Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

Project Overview

– Overall Project Performance Dates: 10/1/18 to 9/30/21

– Project Participants: University at Buffalo (UB), State University of New York; Los Alamos National Laboratory (LANL); Trimeric Corporation

– Funding (DOE and Cost Share)

Team Members	Federal Share	Cost-share	Total	Roles
UB	$534,999	$202,225	$737,224	Materials development
LANL	$200,000	$0	$200,000	Membrane development
Trimeric	$ 65,000	$0	$ 65,000	Techno-economic analysis
Total:	$799,999	$202,225	$1,002,224	

Project Overview

Overall Project Objectives: Develop CMS hollow fiber membranes with H_2 permeance of 1000 GPU and H_2/CO_2 selectivity of 40 at 200-300 ^oC, enabling membrane-based systems capturing 90% CO_2 from coal-derived syngas with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches.

- **Milestone 1: CMS films with H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 40;**
- **Milestone 2: Hollow fiber membranes (HFMs) based on PBI doped with polyprotic acids exhibiting H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40.**

Project Schedule and Milestones

BP 1 Materials development (10/1/18 – 3/31/20; 18 months)

•Optimize CMS materials with an H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 40 with simulated syngas;

•Optimize the hollow fiber membranes based on PBI doped with polyprotic acids.

BP 2 Membrane development (4/1/20 – 9/30/21; 18 months)

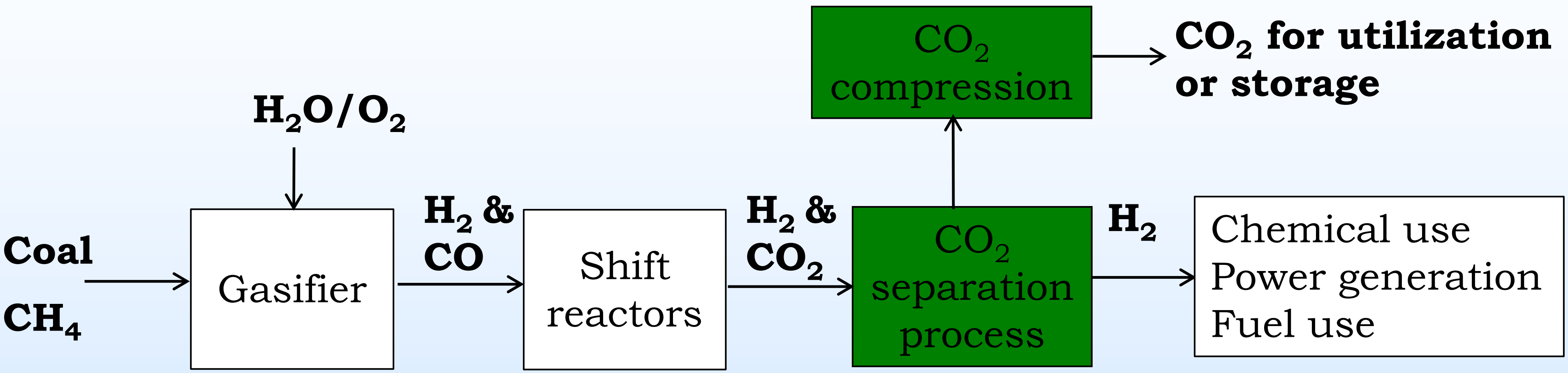
•Prepare and optimize CMS hollow fiber membranes with an H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40 at 200-300 °C ;

•Test membranes using simulated syngas containing H_2S, CO and water vapor;

•Determine the efficiency of the membrane reactors for the WGS reaction;

•Conduct the techno-economic analysis (TEA).

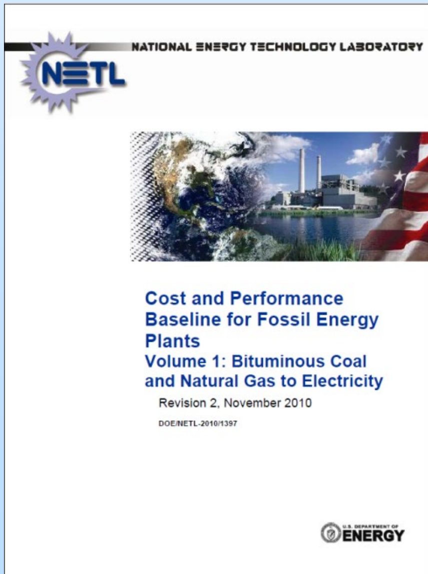
CO_2 separation is energy-intensive and expensive



GEE IGCC/Selexol 543 MWe plant (Case 2)

	CO_2 capture
Power consumption	50 MWe
Capital cost	$252 MM

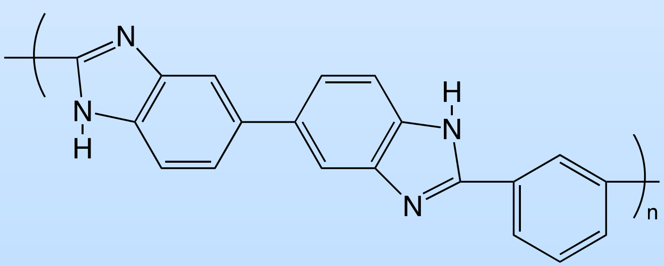
Lower cost and more energy efficient separation technology is needed.


NATIONAL ENERGY TECHNOLOGY LABORATORY
NETL
Cost and Performance Baseline for Fossil Energy Plants
Volume 1: Bituminous Coal and Natural Gas to Electricity
Revision 2, November 2010
DOE/NETL-2010/1397
U.S. DEPARTMENT OF ENERGY

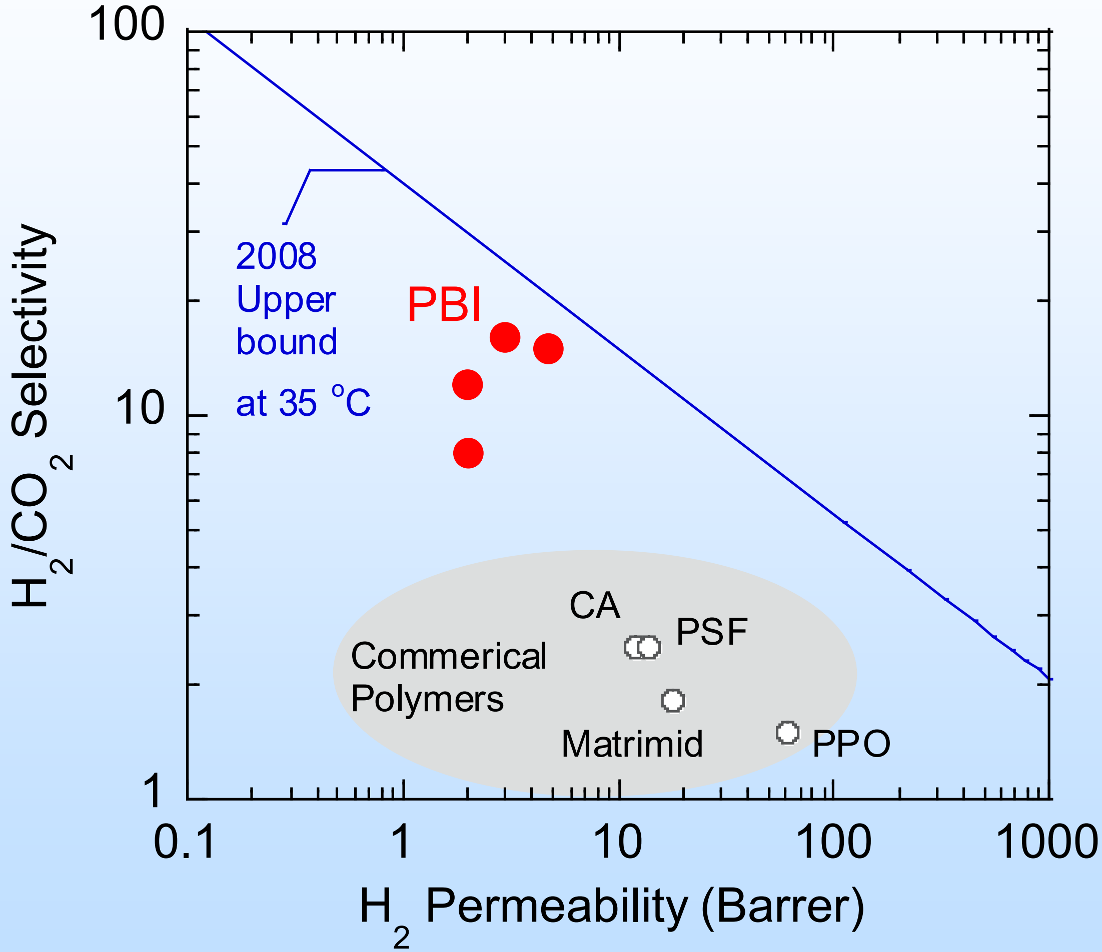
Permeability/Selectivity Tradeoff

	Critical temperature (K)	Kinetic diameter (Å)
H_2	33	2.89
CO_2	304	3.3

$$\frac{S_{H_2}}{S_{CO_2}} << 1 \quad \text{and} \quad \frac{D_{H_2}}{D_{CO_2}} >> 1$$

