

Sorption Enhanced Mixed Matrix Membranes for H₂ Purification and CO₂ Capture (DE-FE0026463)

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NETL CO₂ Capture Technology Project Review Meeting
Pittsburgh, PA
8/27/2019

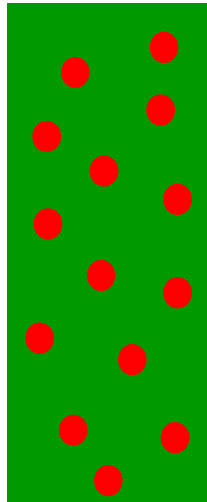


Sorption Enhanced Mixed Matrix Membranes for H₂ Purification and CO₂ Capture

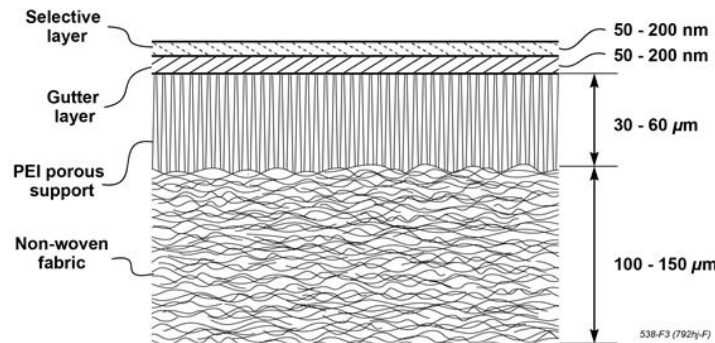
- Award number:** DE-FE0026463
- Project period:** 10/1/15 to 9/30/19
- Funding:** \$1,485,099 DOE
\$ 376,837 UB and MTR contribution
\$1,861,936 total
- Project manager:** Isaac Aurelio (formerly Steve Mascaro)
- Participants:** University at Buffalo (**UB**);
Membrane Technology and Research, Inc. (**MTR**);
and University of Kentucky (**CAER**)
- Project Objectives:** Develop membranes with H₂ permeance of 500 GPU and H₂/CO₂ selectivity of 30; and
Conduct parametric tests with real syngas at CAER.

Project Scope

- BP1:** Prepare mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 **(10/2015-9/2016)**
- BP2:** Prepare thin film composite membranes with H_2 permeance of 500 GPU and H_2/CO_2 selectivity of 30 **(10/2016-3/2018)**
- BP3:** Conduct a 20-day field test of membranes with real syngas at CAER **(4/2018-9/2019)**



**Nanostructured
materials**



**Industrial
membranes**



**Field
test**

Our Approach:

H₂/CO₂ Solubility Selectivity

$$\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}$$

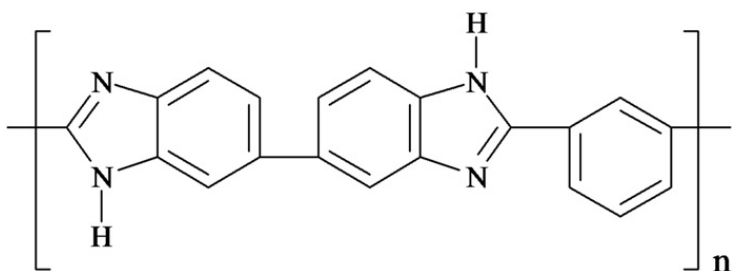
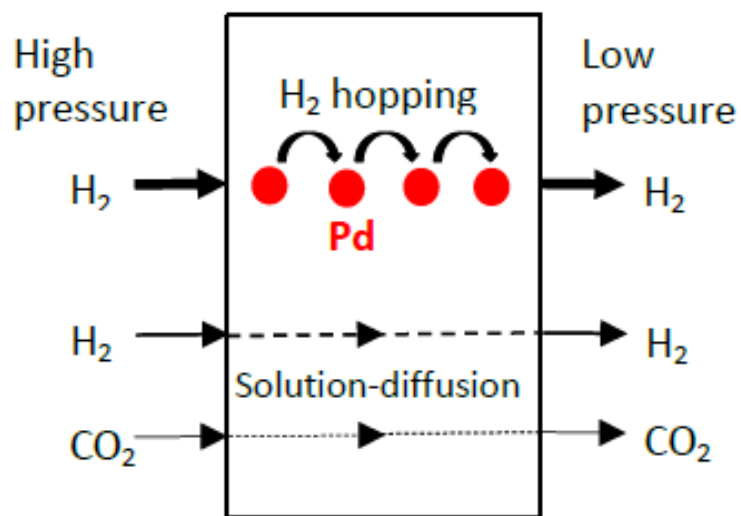
Materials	Temp. (°C)	H ₂ solubility cm ³ (STP)/(cm ³ atm)	H ₂ /CO ₂ solubility selectivity
Poly(dimethyl siloxane)	35	0.10	0.078
Polysulfone	35	0.075	0.036
Matrimid®	35	0.12	0.035
Pd metal*	25	38,000	> 1,000

* Calculated at 0.02 bar H₂

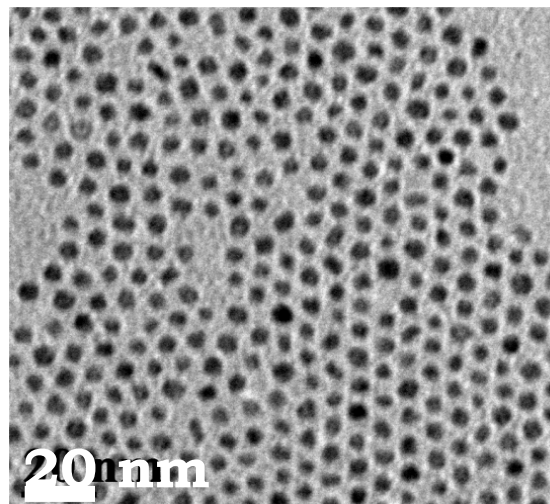
Adams and Chen, *Materials Today*, 14 (2011) 282-289



