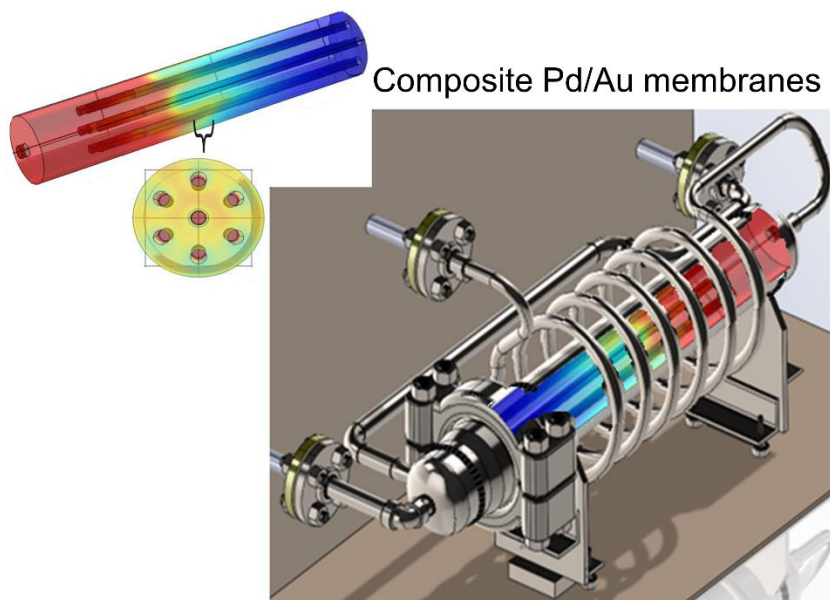


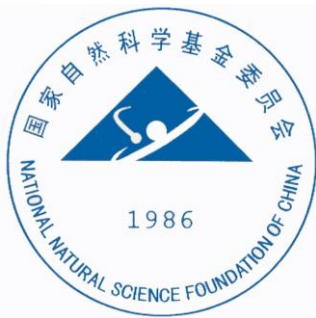
# Development of a Large-scale Multitube Membrane Module for H<sub>2</sub> Separation

Dr. Bernardo Castro-Dominguez

October 15<sup>th</sup>, 2018



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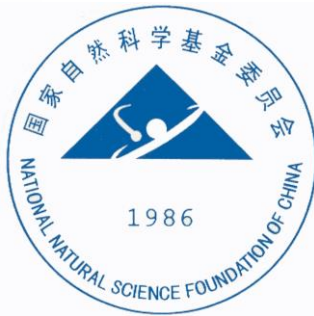


Interested and experience:

- Catalysis
- Membranes
- Gas separation
- Hydrogen production
- CO<sub>2</sub> sequestration



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long-term thermal and mechanical stability.



**METALLIC**  
Ma (fourth from right) discusses synthesis of palladium alloy membranes with his group. Credit: COURTESY OF YI HUA MA

**THE GROUP** has developed unique technologies to synthesize palladium membranes that are stable for thousands of hours (*Ind. Eng. Chem. Res.* 2004, 43, 2936). "One of our membranes was tested for 6,000 hours under steam-reforming conditions in a Shell laboratory," Ma says.

In recent work, Ma and colleagues investigated the hydrogen-permeability and hydrogen-selectivity stability of a low-copper-content Pd-Cu membrane with a thickness of less than 10  $\mu\text{m}$  supported on a porous stainless steel substrate. "Porous stainless steel supports, unlike porous ceramic or glass supports, resist cracking," he observes. "Palladium-porous stainless steel membranes are also easily assembled, and the thermal expansion coefficient of stainless steel is very close to that of palladium, ensuring good mechanical properties of the composite membrane during temperature cycling.

"Composite Pd-Cu alloys have the advantage over other types of palladium membranes of being mechanically stable and sulfur resistant," Ma adds. "Pd-Cu alloys with a relatively high copper content have higher hydrogen permeability but lose their hydrogen transport properties at temperatures above 450  $^{\circ}\text{C}$  because of a phase transformation of the alloy at high temperatures."



**COMPOSITES**  
Virginia Tech group has prepared

The group measured the hydrogen permeation rate of a porous stainless-steel-supported, 10- $\mu\text{m}$ -thick Pd-Cu membrane containing around 10% copper by weight and observed no decline in the rate at 450  $^{\circ}\text{C}$  over 500 hours.

Chemical engineering professor S. Ted Oyama and research professor Yunfeng Gu at Virginia Polytechnic Institute & State University, Blacksburg, have been working on highly permeable

## Prof Yi Hua Ma

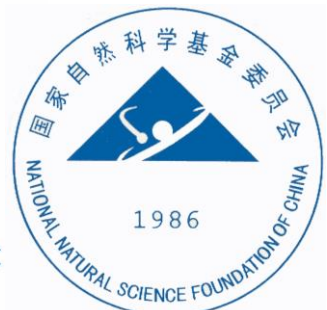


World's leading membrane research labs

## Prof Ted Oyama



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Dr. Bernardo Castro

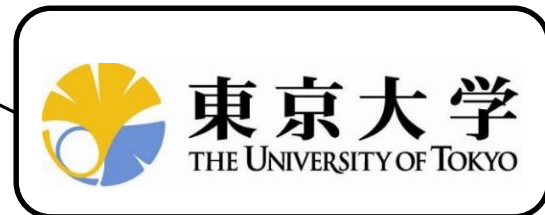
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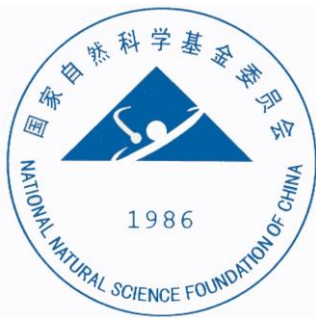
Lecturer / Assistant  
Professor



UNIVERSITY OF  
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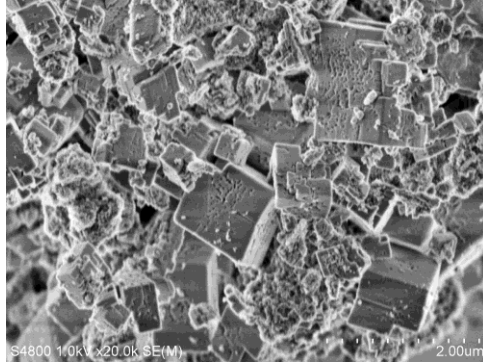


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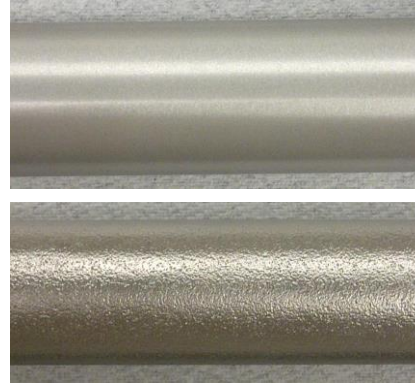