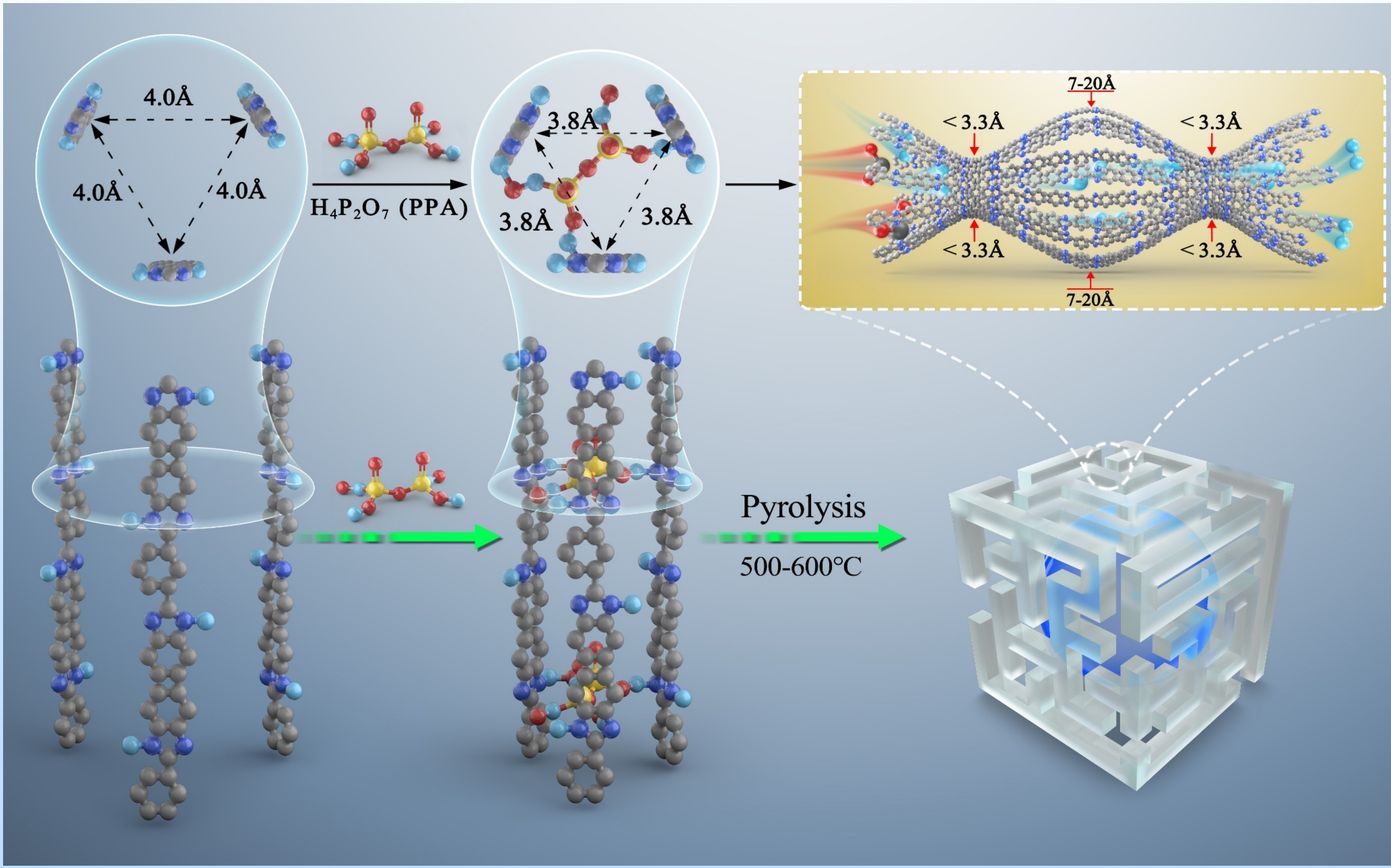


Polybenzimidazole (PBI)
(Celazole®)

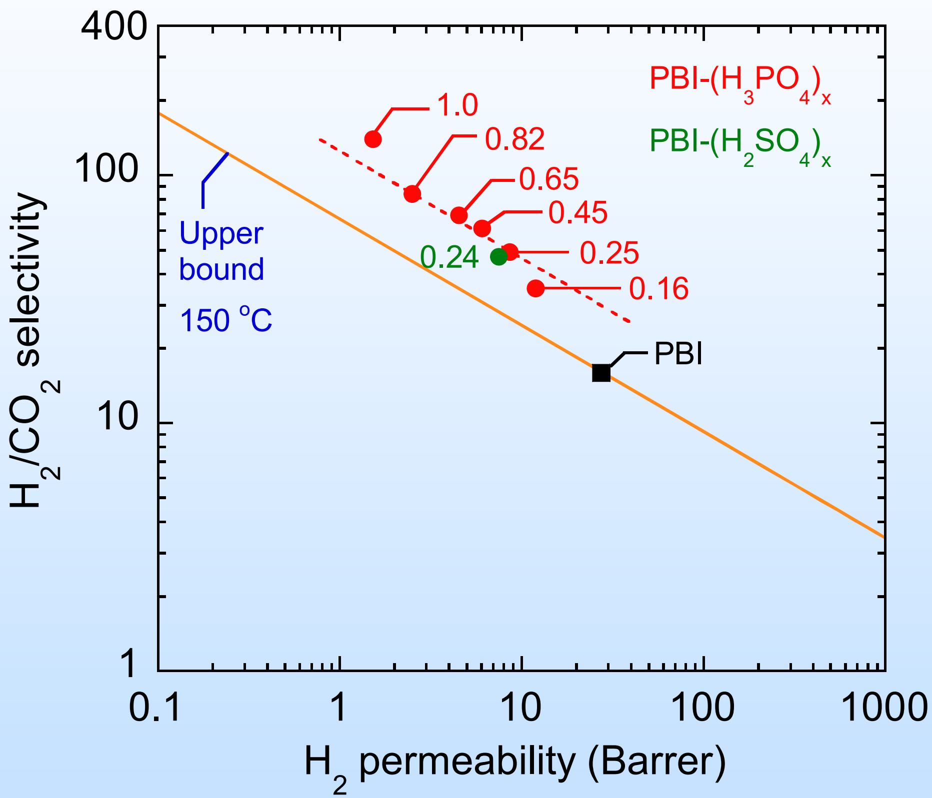


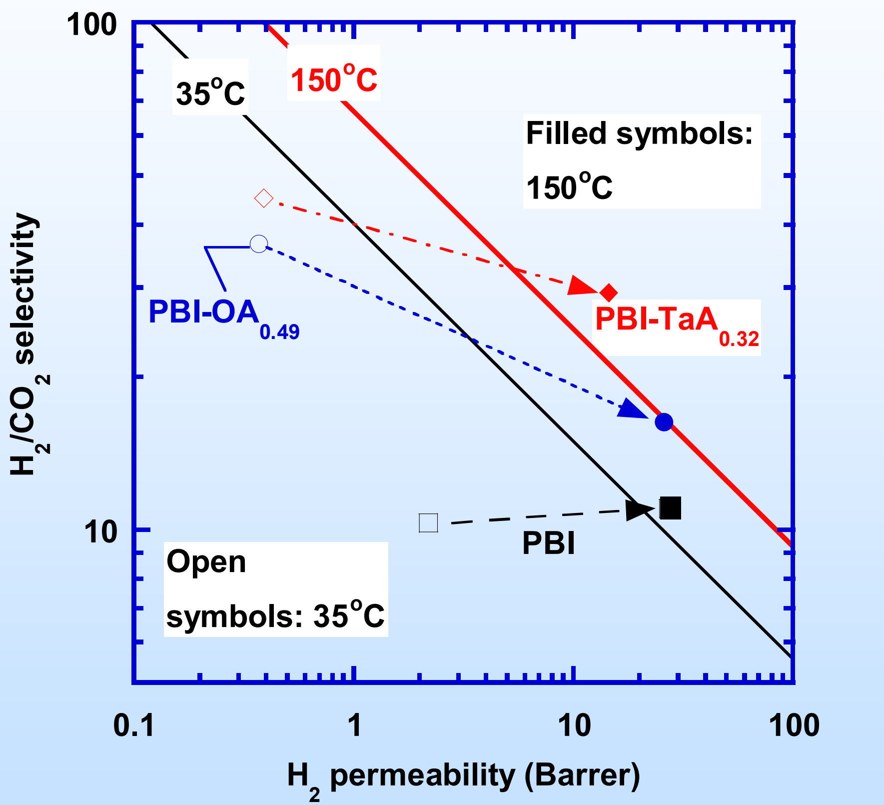
- Commercially available
- High T_g (417 °C), T_d : 550 ° C

Our Approach to Meet Milestones:
Carbonization of Polyprotic Acid Doped PBI



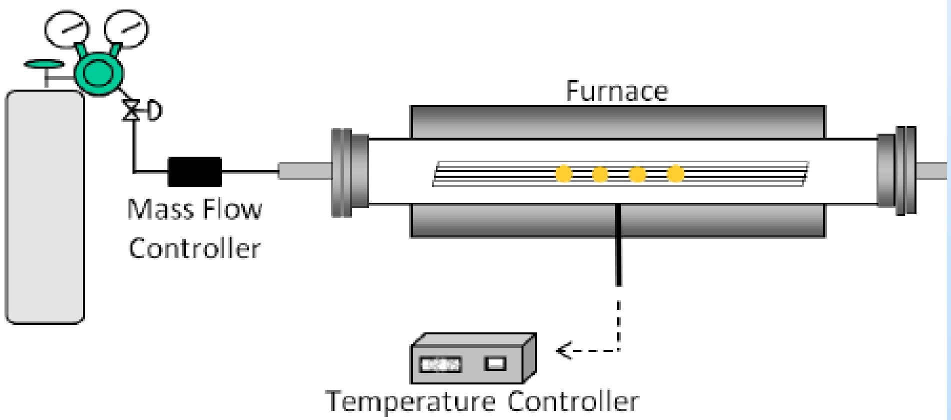
Polymeric Membranes for H_2/CO_2 Separation



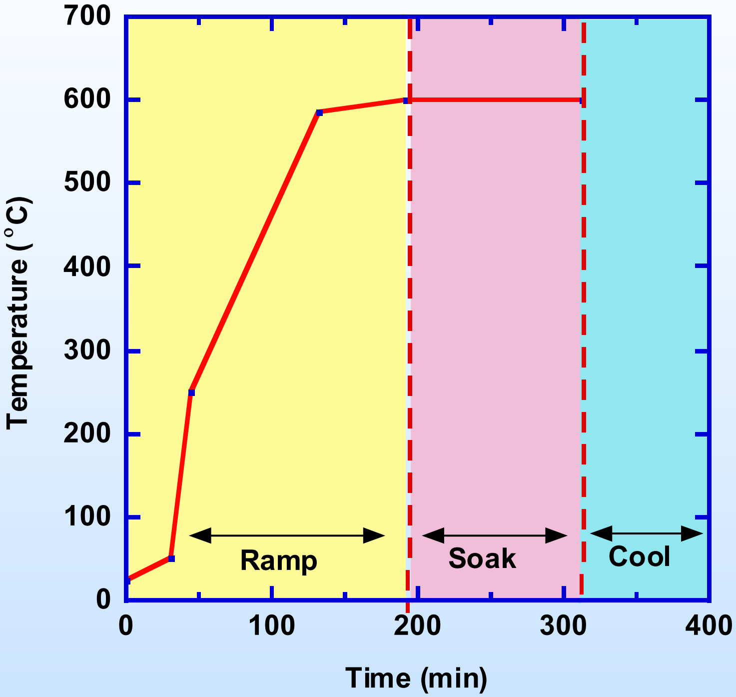


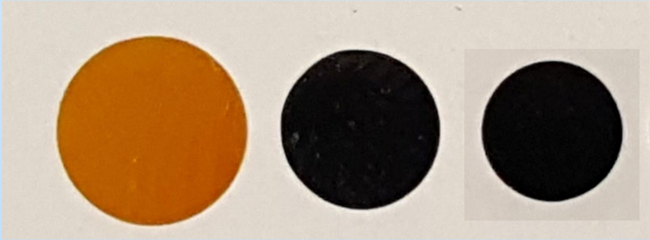
Zhu, Swihart, and Lin, *Energy Environ. Sci.* 2018, 11 (1), 94-100.
Hu, et al., *ACS Appl. Mater. Interface.* 2021, 13(10), 12521-12530.