Our Approach: Sorption Enhanced Mixed Matrix Materials

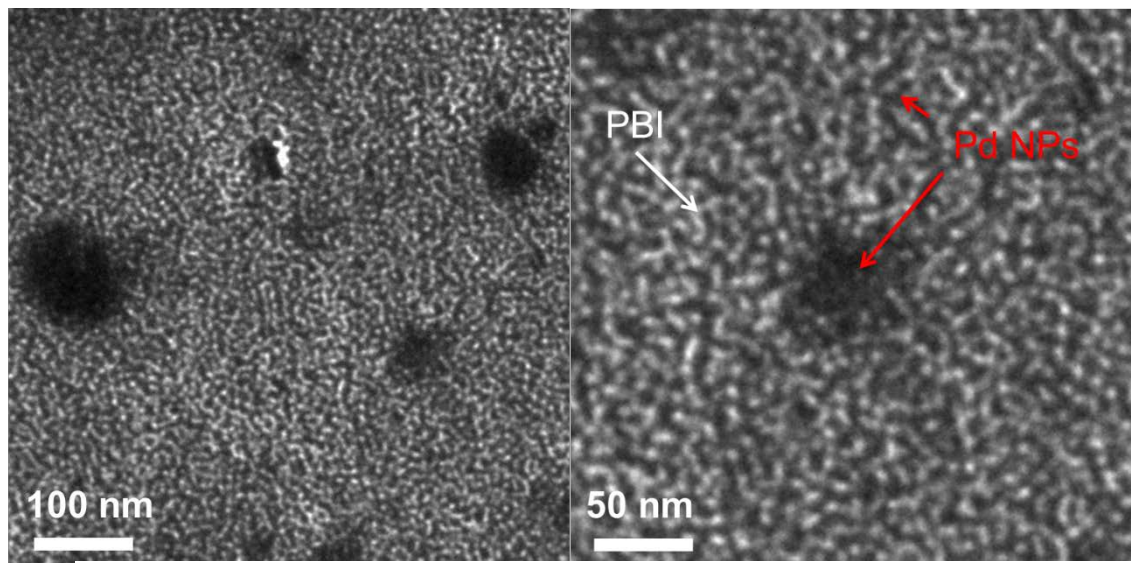


Polybenzimidazole
(PBI)



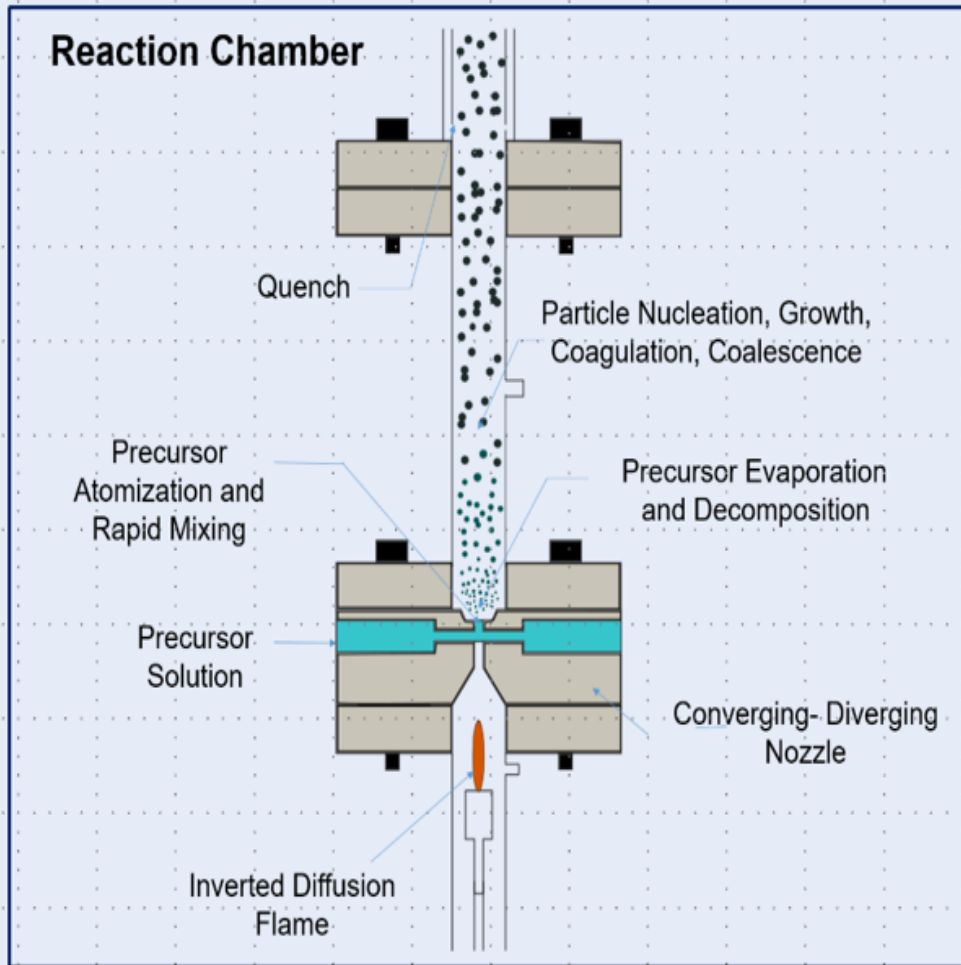
Pd nanoparticles

Konda, Lin, Swihart,
et al., *AIChE J.*, 64(11)
3826 (2018)



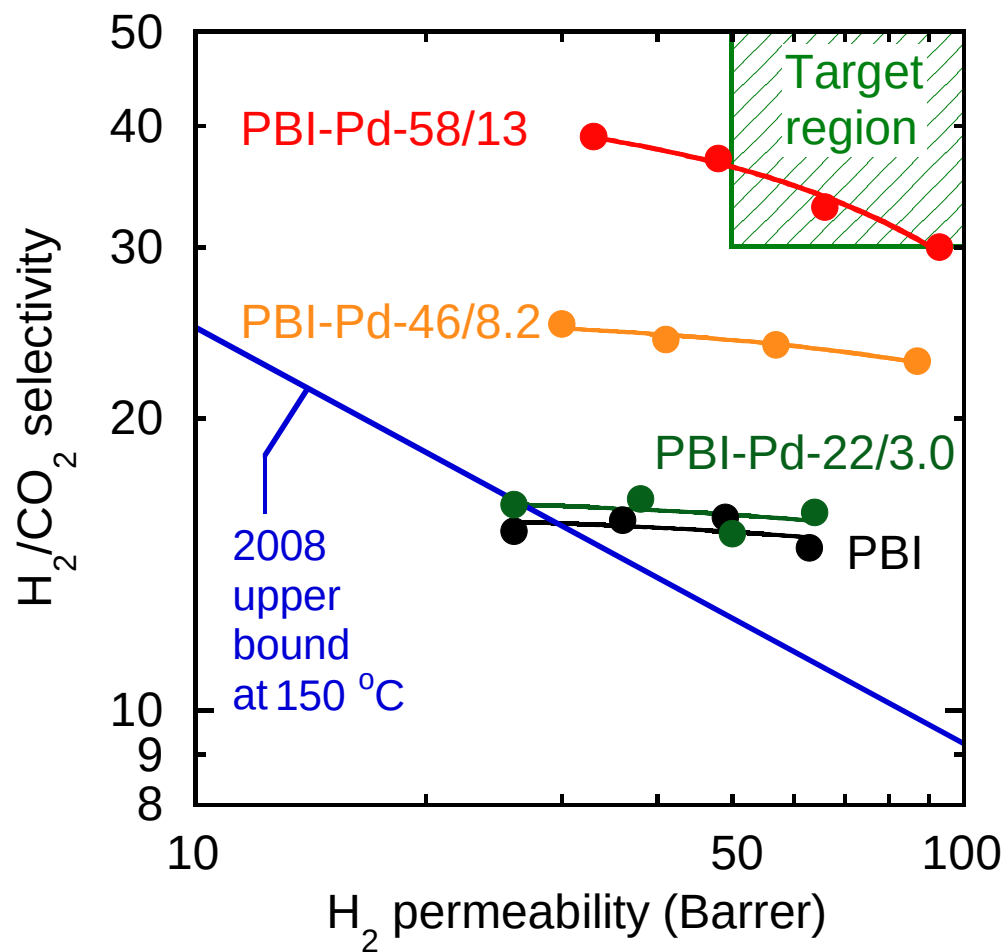
Mixed matrix materials (MMMs)