# Membrane Research Overview

Zeolite and MOF membranes



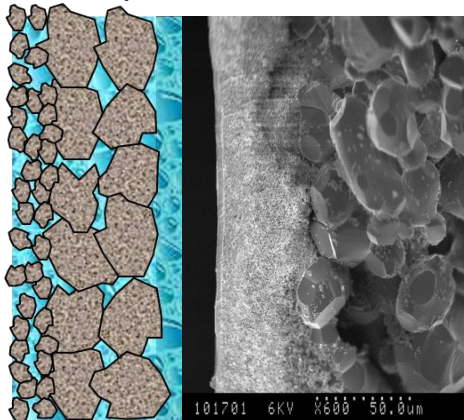
Metallic membranes



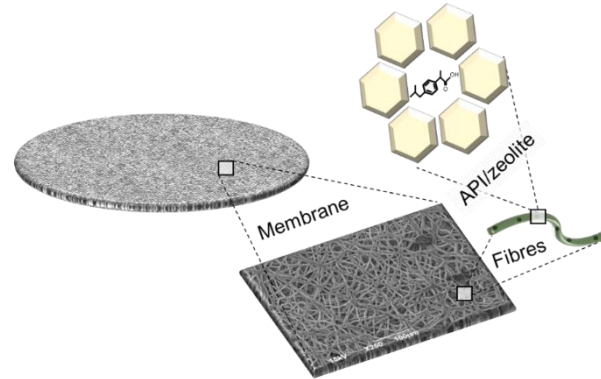
Membranes from natural materials



Liquid membranes



Drug delivery membranes

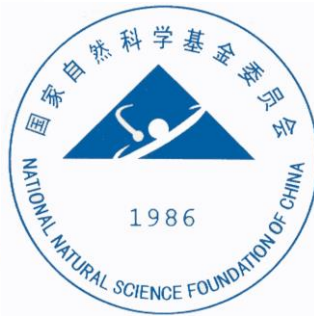


Other membranes:

- Graphene oxide membranes
- Silica membranes
- Mixed matrix membranes
- Carbon membranes



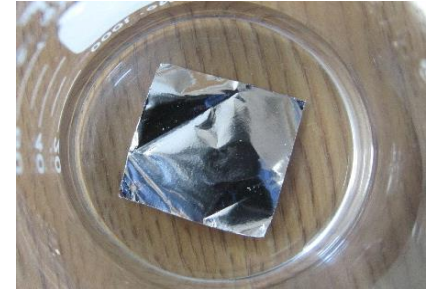
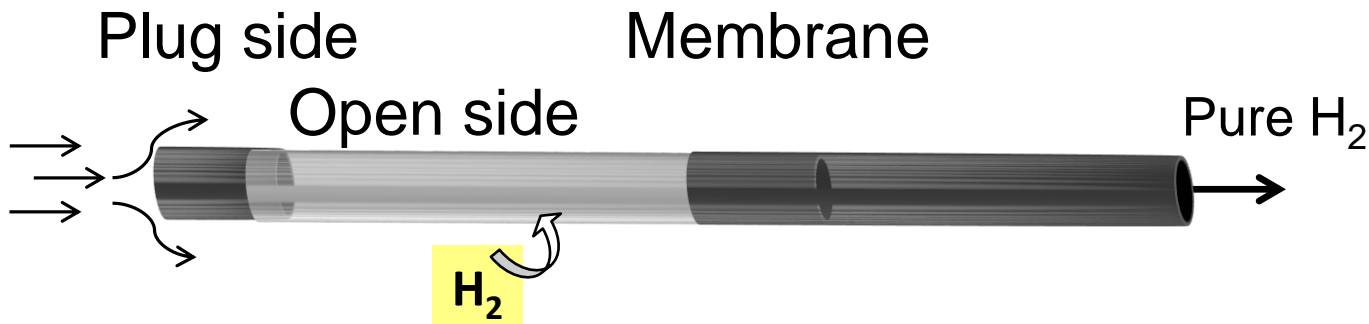
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# Brief on Palladium Membranes



Au and Pt deposition > Electroplating  
Pd deposition —————> Electroless Plating

Intermetallic diffusion barrier { Al<sub>2</sub>O<sub>3</sub> particles cemented w/  
Pd  
Oxidation in air

316L PSS Support



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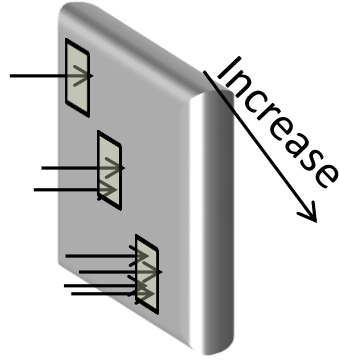


Newton  
Fund



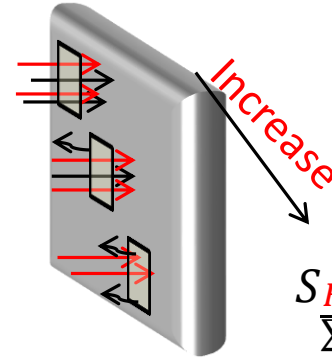
# Membrane Properties

Permeance

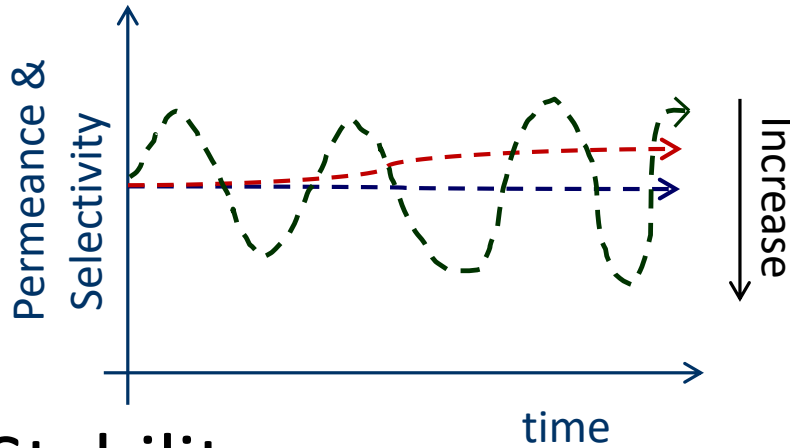


$$\bar{P}_{H_2} = \frac{\text{flow rate}}{\text{area} \times \sqrt{H_2 \text{ partial pressure}}}$$

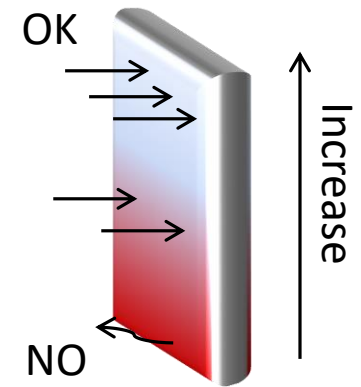
Selectivity



$$S_{\frac{H_2}{\sum i}} = \frac{H_2 \text{ flow rate}}{\sum \text{gas } i \text{ flow rate}}$$