Our Approach: Carbonizing PBI/Acid to Enhance H_2/CO_2 Separation Performance



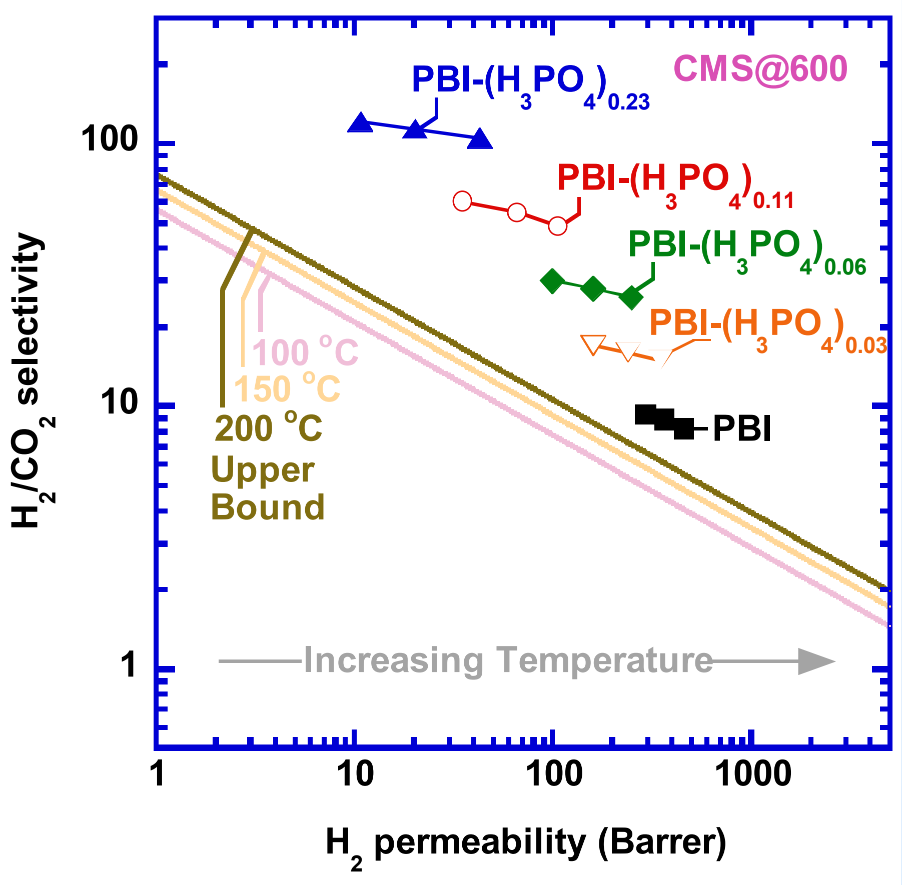
T_{max}: 600-900 °C



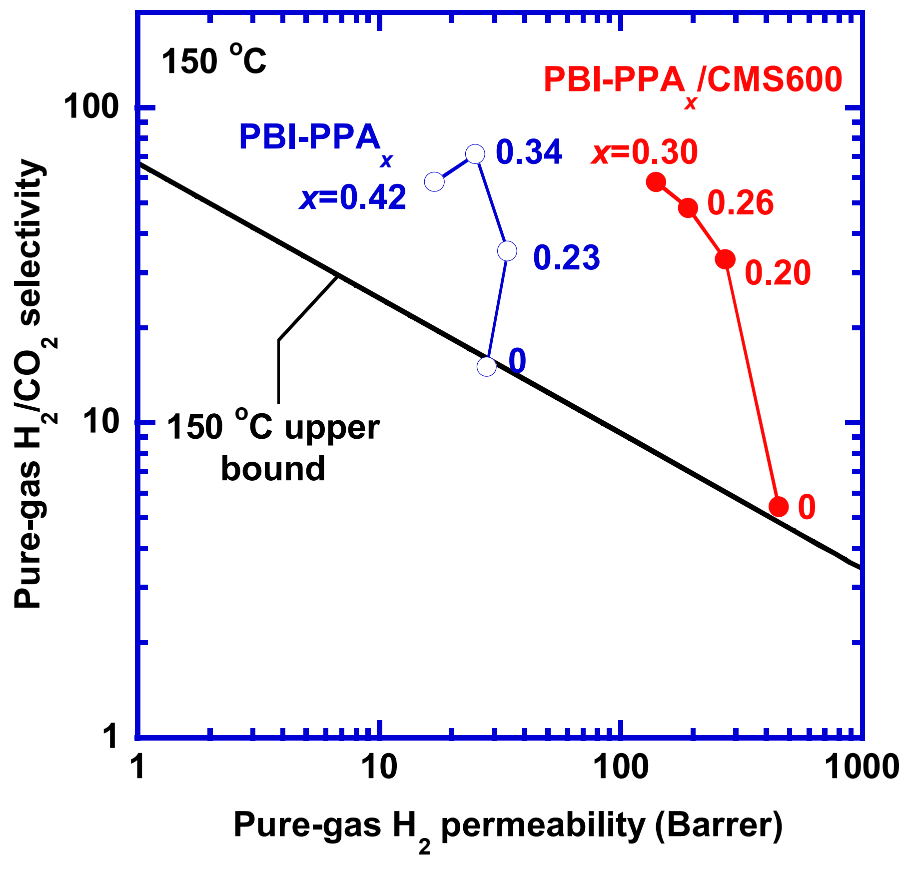


Meeting Milestone I: H_2 permeability of 200 Barrer and H_2/CO_2 selectivity of 40