Nanoparticle Synthesis Scale-up: Gas Phase Synthesis



- ❑ Scaled up the nozzle diameter
- ❑ Achieved plugging-free production
- ❑ Can produce 2 g of Pd-Cu alloy NPs in 8 h

Membrane Materials Meeting the BP1 Target



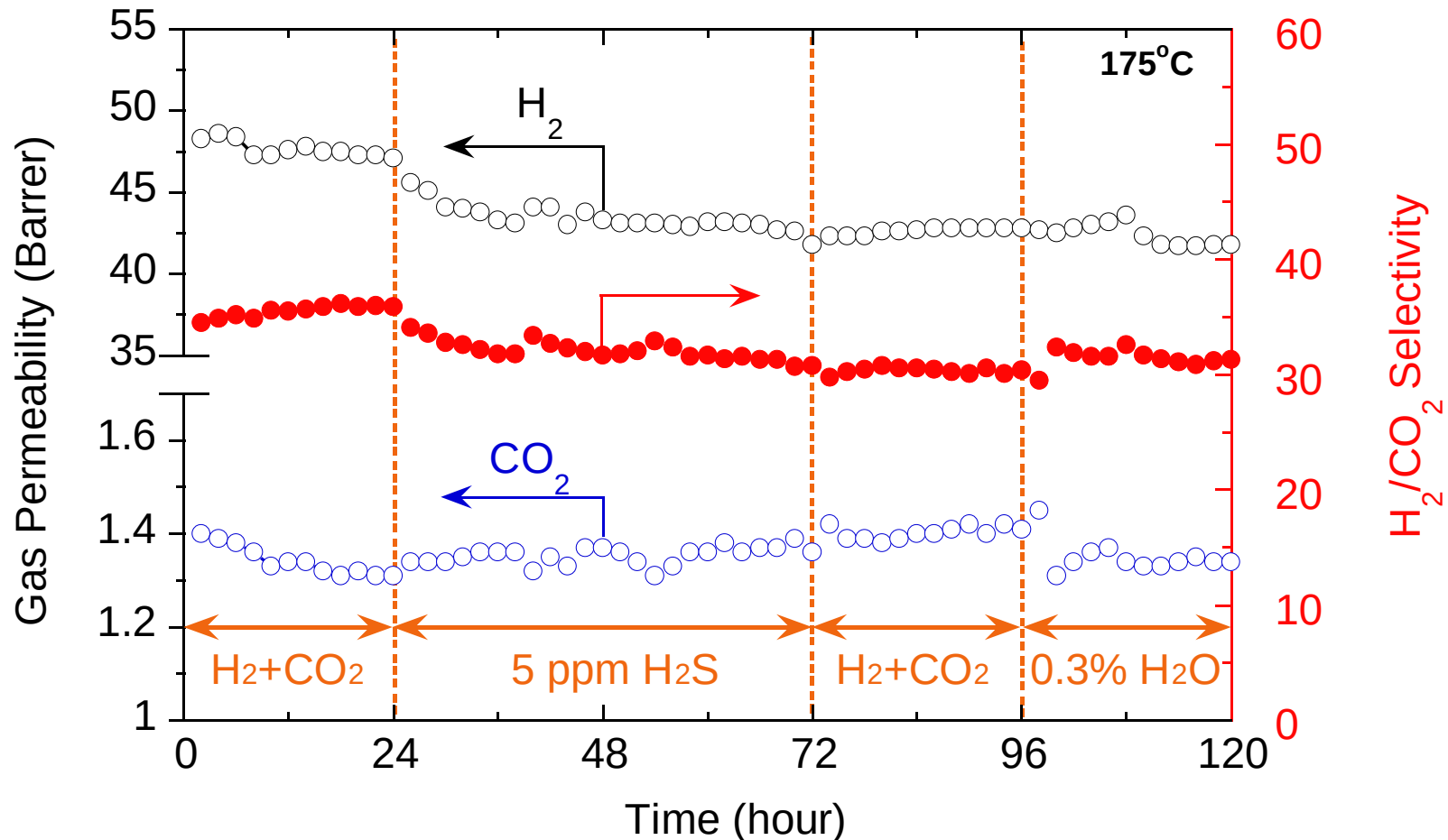
Mixed-gas:
50% H_2 /50% CO_2

Temperatures:
150-175-200-225 °C
from left to right.

Zhu, Swihart, Lin, et al., *Adv. Funct. Mater.*, 1904357 (2019)

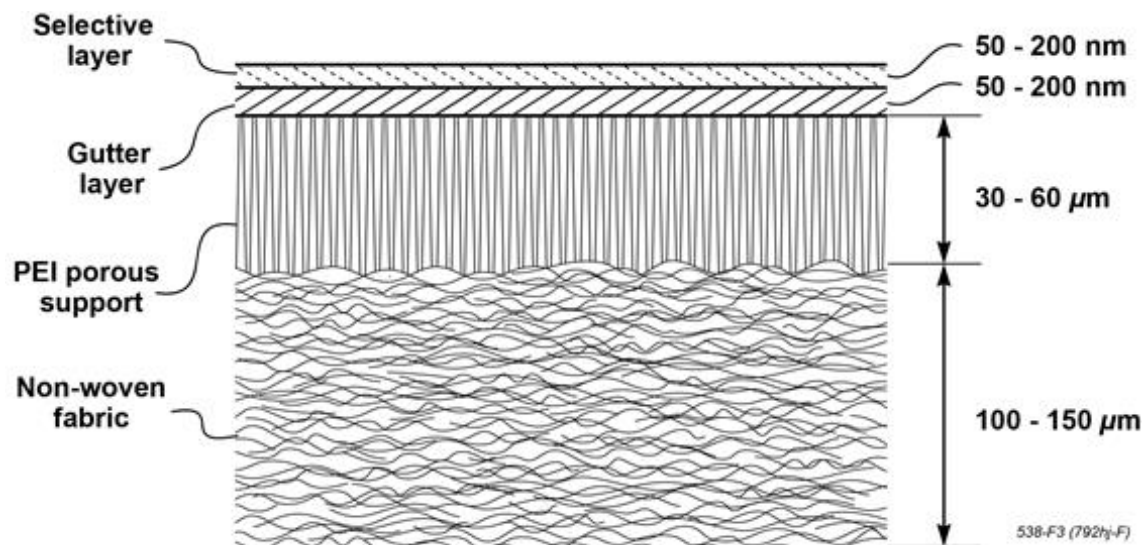
Zhu, Swihart and Lin, *Energy Environ. Sci.*, 11 (1), 94-100 (2018)