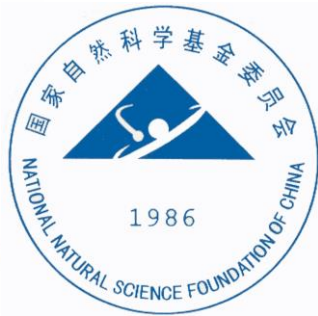
Stability



Robustness



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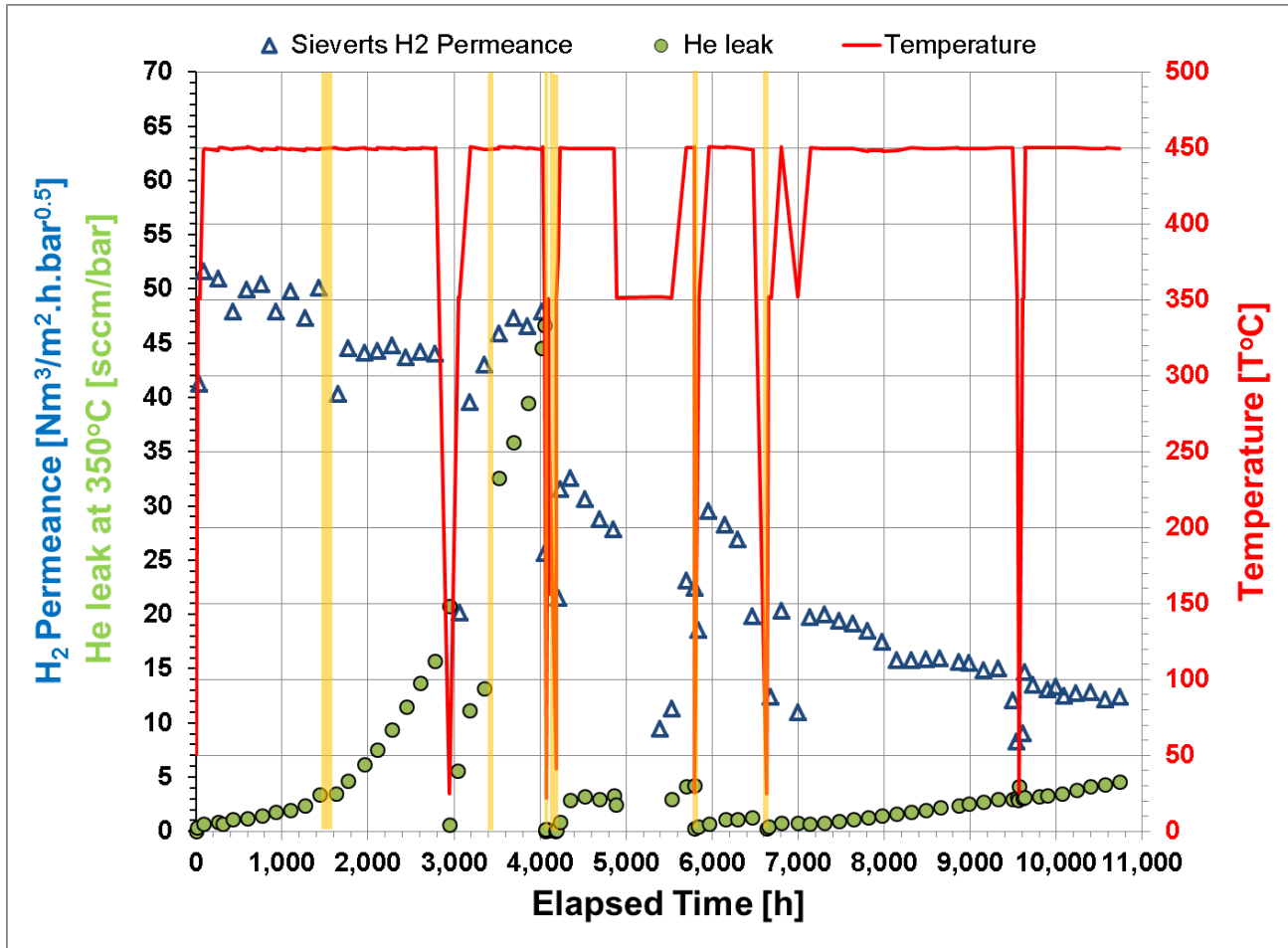


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# Long-Term Lab-scale Tests



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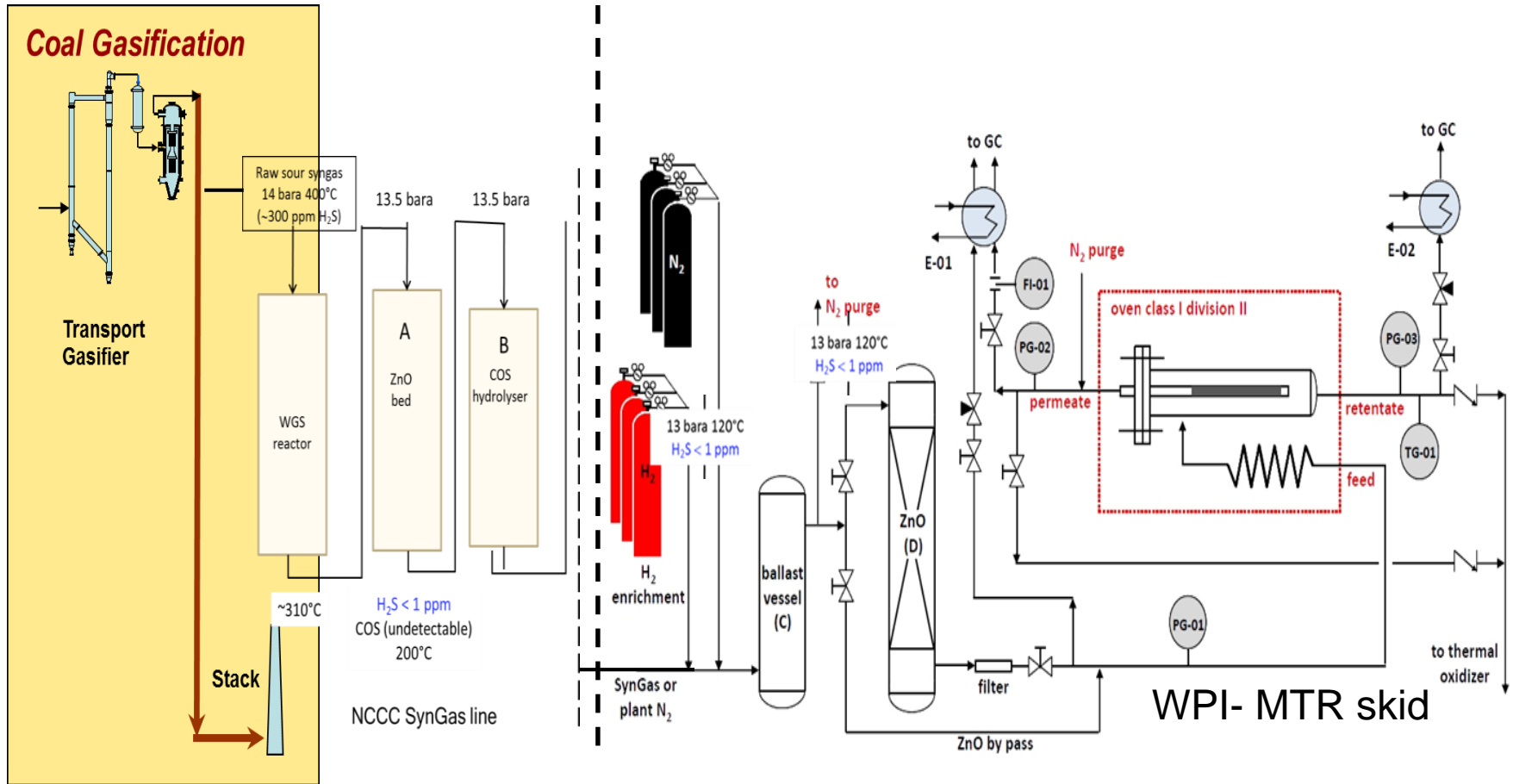
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# Pd and Pd/Alloy Membrane Testing