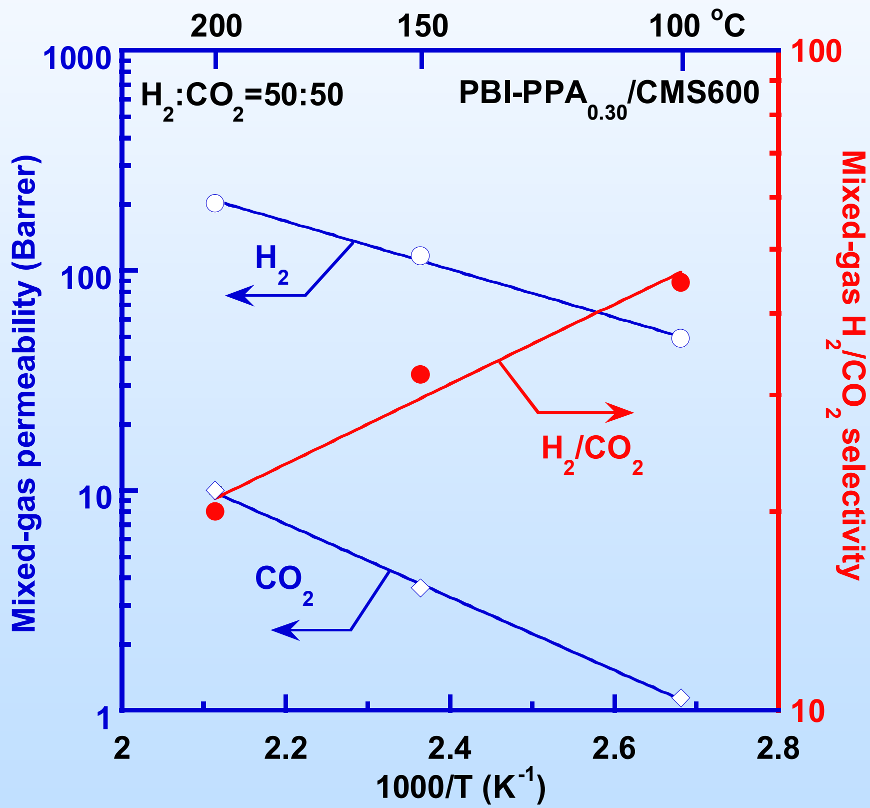
PBI-H_3PO_4 CMS@600

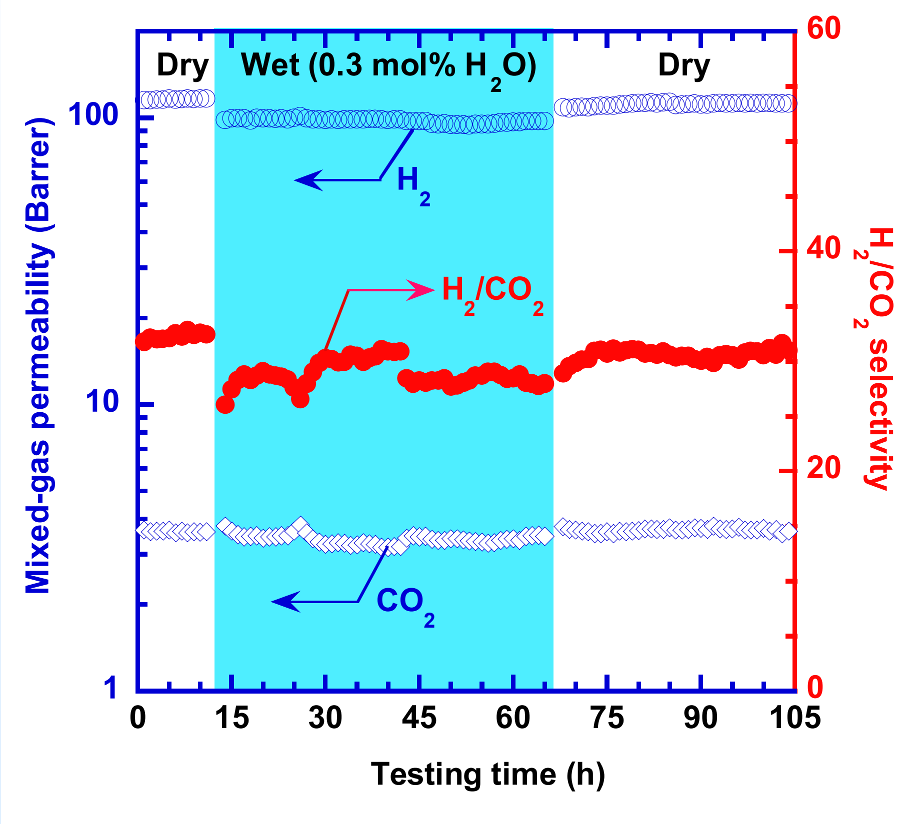


PBI-$H_4P_2O_7$ CMS@600

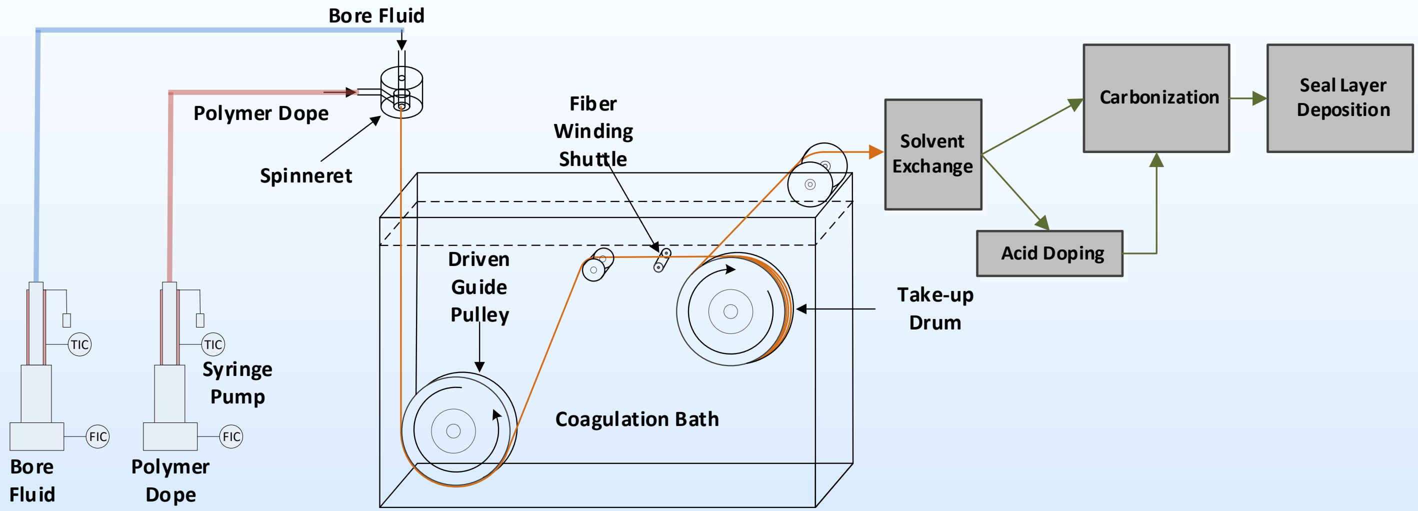


Stable H_2/CO_2 Separation Performance of PBI-PPA CMS@600 at 150 °C

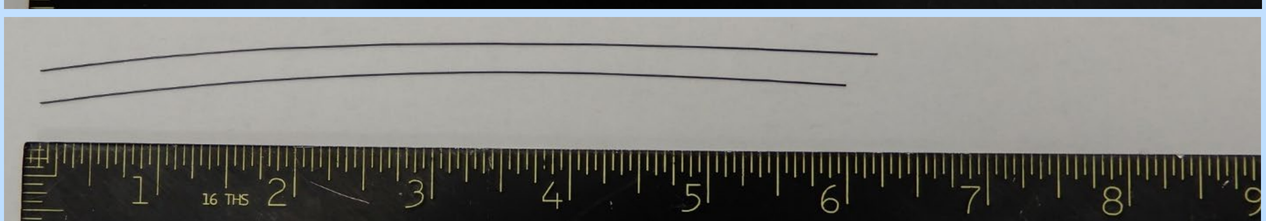




Fabrication of PBI CMS HFMs



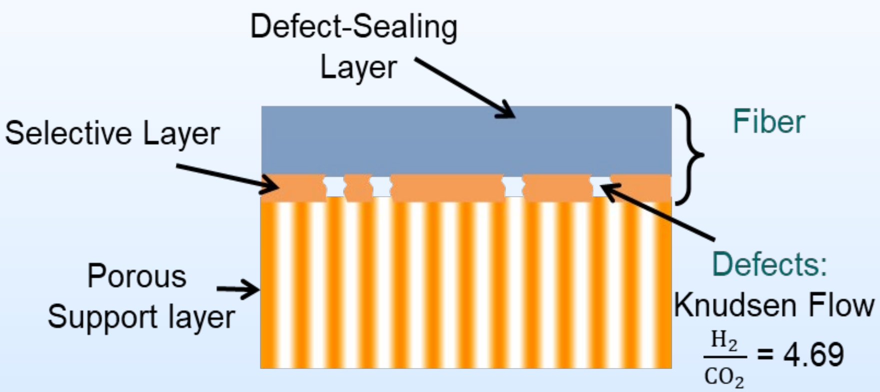
Base PBI HFM

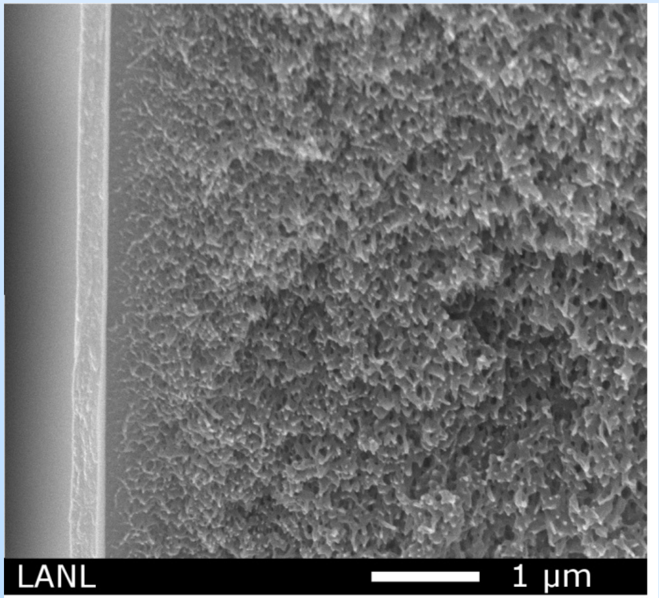


Carbonized PBI HFM[12]

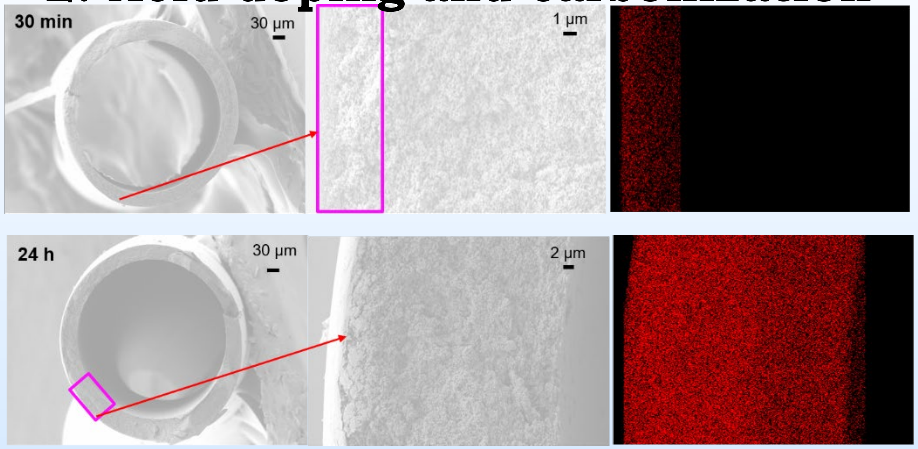
Improve Separation Performance of PBI CMS HFMs