Stability of Mixed Matrix Materials against H_2S and H_2O



PBI-Pd-58/13: 58 wt% or 13 vol% Pd nanoparticles

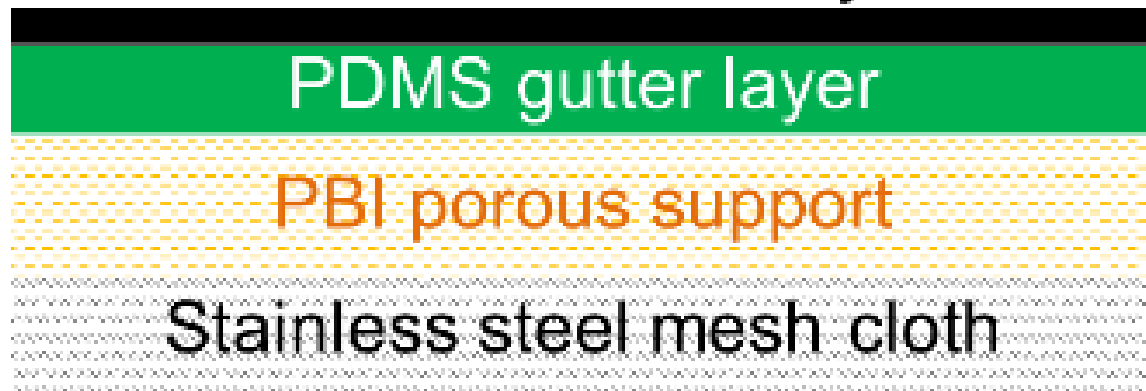
Thin Film Composite (TFC) Membranes



Conventional
TFC
membranes

Baker and Low,
Macromolecules, 47 (2014)
6999-7013.