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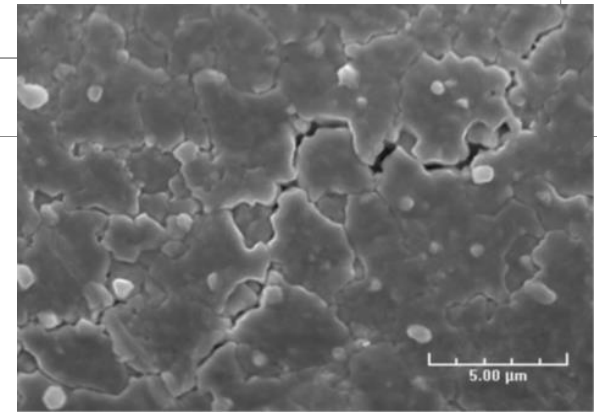
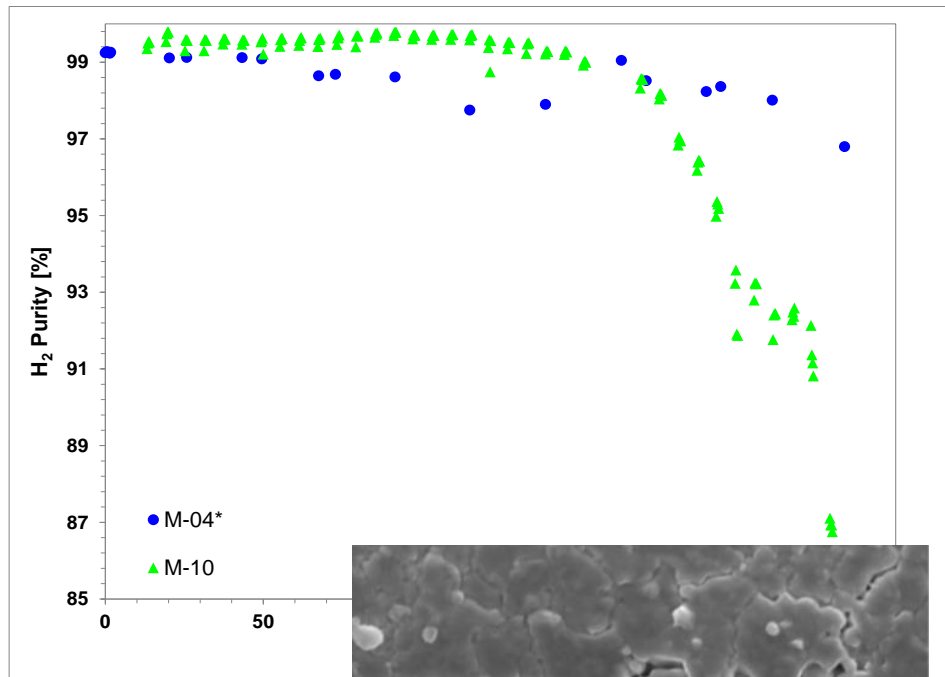
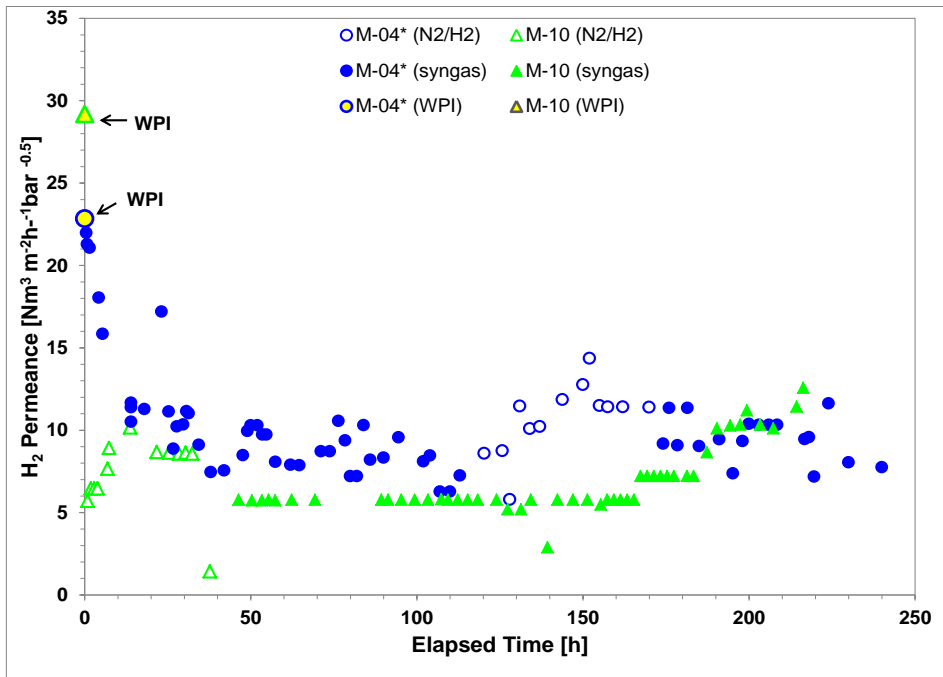


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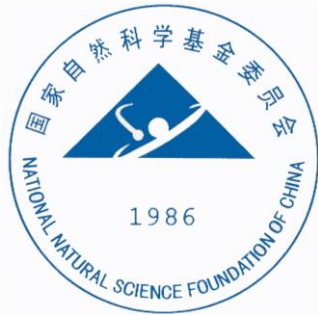
# Pure Palladium Membranes



I. Mardilovich, B. Castro-Dominguez, N. Kazantzis, T. Wu, Y.H. Ma, A comprehensive performance assessment study of pilot-scale Pd and Pd/alloy membranes under extended coal-derived syngas atmosphere testing, Intl. J. Hydr. Energy 40 (2015) 6107-6117



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# Membranes Tested

Total testing time: 4275 hours

Permeance:

Pd/Au > Pd/Au/Pt > Pd > Pd/Pt

Maximum selectivity:

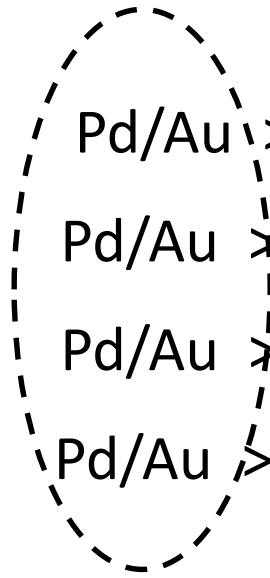
Pd/Au > Pd/Au/Pt > Pd > Pd/Pt

Robustness:

Pd/Au > Pd/Pt > Pd/Au/Pt > Pd

Stability:

Pd/Au > Pd/Au/Pt > Pd > Pd/Pt



I. Mardilovich, B. Castro-Dominguez, N. Kazantzis, T. Wu, Y.H. Ma, A comprehensive performance assessment study of pilot-scale Pd and Pd/alloy membranes under extended coal-derived syngas atmosphere testing, Intl. J. Hydr. Energy 40 (2015) 6107-6117



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# Successful Single Membrane Tests

- Showed **outstanding H<sub>2</sub> permeance stability under industrial conditions**.
- Achieved a **H<sub>2</sub> purity level of 99.85 – 99.95 %** for several hundred hours in syngas.
- Demonstrated **the robustness and physical integrity** of the membranes.
- Suspected that **Au is responsible for the protection of the membrane**, acting as a patch paste blocking any defects at the surface of the Pd layer.

Next: Scale up!



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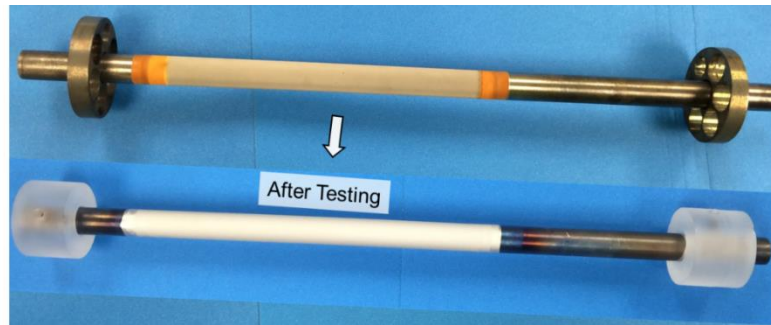