1. Defect-Sealing



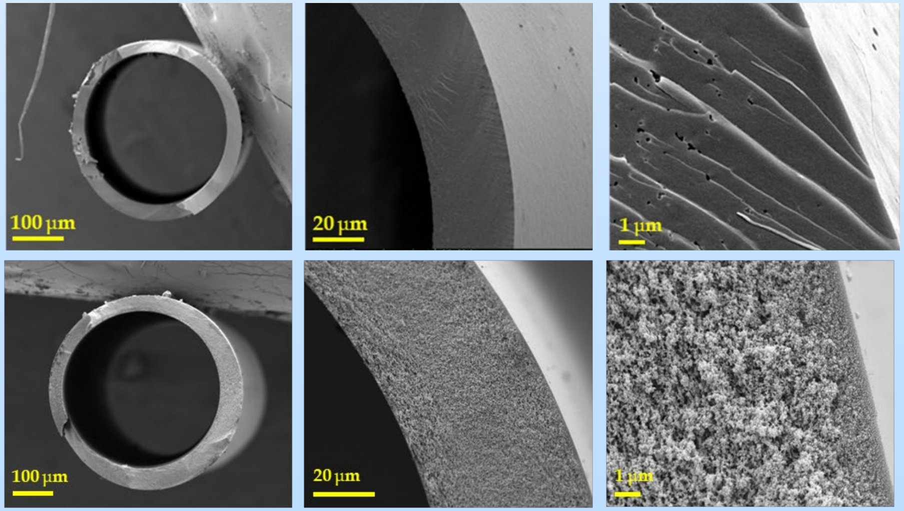


2. Acid doping and carbonization

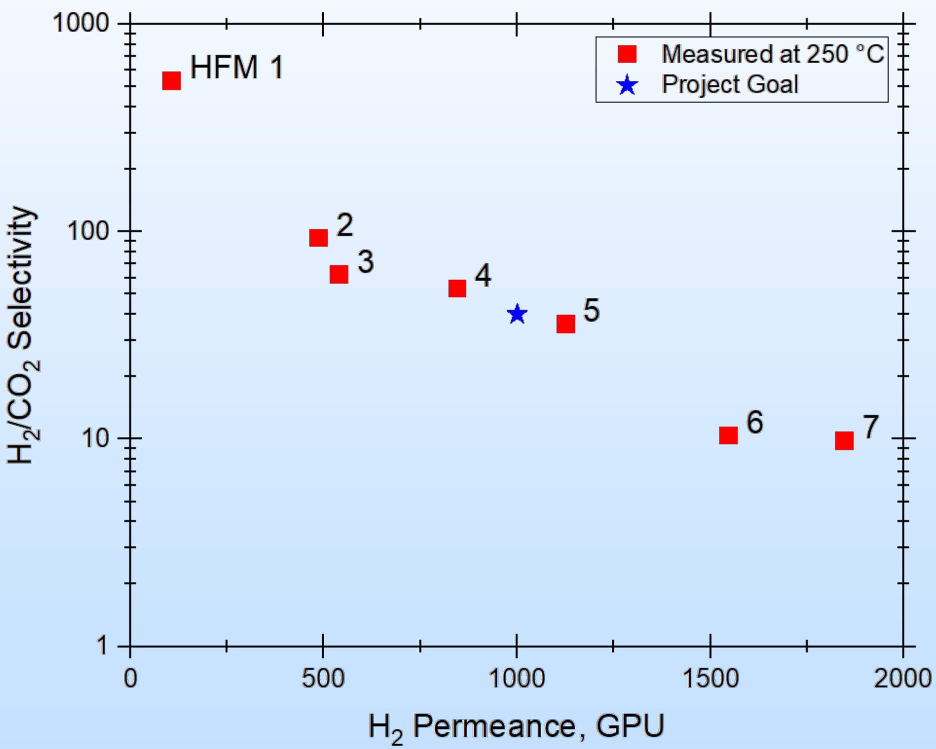


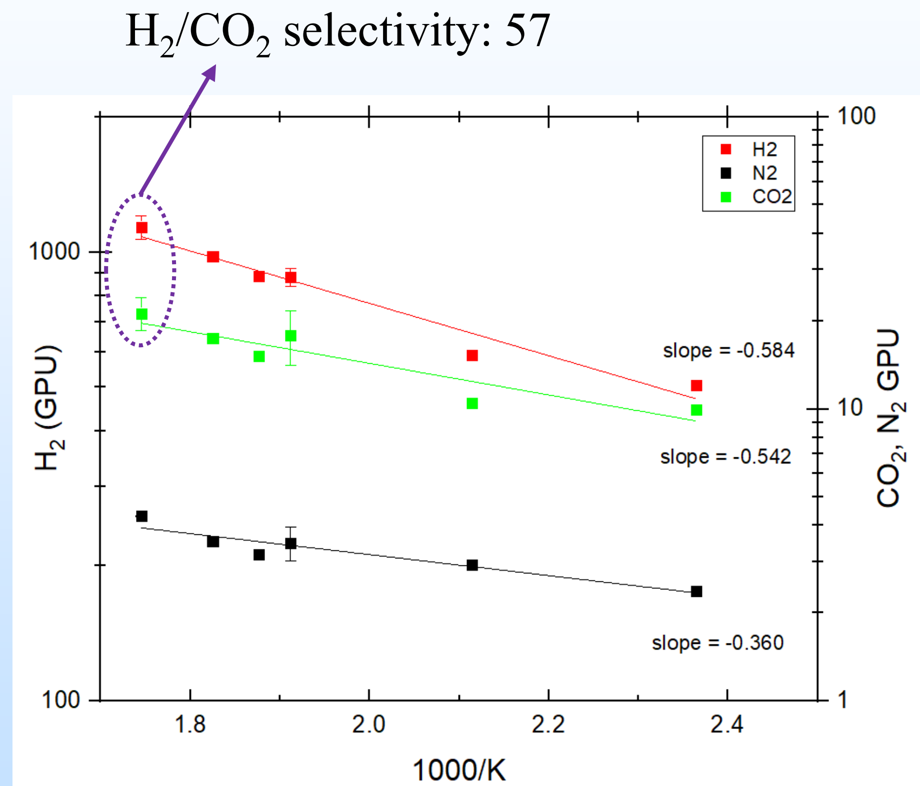
Symmetric – Low Permeance

Asymmetric – High Permeance

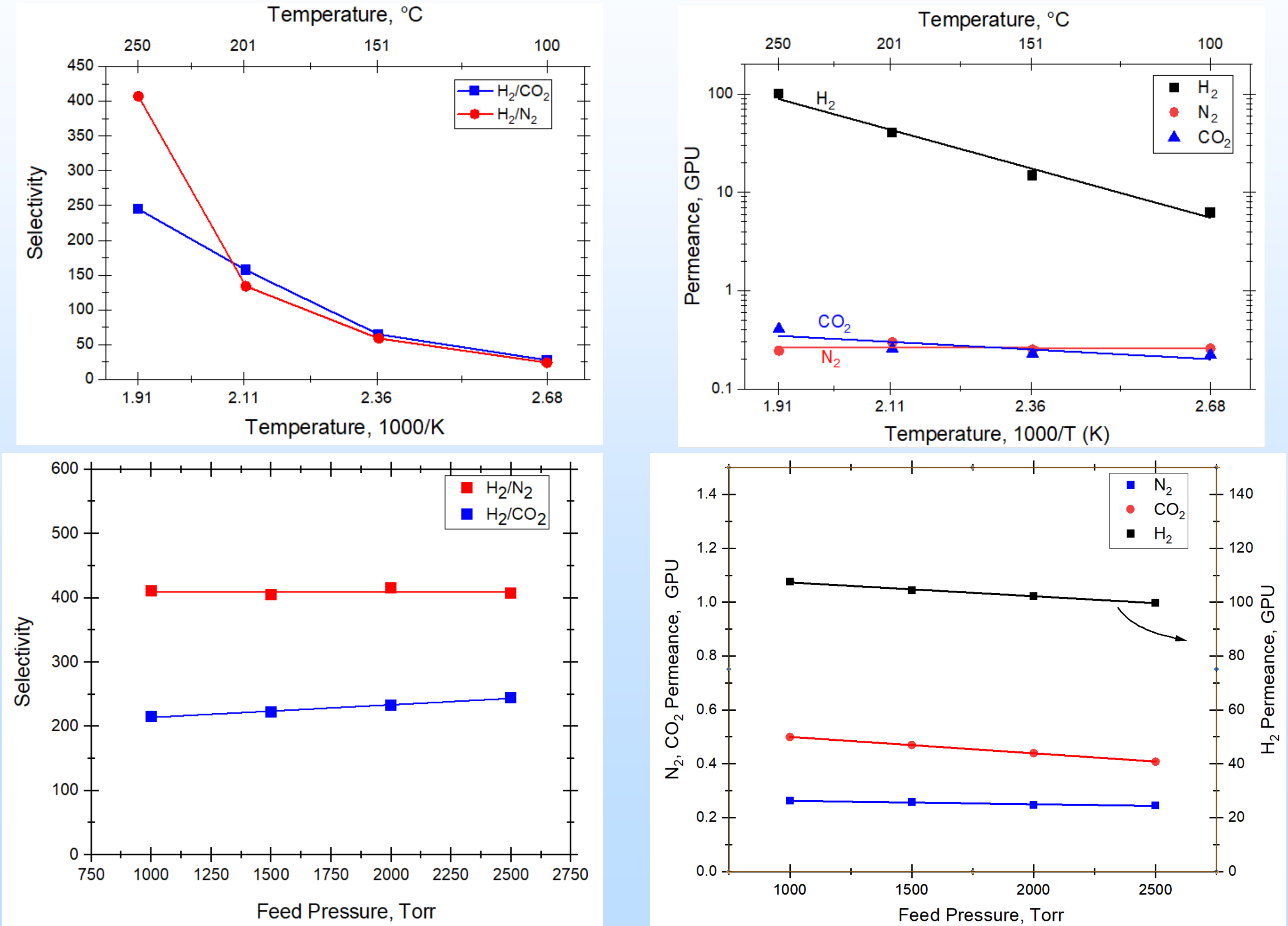


Meeting Milestone 2: H_2 permeability of 1000 GPU and H_2/CO_2 selectivity of 40