PBI/Pd selective layer



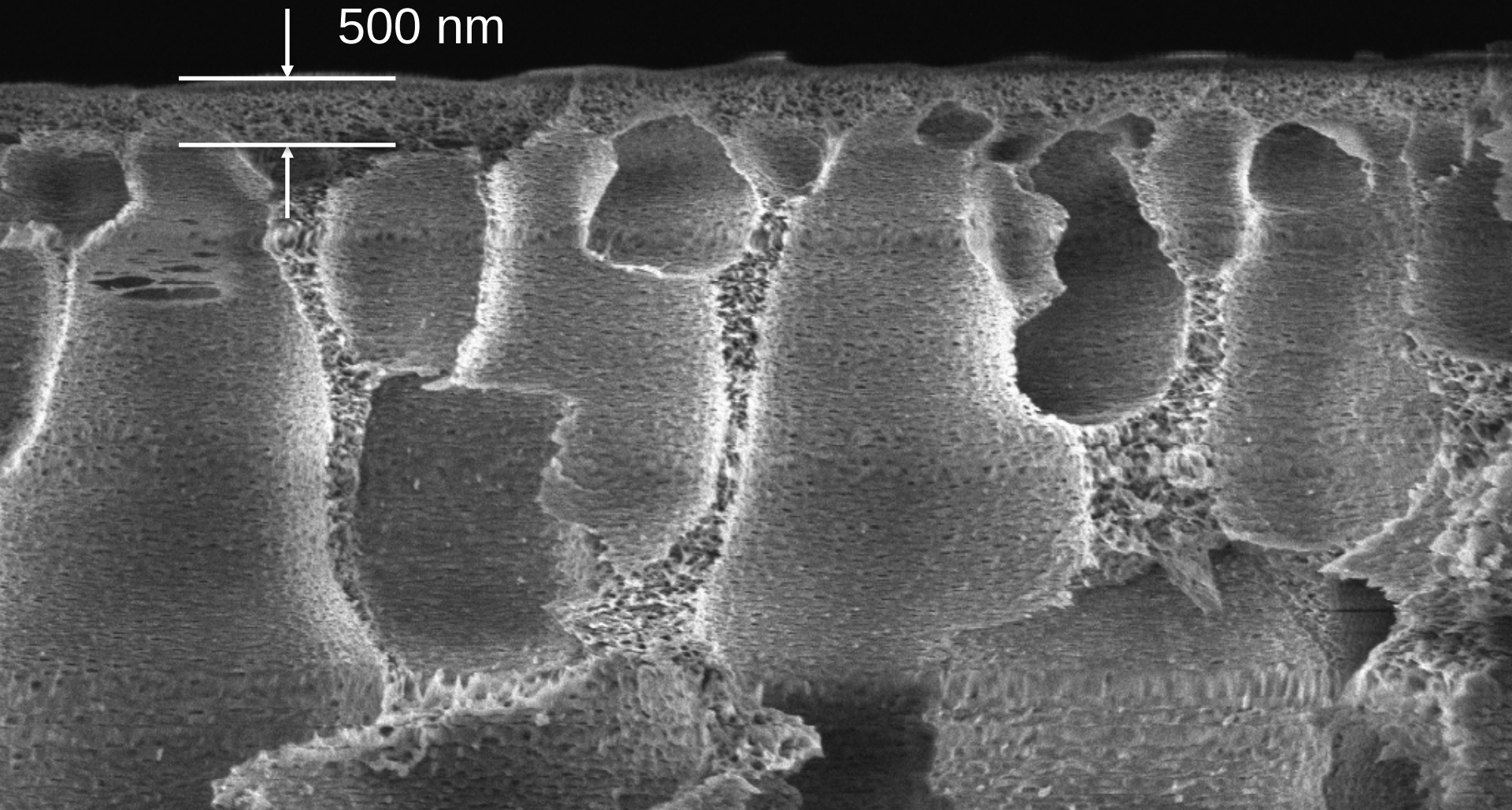
**Thermally
stable TFC
membranes**

Surface of PBI-supports: SEM Characterization

Aver. pore size: 14 nm
Surface porosity: ~15%



Cross-section of PBI-supports: SEM Characterization



Mag = 15.00 K X 1 μ m
Auriga-39-38

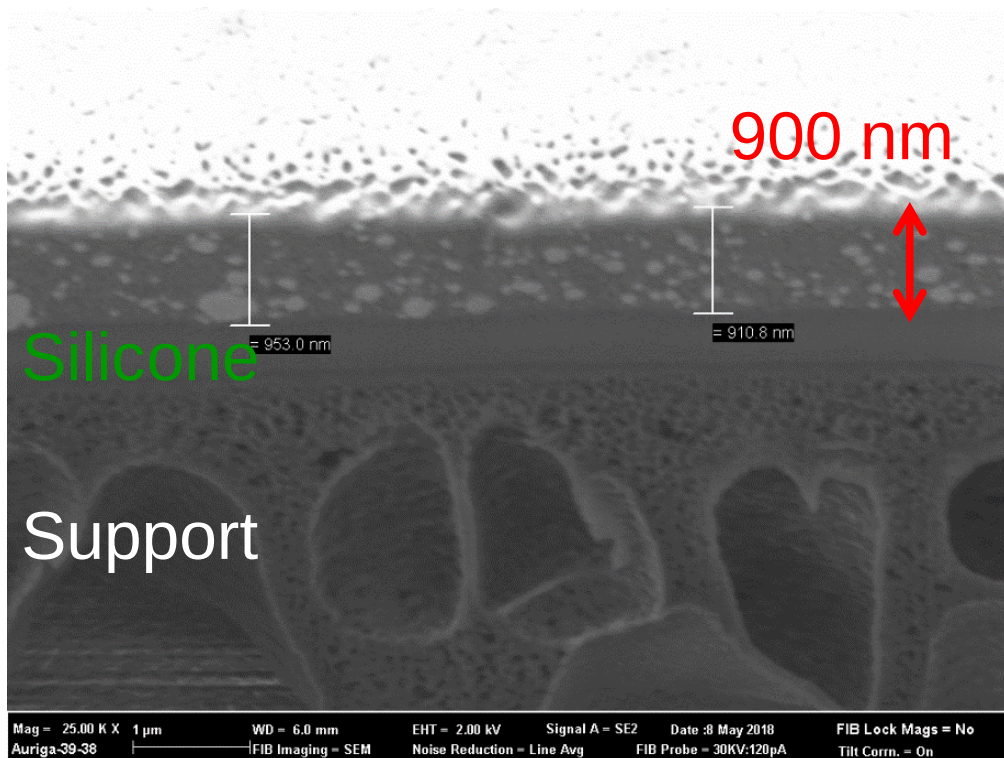
WD = 6.1 mm
FIB Imaging = SEM

EHT = 2.00 kV
Noise Reduction = Pixel Avg.