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# Scale-up Membranes



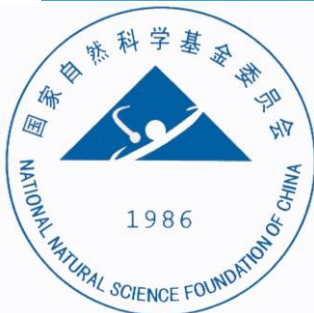
Diameter: 0.5 in  
Length: 6 in



Diameter: 0.5 in  
Length: 15 in



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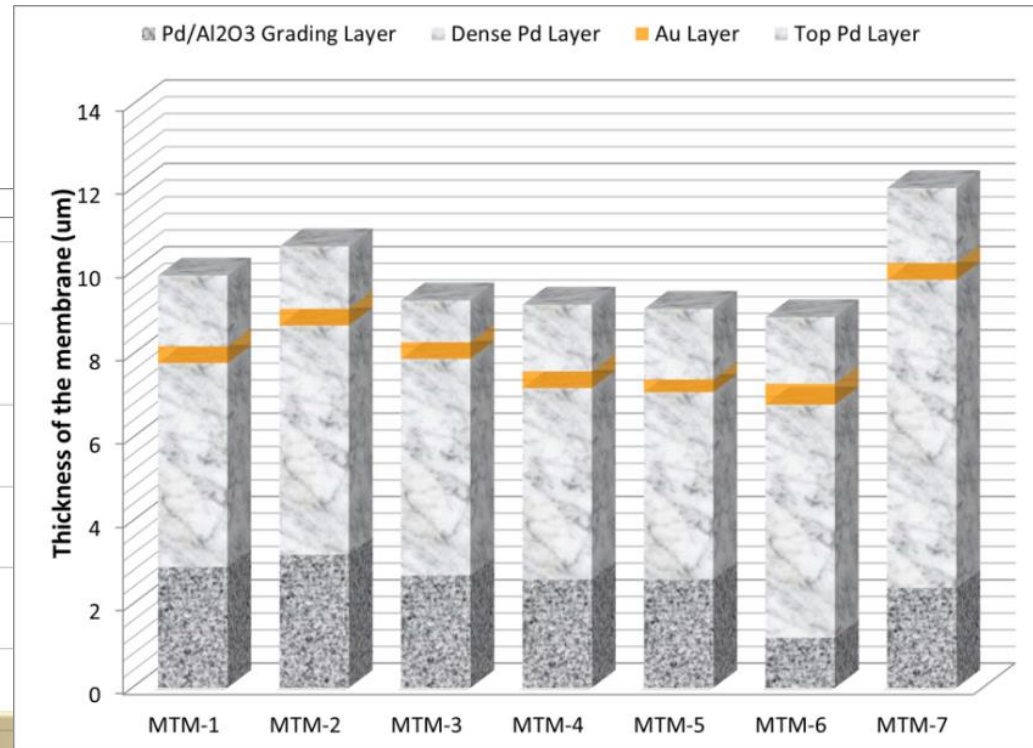
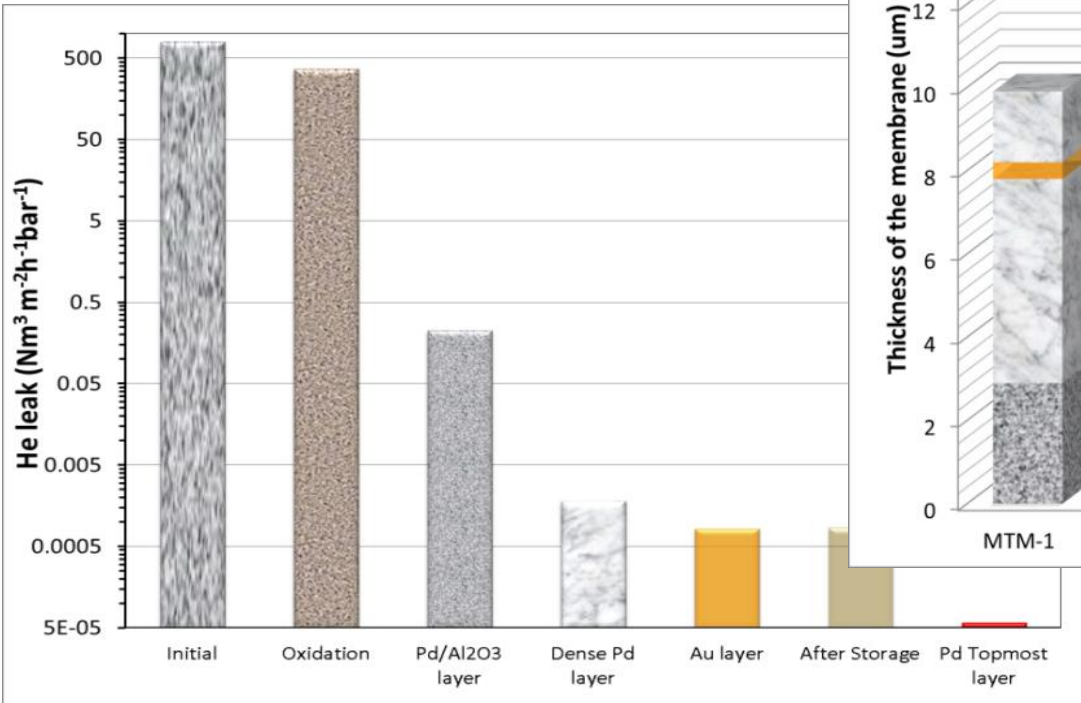


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# Manufacture



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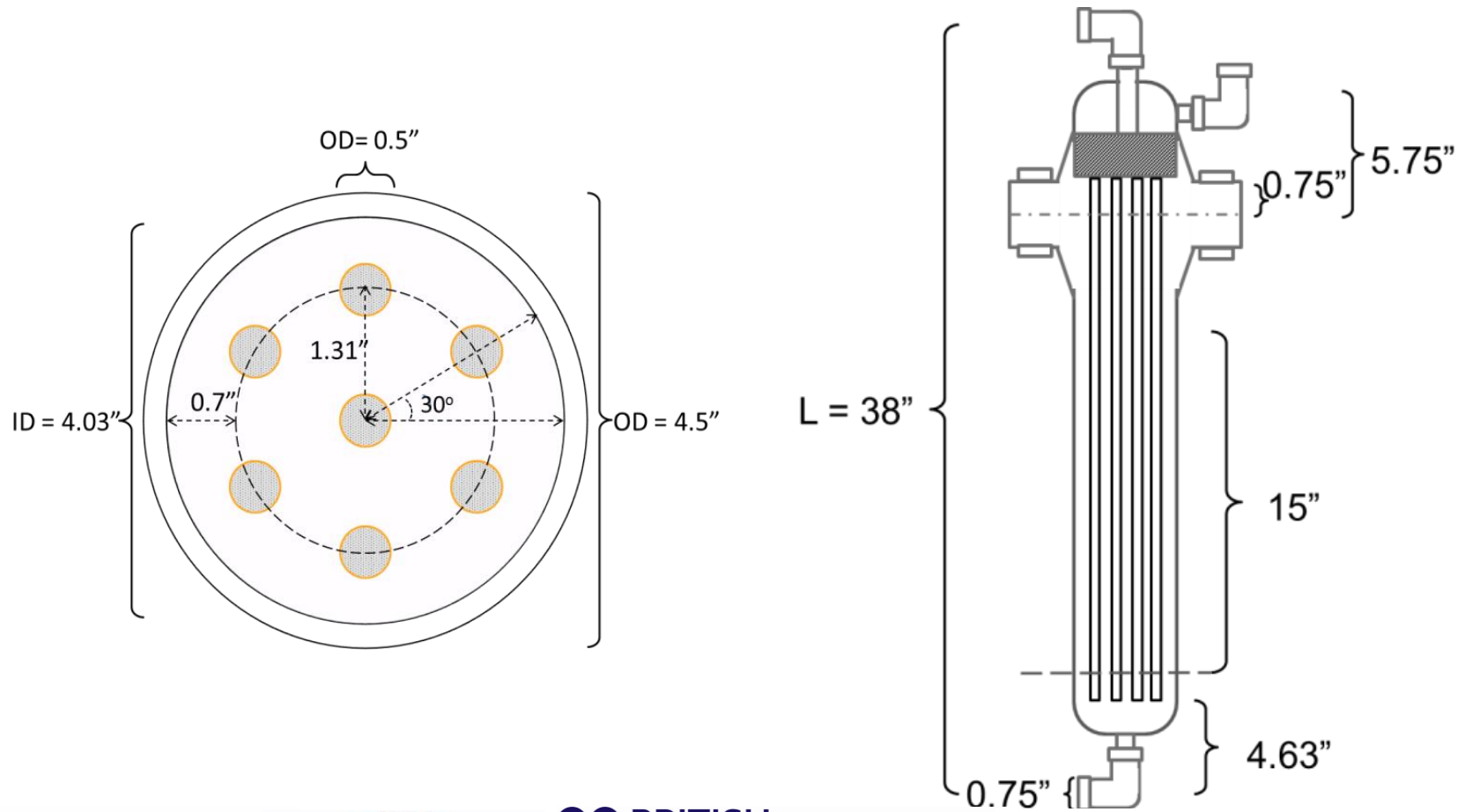
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# Multitube Pd/Au Configuration