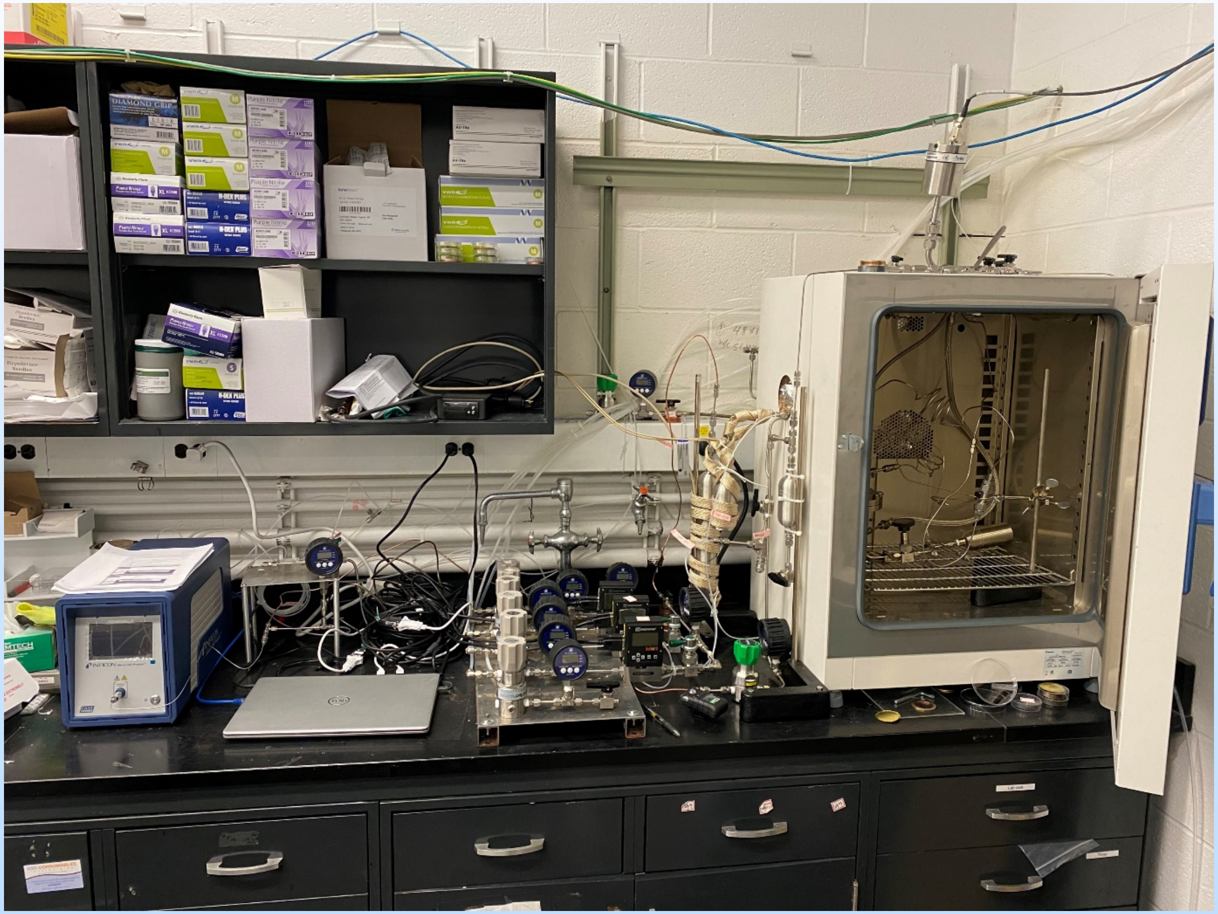




Activated Diffusion Dominant Gas Transport Phenomena

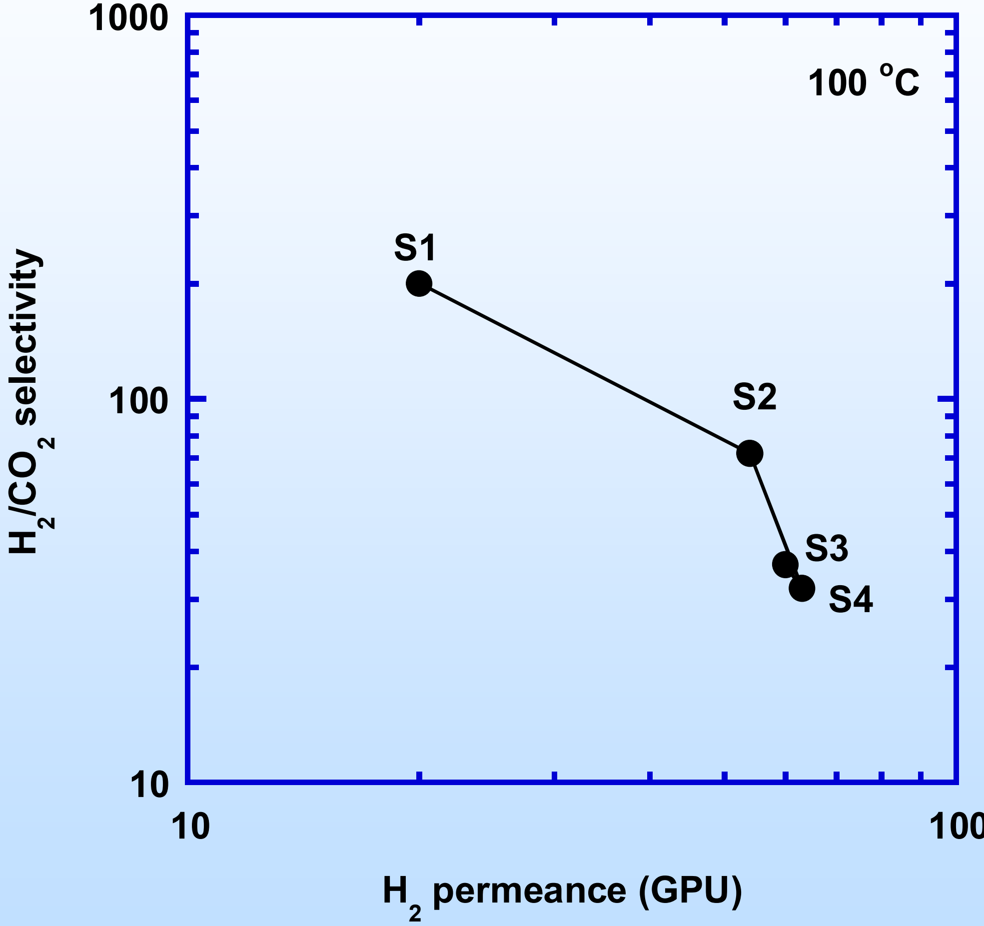


Membrane Reactor and Testing Platform for WGS Reaction

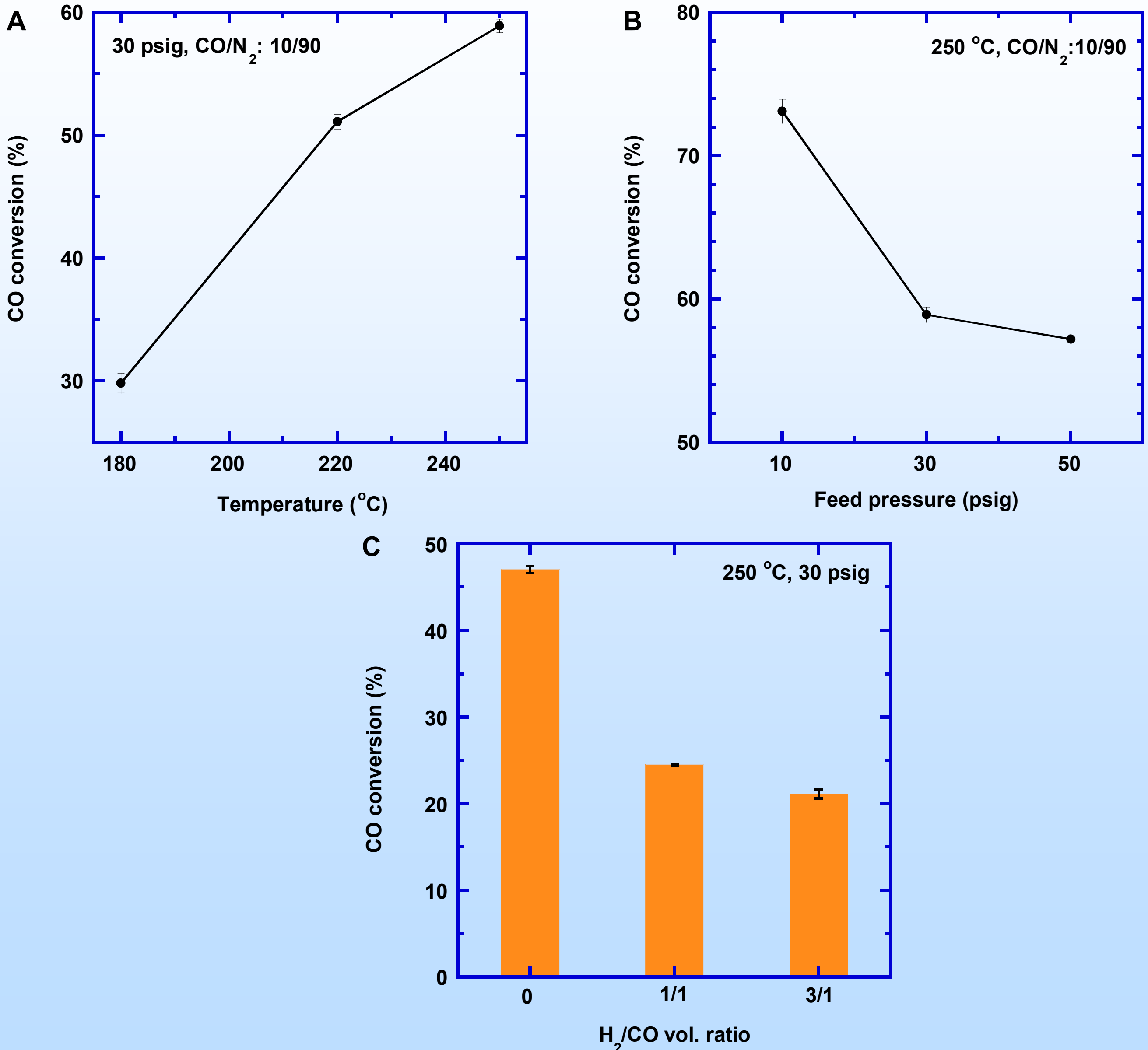


Optimize Performance of Hollow Fiber Membranes

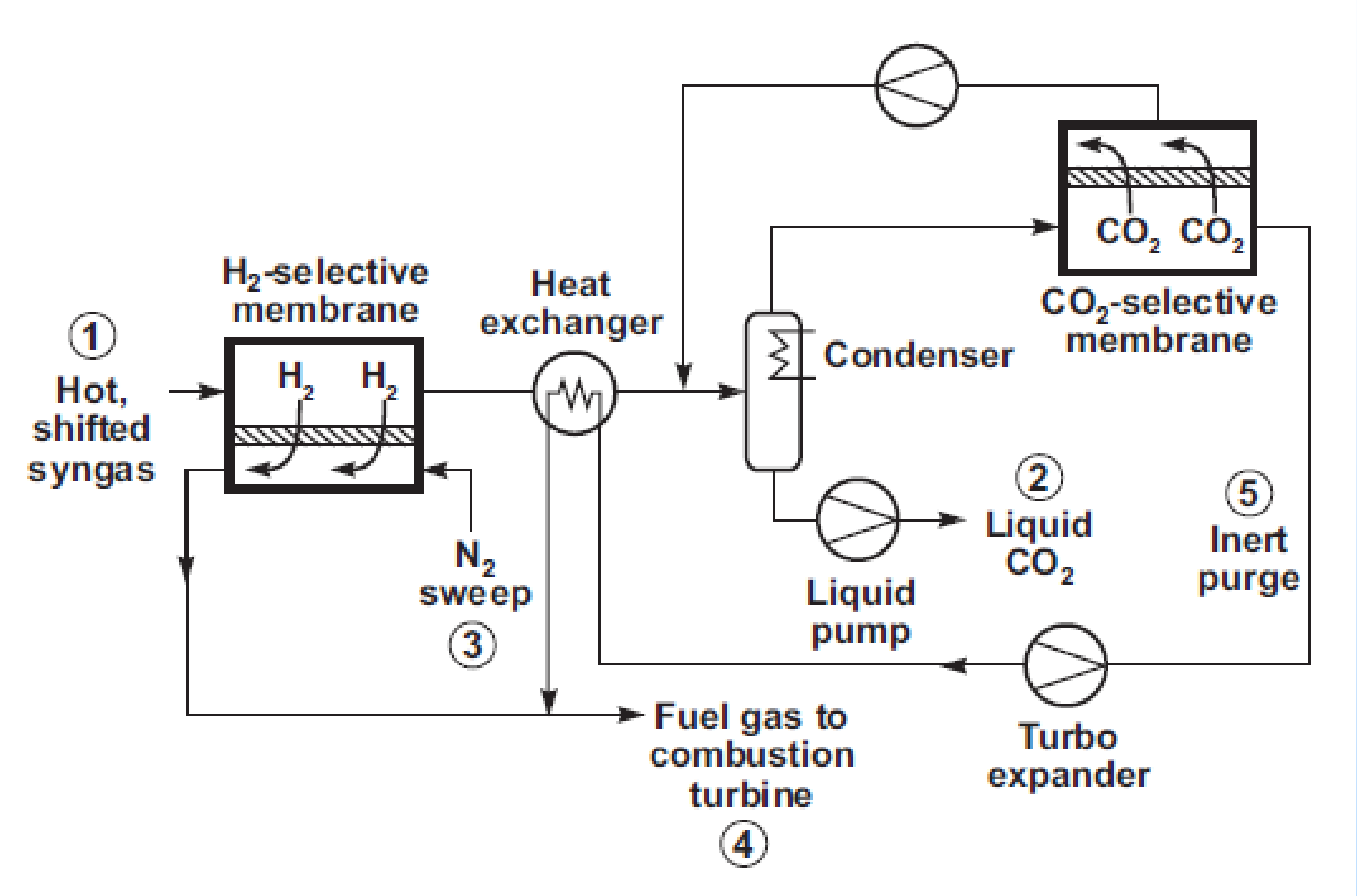
Ceramic-support PBI-PPA Carbon molecular sieve (CMS) composite membranes