Signal A = InLens Date :7 Jul 2017
FIB Probe = 30KV:600pA

FIB Lock Mags = No
Tilt Corr. = Off

Reduce PBI/Pd Selective Layer Thickness to below 900 nm



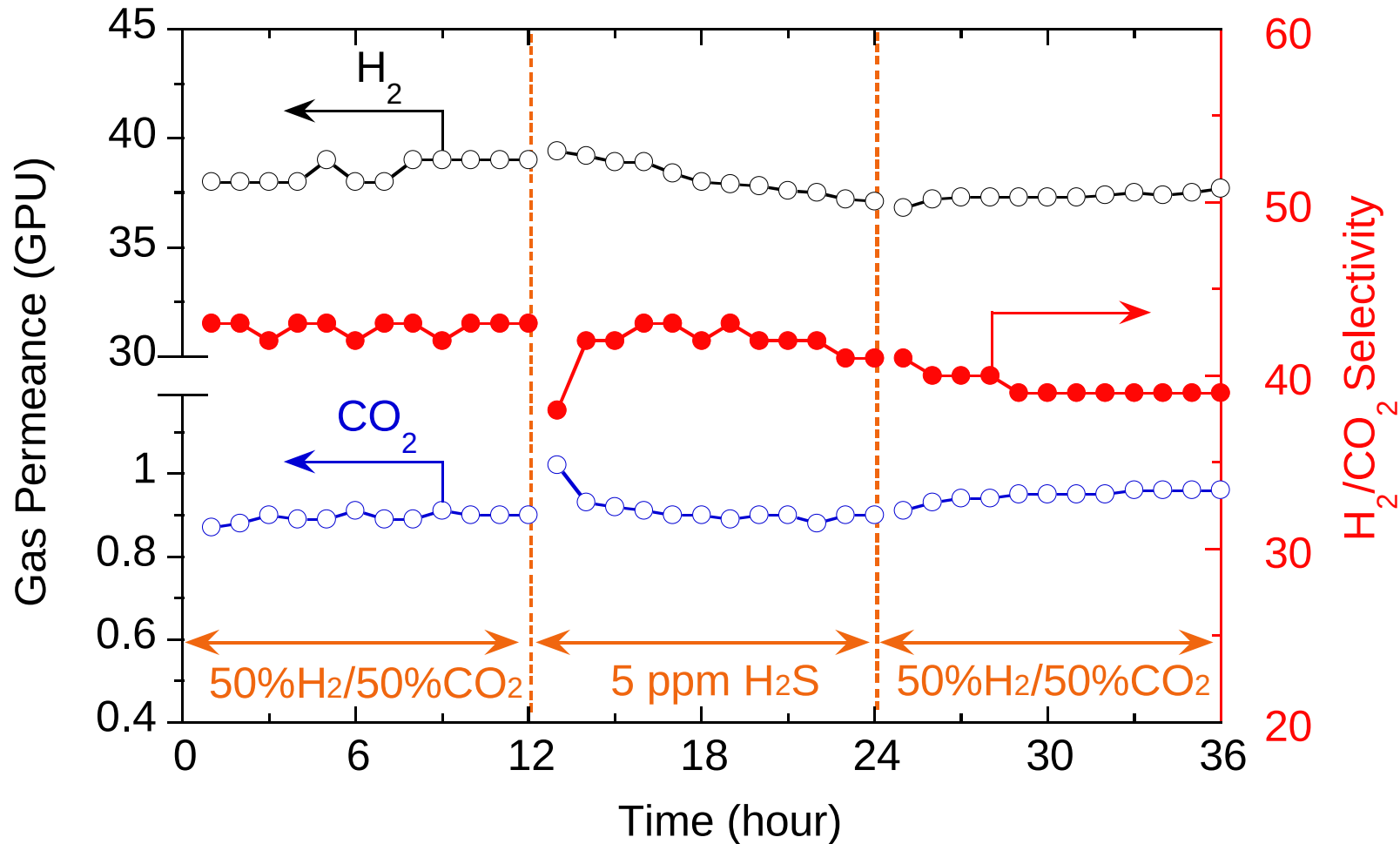
PBI-Pd-58/13

H₂ permeance: ca. 40 GPU
H₂/CO₂ selectivity: 40

Note: The PDMS gutter layer has an H₂ permeance of ~400 GPU

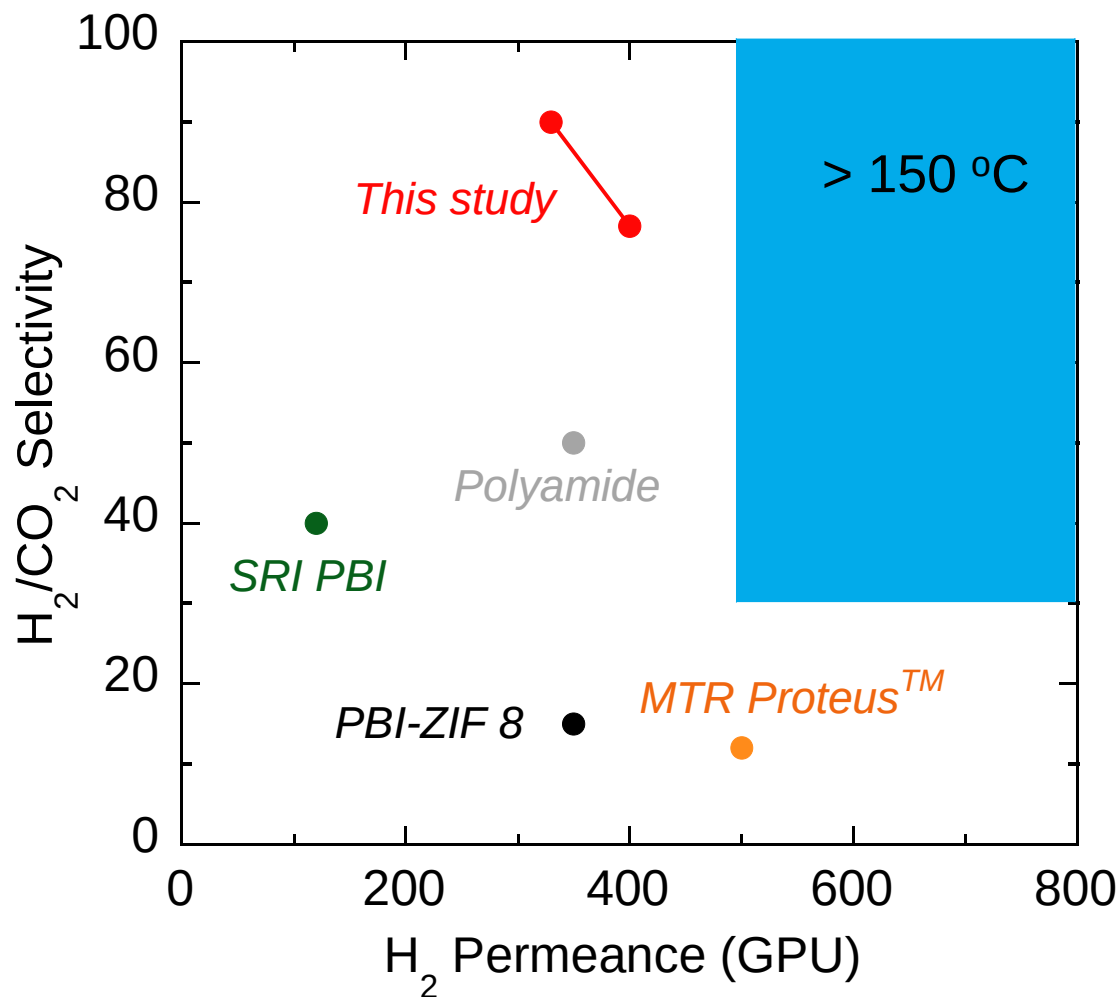
Measurement condition: 150 °C, 150 psig; 50% H₂/50% CO₂

Stability with H₂S for PBI-Pd-58/13-based TFC Membrane



PBI-Pd-58/13: 58 wt% or 13 vol% Pd nanoparticles
175 °C; 150 psig

Membrane Properties Meeting BP2 Target



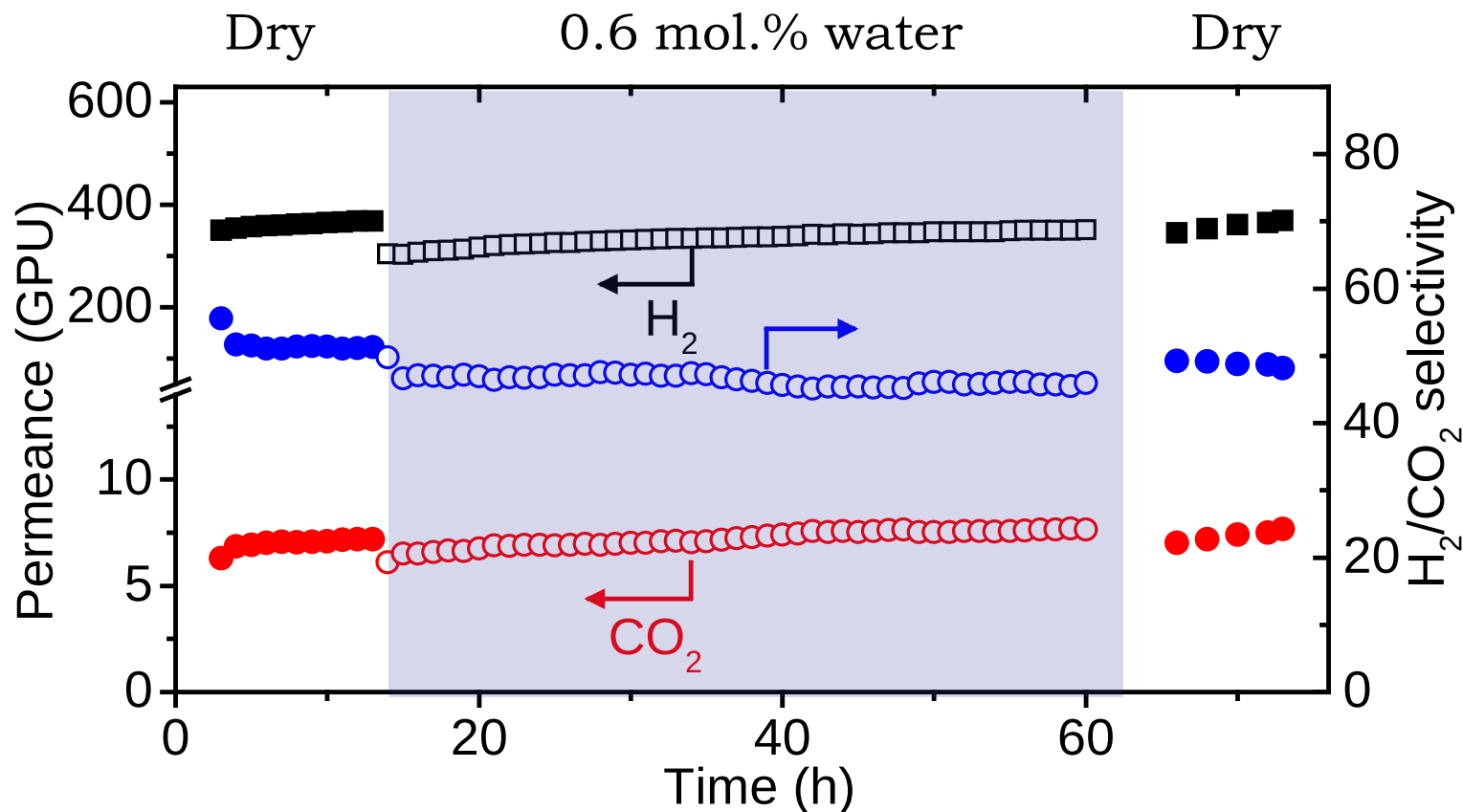
- Thin film (70 nm)
- 230 °C

New Inorganic Membranes

Temp (°C)	H ₂ permeance (GPU)	CO ₂ permeance (GPU)	H ₂ /CO ₂ Selectivity
40	1.8	3.3	0.54
63	7.5	3.4	2.2
106	40	3.8	10
154	163	3.3	50
178	229	5.4	42
202	369	7.7	48

The feed gas is H₂/CO₂ (50/50) mixture at 100 psig.

Long-Term Stability and Effect of Water Vapor



The feed gas is H₂/CO₂ (50/50) mixture
at 100 psig and 200 °C.