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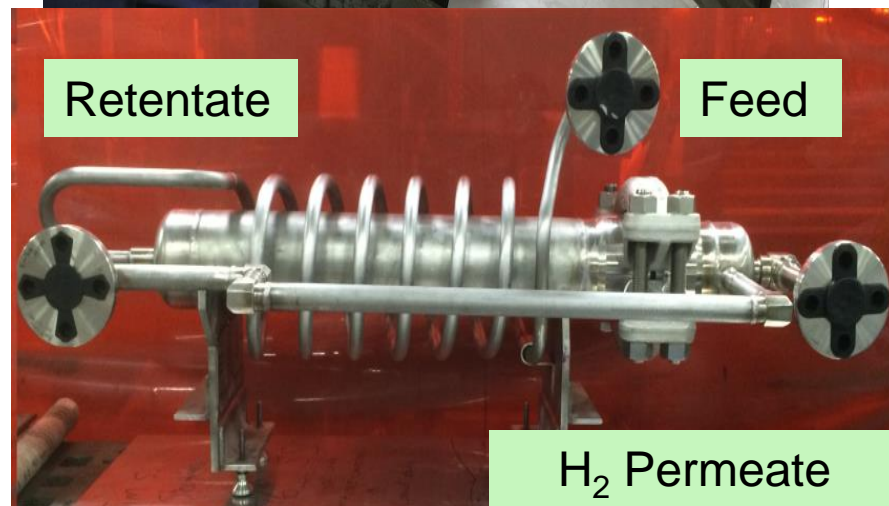
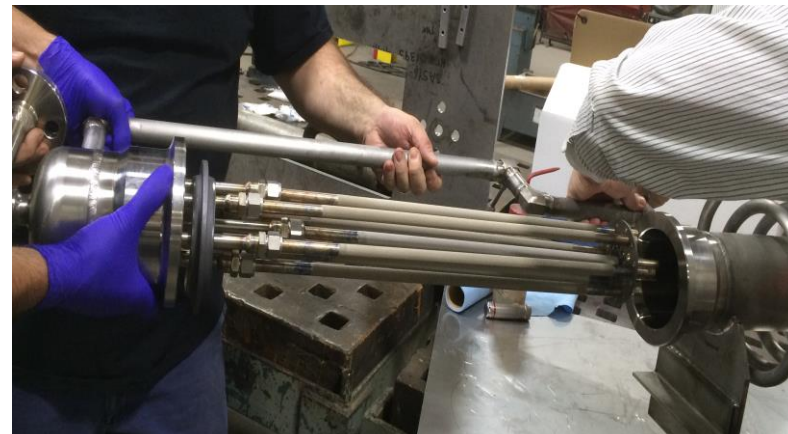
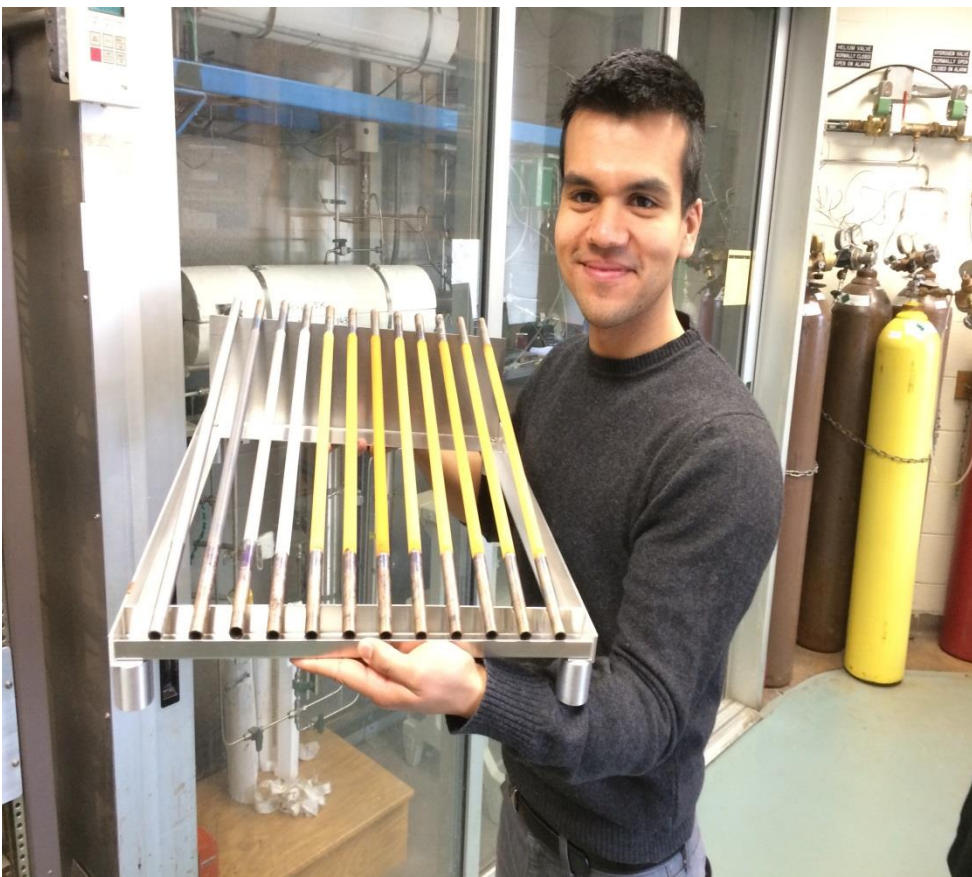


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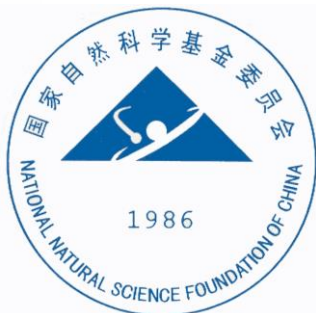


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# Scaling-up Pd/Au Membranes