Activity of Commercial Catalysts

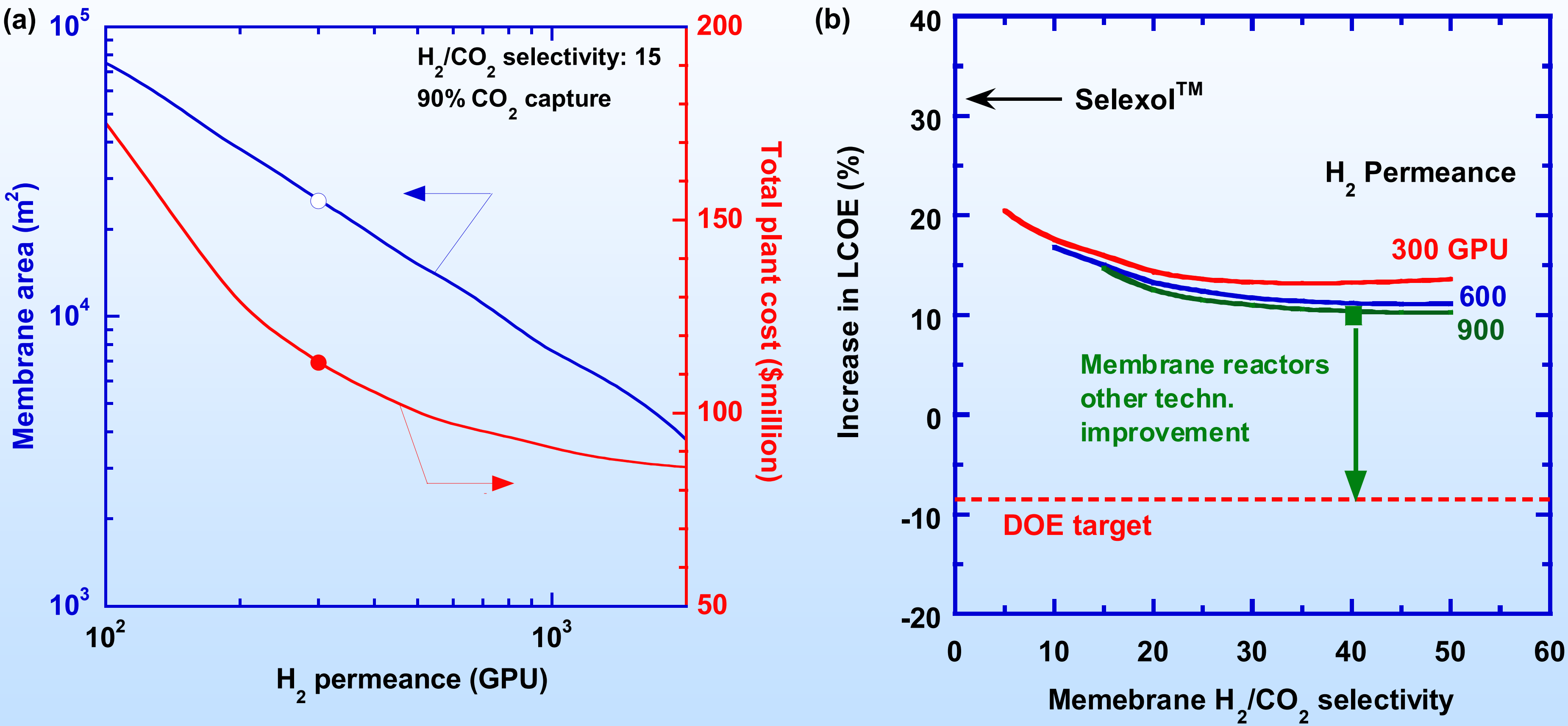


MTR's Membrane Process Design



Merkel, Zhou and Baker, *J. Membr. Sci.*, 389, 442 (2012)
Merkel, et al., *NETL CO_2 Capture Technology Meeting*, 2011.

MTR's Techno-Economic Analysis



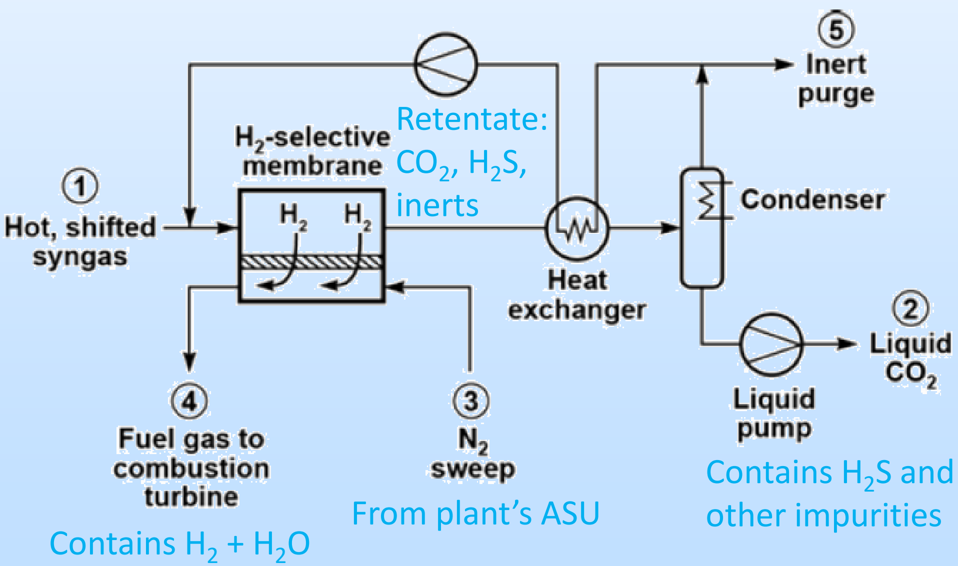
Merkel, Zhou and Baker, *J. Membr. Sci.*, 389, 442 (2012)
Merkel, et al., *NETL CO_2 Capture Technology Meeting*, 2011.

TEA: Process to be Simulated

TEA Focus: effect of key membrane improvements on CO_2 capture design and costs

- **Improved permeability and selectivity:** Reduce CO_2 processing costs downstream of membrane
- **Increased operating temperature (200-300°C vs 150°C)**: Reduce cost of cooling gas upstream of the membrane

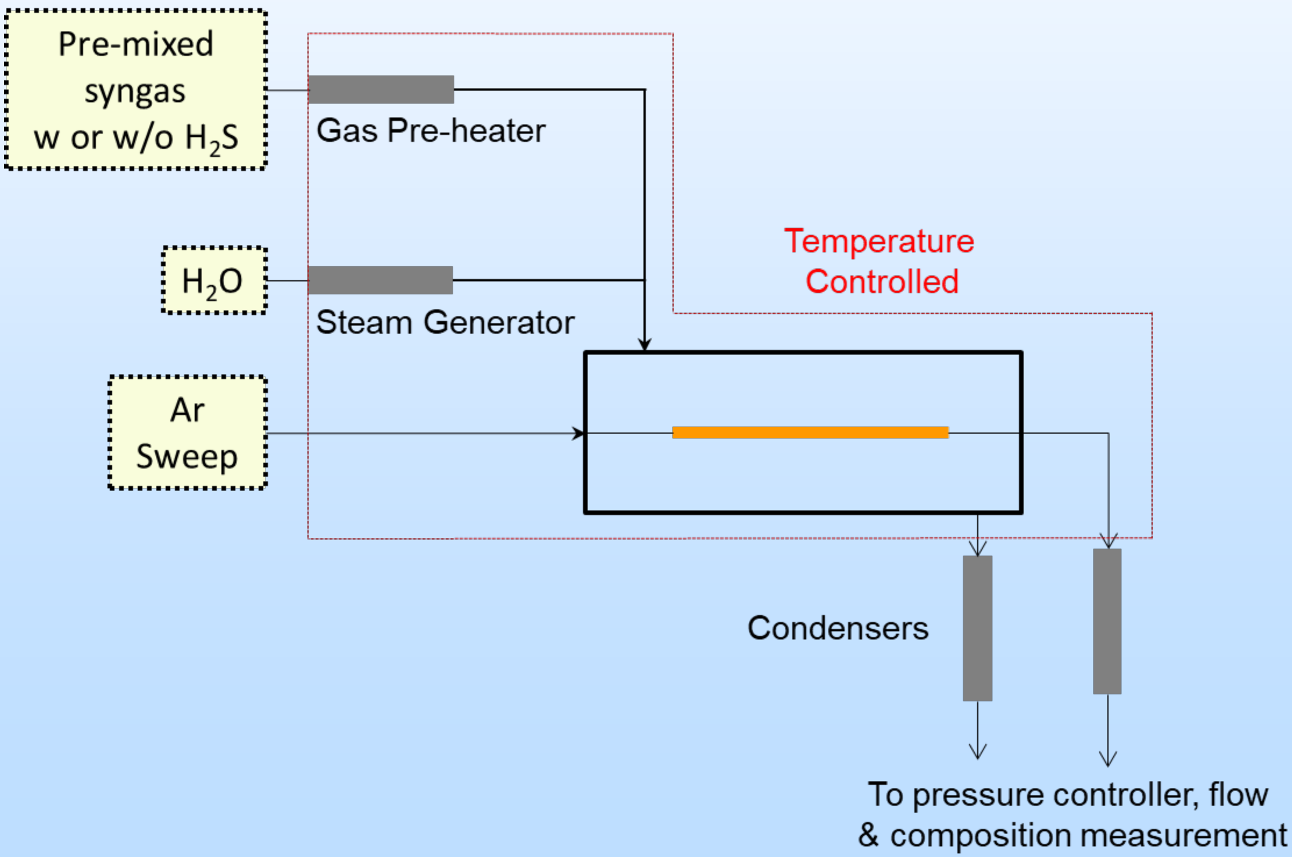
Incorporating membrane performance into process model:



Source: MTR, Final Report to DOE-NETL for DE-FE0001124, December 2011

Plans for Future Testing/Development/ Commercialization

LANL: syngas evaluations in a pencil module

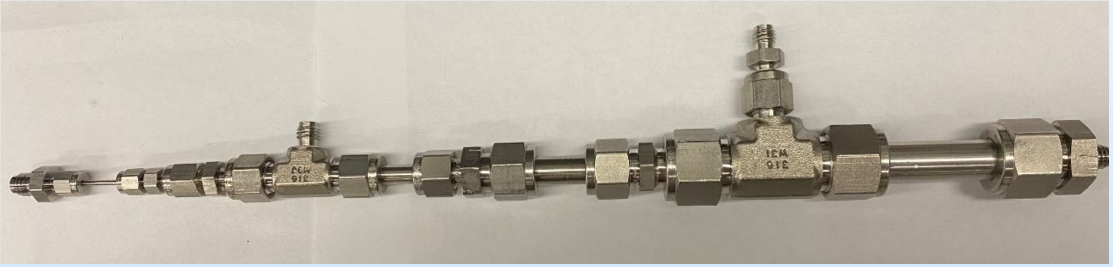


Feed composition	Test 1	Test 2
H_2 (%)	50	50
CO_2 (%)	30	30
H_2O (%)	19	19
CO (%)	1	1
H_2S (ppm)	0	20
Total Feed Pressure (psia)	200	200
Temp (°C)	200-350	

Ref: NETL Test protocol – Testing of hydrogen separation membranes, 2008.