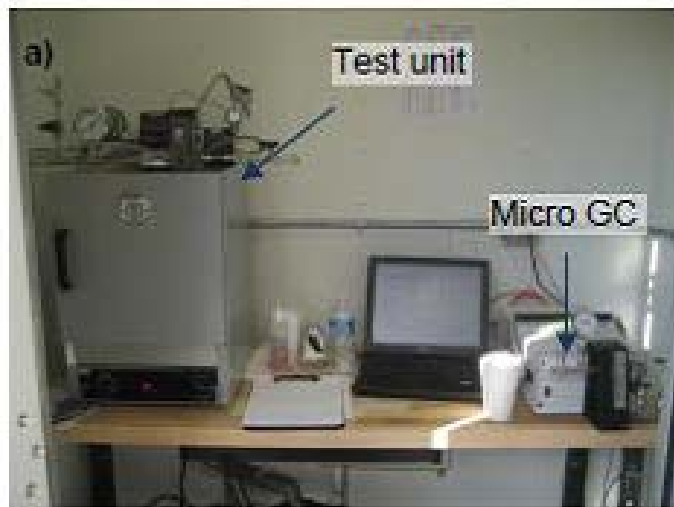
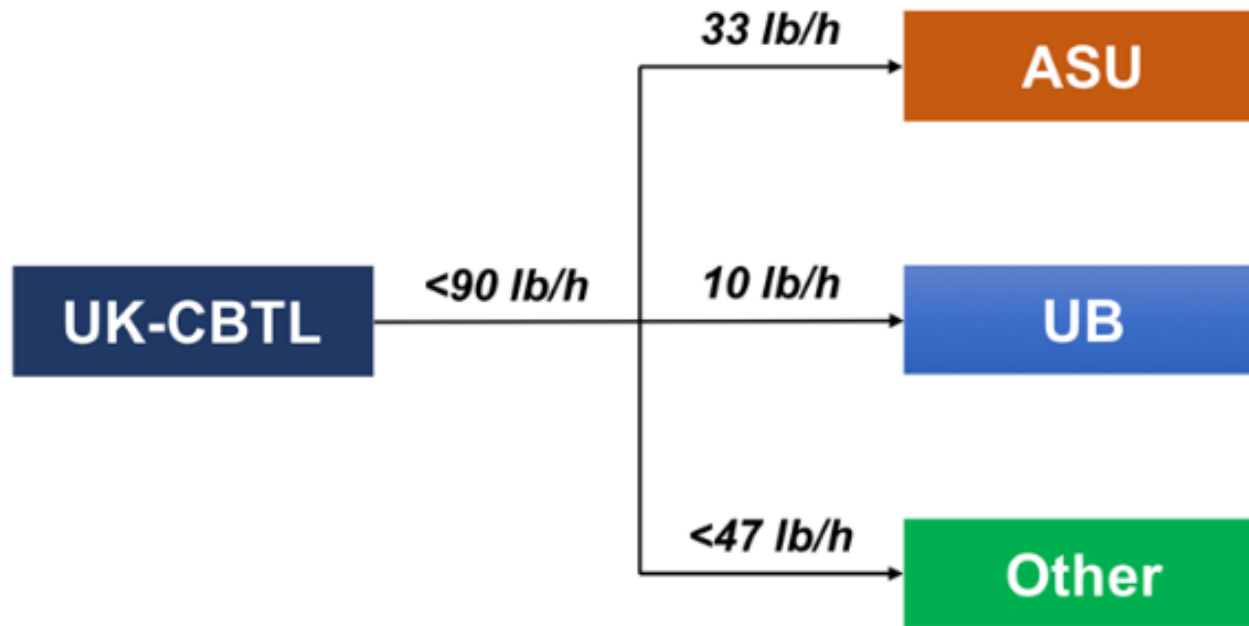
Gasifier at University of Kentucky Center for Applied Energy Research (CAER)



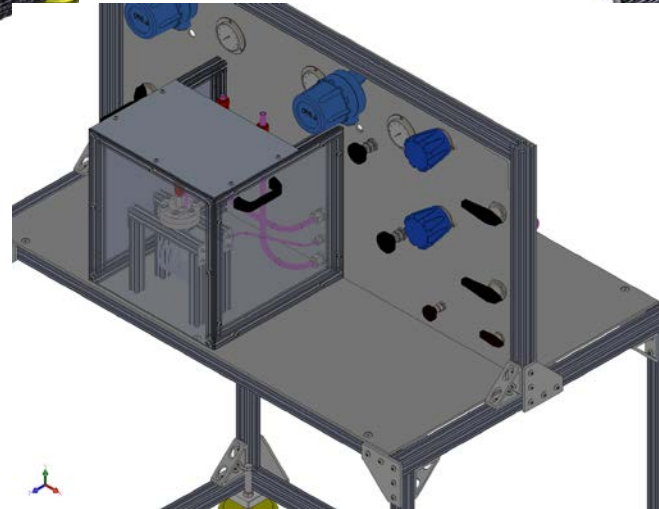
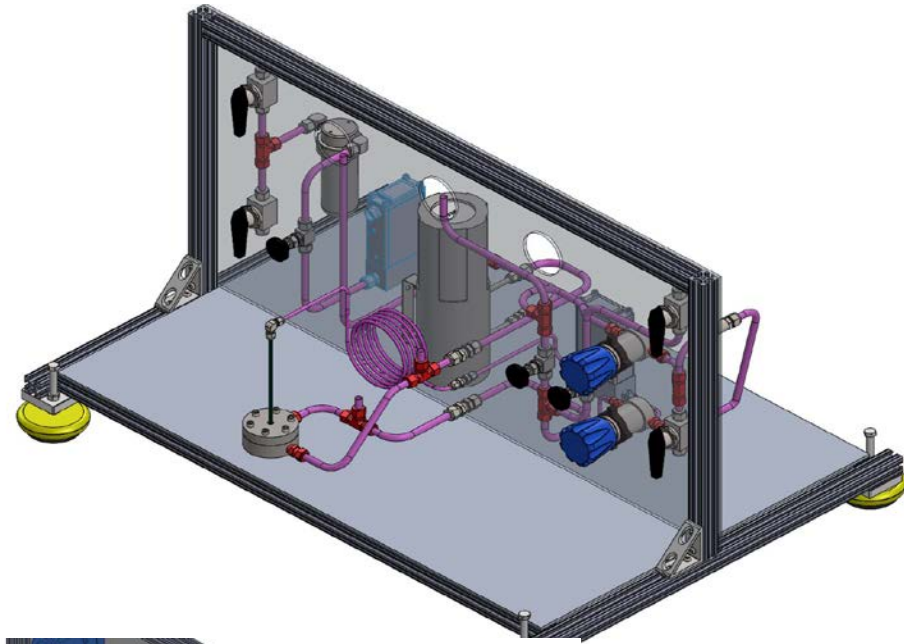
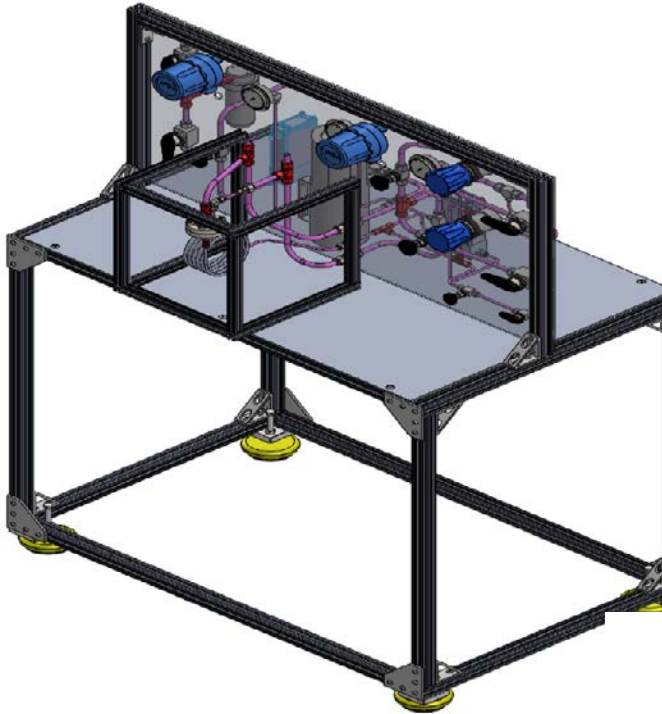
Syngas produced at atmospheric pressure, cooled to 40 °C, and then compressed to 450 psig