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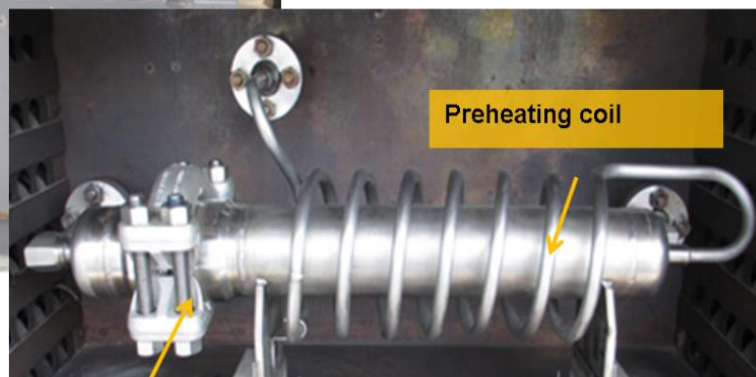
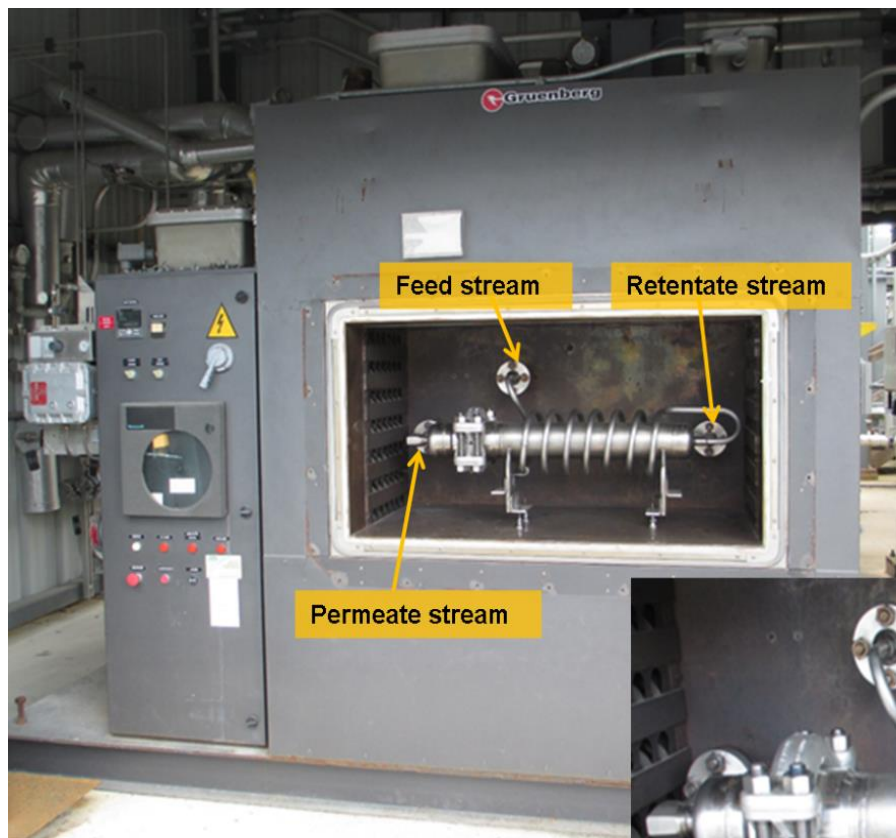


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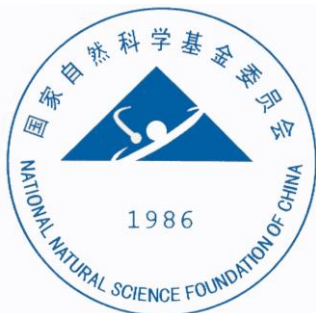


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# Scale-up : Multitube Pd/Au Module



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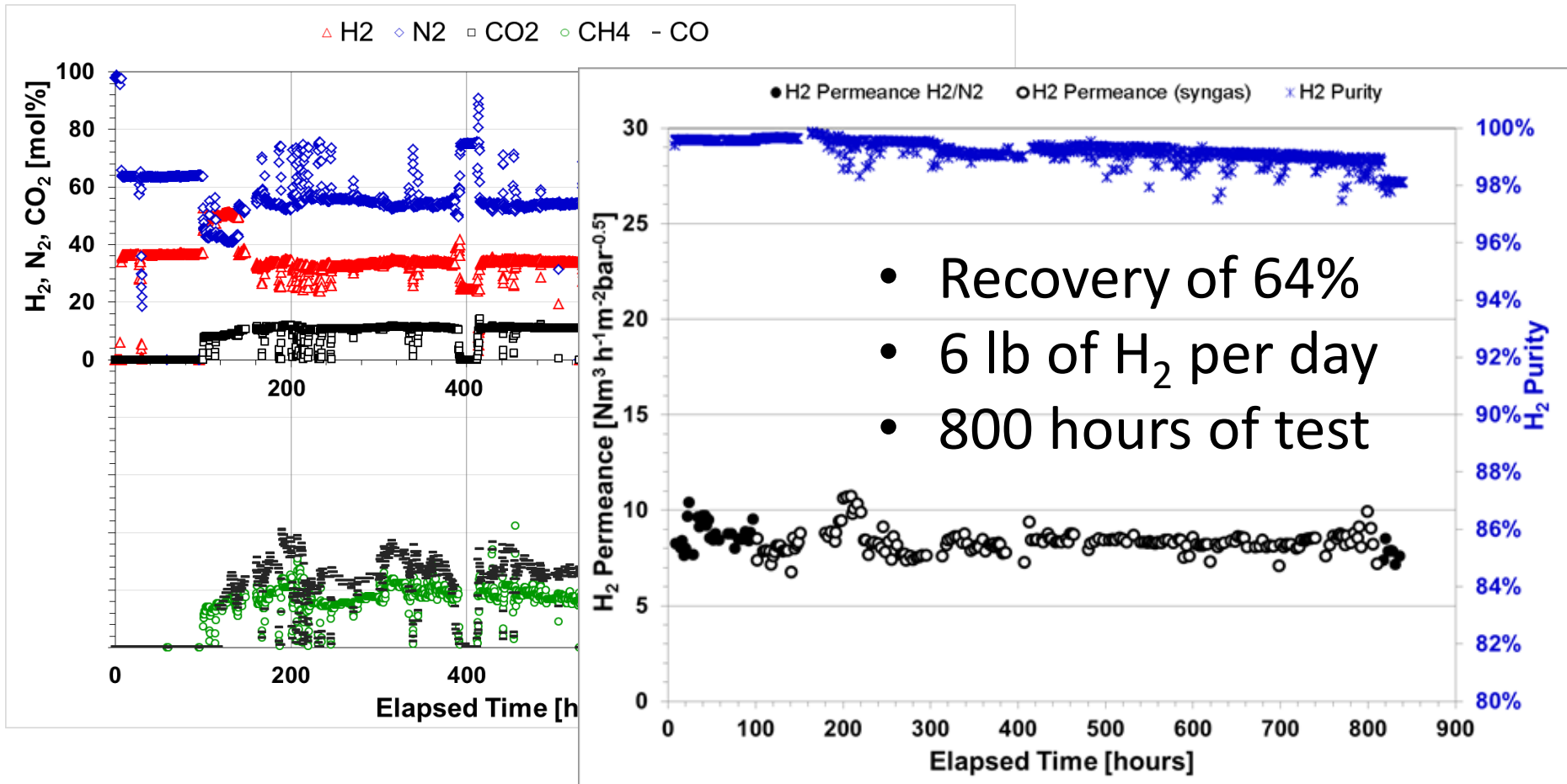
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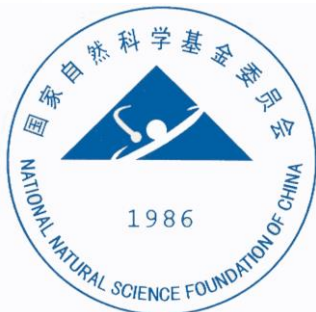
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# Multitube Membrane Module



