
- Wil be explored with 50 nm thick $\text{ZrO}_2$
Deposition control: surface chemistry

**Aqueous** medium:
- Spontaneous ion sorption
- **Charges** the surface
- Diffuse counter-charge

Control surface charge:
- By specific ions, $p_H$
- Colloidal stability:
  - Homogeneous dense packing
- **Affinity**: orientation

Characterization: $\zeta$-potential
Zeolite Y deposition

Effect $p_H = 8.5$ (left) vs $p_H = 11.5$ (right)
And finally: one very new result

200 nm electroless Pd on:
120 nm layer
560 nm γ-alumina ($\varnothing_p = 4$ nm)
5 $\mu$m $\alpha$-$\text{Al}_2\text{O}_3$ ($\varnothing_p = 80$ nm)
2 mm $\alpha$-$\text{Al}_2\text{O}_3$ ($\varnothing_p = 700$ nm)

**Stable** $j_{H_2} = 0.1...1$ (mol/m$^2$/s): 260...320°C; 2→0 Bar.
- Appears surface controlled

**Selectivity** $>100$

**Further stabilization:** alloys, meso-porous top layer
And the first tubes

\(\gamma\)-alumina on AKP30 on coarse \(\alpha\)-\(\text{Al}_2\text{O}_3\)

- Green/magenta: \textit{homogeneity}

Pd on \(\gamma\)-alumina

- Brown \textit{intermediate}:
  - Gray <500 nm Pd:
  - \(\text{N}_2\)-dense at RT
Conclusions; status

Viable multi-layer syntheses become available:
• Several membrane separation concepts
• Surface pore $\varnothing < 1 \mu m$
• Defects are becoming under control

Abundant use of colloidal, US-based methods

Further development defect detection needed

Further development of rapid methods needed

Now trying several membrane/fuel cell concepts
Acknowledgement

DOE

- Hydrogen Production and Storage program
- BES Hydrogen Fuel Initiative
- EMTEC hydrogen program

NSF

- IGERT MEMD

State of Ohio/OSU

- Third Frontier program
- Hayes Investment program
Questions?