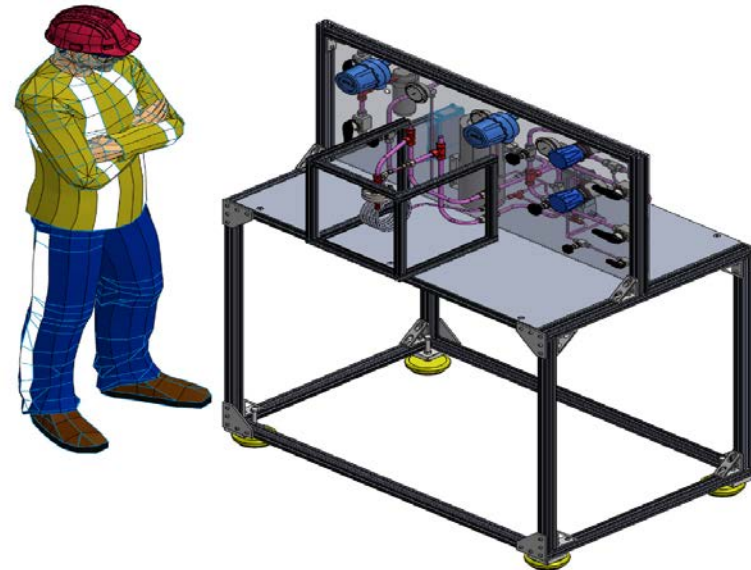
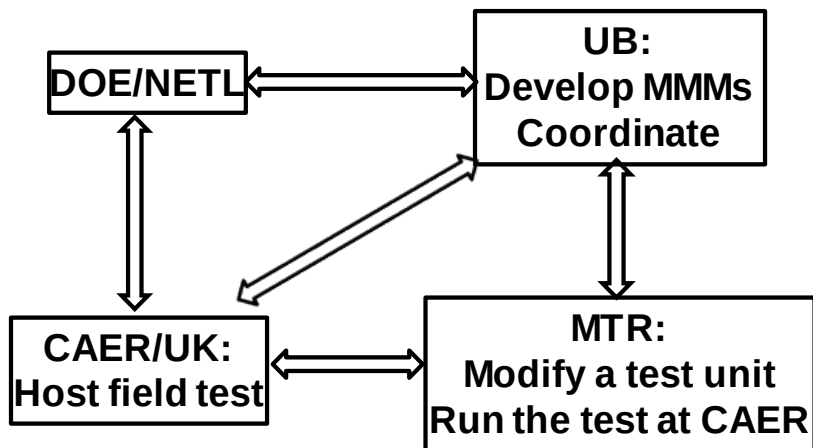
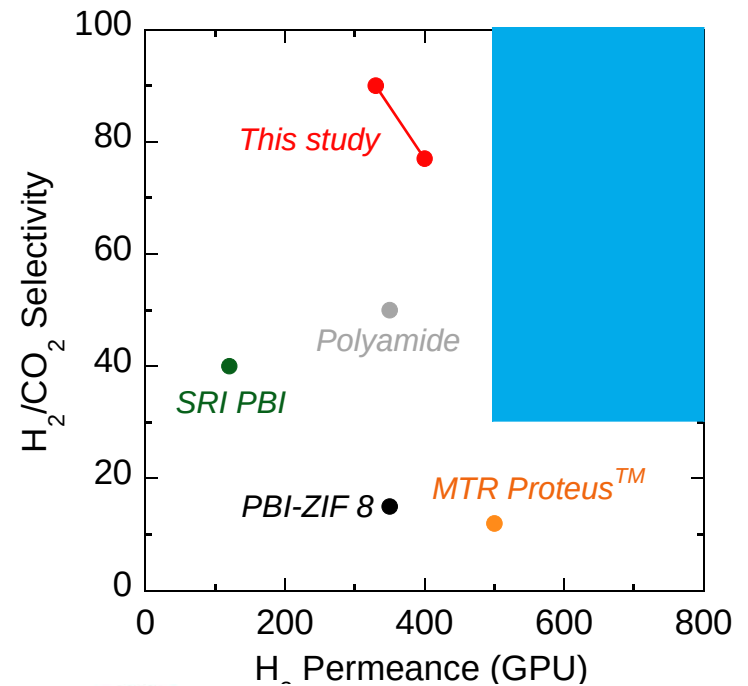
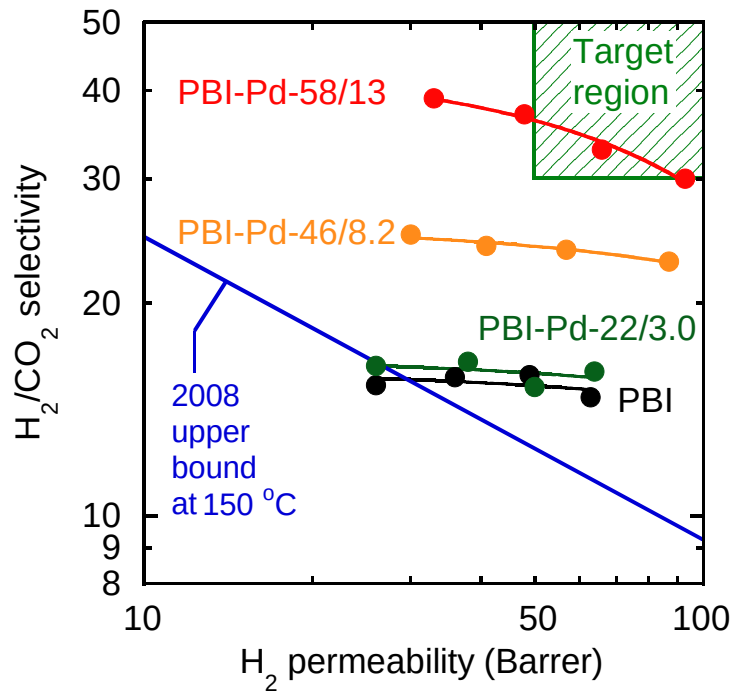
Field Test of Membrane Stamps



Membrane Testing Unit



Summary



Acknowledgments



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ENERGY



Isaac Aurelio
Steve Mascaro



Jay Kniep
Tim Merkel



Landon Caudill
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