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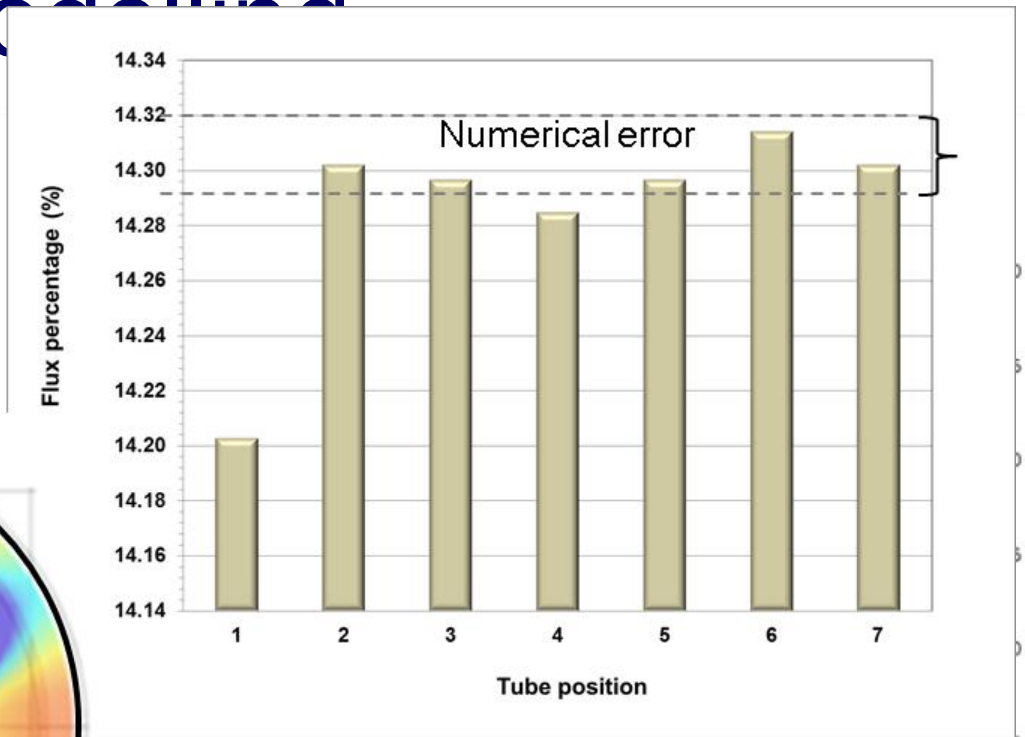
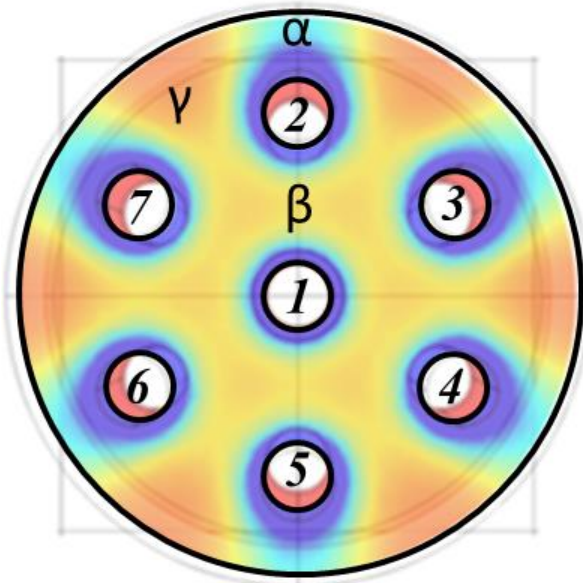
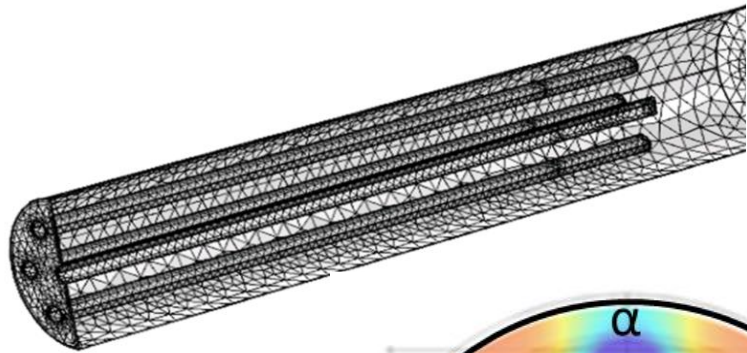


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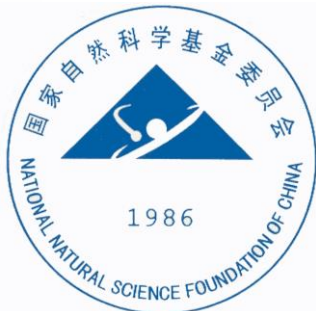


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# Modelling



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# Successful Scale-up!

- The membranes showed replicability with thicknesses deviating by only 1%
- Tested for 850 h producing 6 lb/day of H<sub>2</sub> with a purity in the range of 99.87-98%
- The membrane located at the center showed a reduced efficiency
- **Proof of concept has been completed!**



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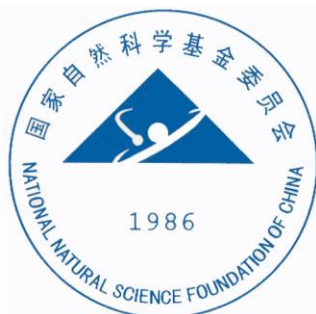
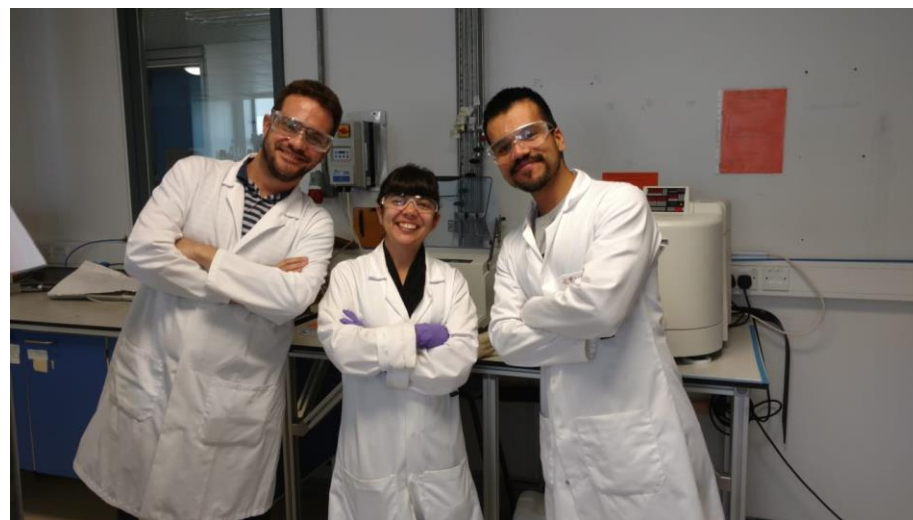


# Acknowledgements



**Centre for Advanced  
Separations Engineering  
(CASE)**

**Center for Inorganic  
Membrane Studies**



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DE-FE0004895



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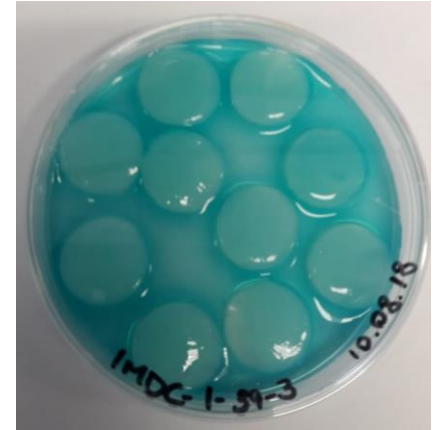


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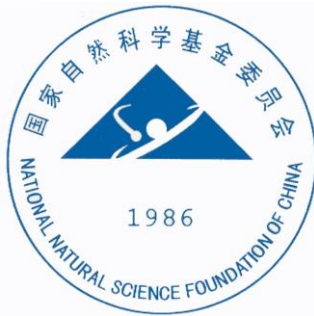
### Membranes:

- Graphene oxide membranes
- Silica membranes
- Mixed matrix membranes
- Carbon membranes
- Liquid membranes
- Zeolite membranes

Membranes from natural materials



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