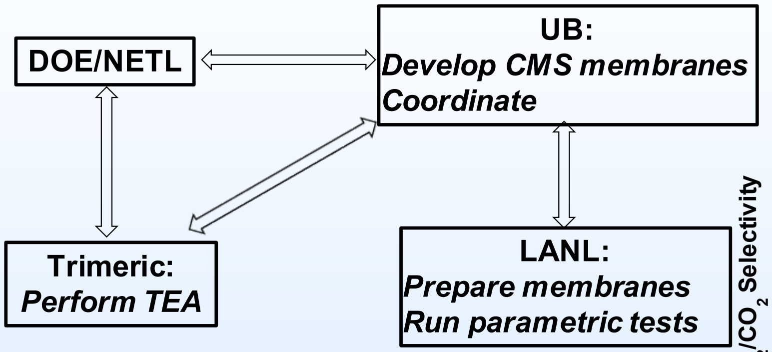
Plans for Future Testing/Development/ Commercialization

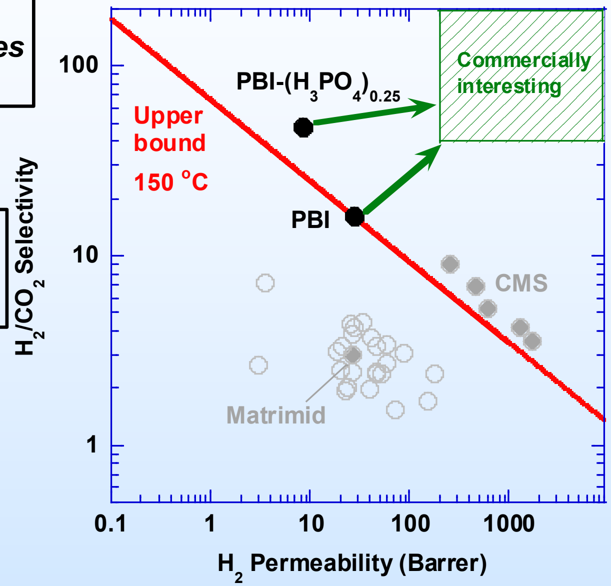
UB: characterize membrane reactors for H_2/CO_2 separation

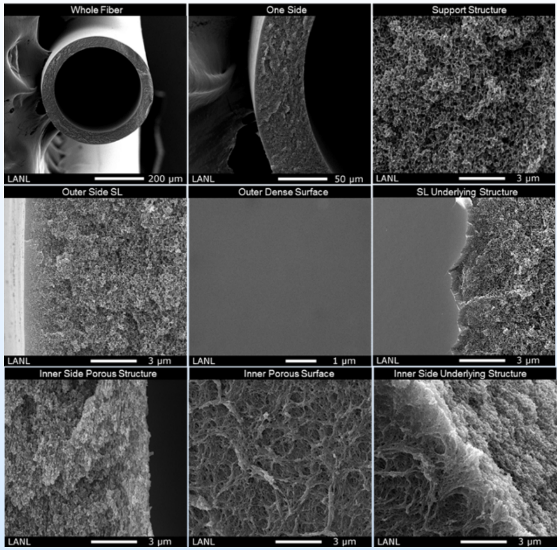


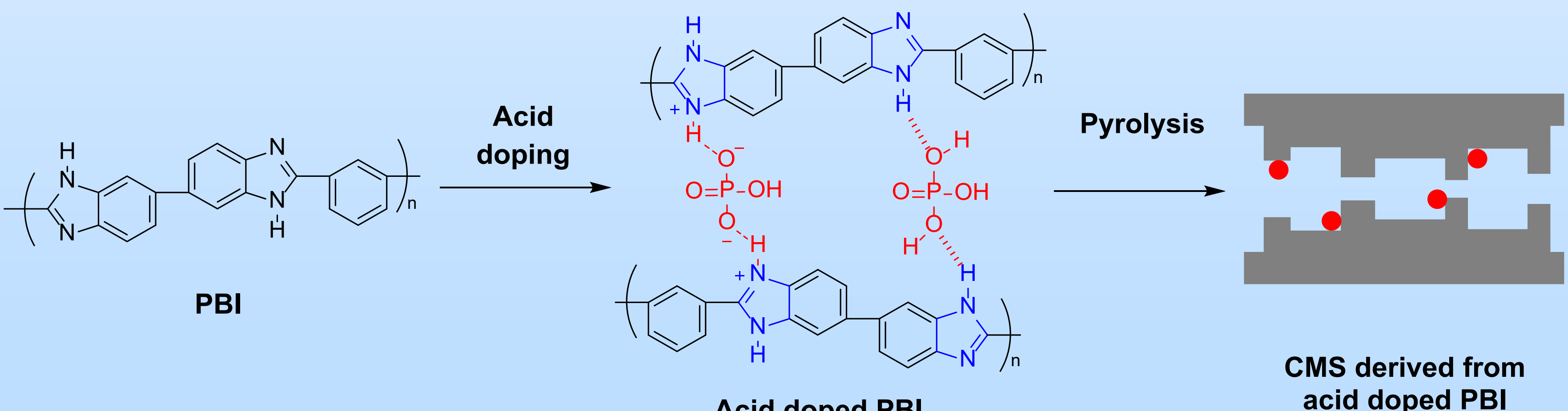
Trimeric: conduct TEA (Impact on COE; Comparison to DOE reference Selexol case)

Summary


DOE/NETL
UB:
Develop CMS membranes
Coordinate
Trimeric:
Perform TEA
LANL:
Prepare membranes
Run parametric tests

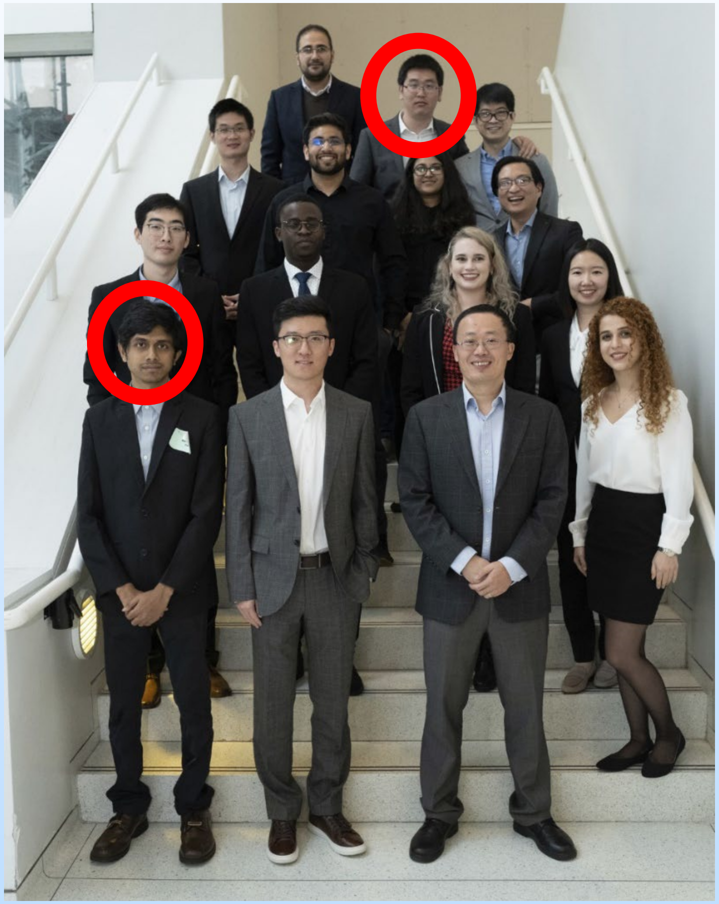

Upper bound
150 °C
PBI-$(H_3PO_4)_{0.25}$
PBI
Commercially interesting
CMS
Matrimid
H_2/CO_2 Selectivity
H_2 Permeability (Barrer)
0.1
1
10
100
1000
1
10
100


Whole Fiber
One Side
Support Structure
Outer Side SL
Outer Dense Surface
SL Underlying Structure
Inner Side Porous Structure
Inner Porous Surface
Inner Side Underlying Structure


Acid doping
Pyrolysis
PBI
Acid doped PBI
CMS derived from acid doped PBI

Organization Chart

University at Buffalo (UB):
Dr. Haiqing Lin (PI)



Project efforts:

- Prepare, optimize and characterize PBI doped with polyprotic acids;
- Prepare, optimize and characterize CMS materials;
- Prepare and optimize hollow fiber membranes based on PBI and PBI doped with polyprotic acids;
- Characterize H_2/CO_2 separation properties;
- Conduct parametric tests of membranes for H_2/CO_2 separation;
- Evaluate the CMS membranes for WGS reactors.

Organization Chart

- Los Alamos National Laboratory(LANL), Carbon Capture and Separations for Energy Applications (CaSEA) Laboratory

Team members

- Rajinder P. Singh (co-PI)
- Jeremy C. Lewis
- JongGuen Seong
- Kathryn A. Berchtold

Project efforts:

- Prepare and optimize hollow fiber membranes based on PBI and PBI doped with polyprotic acids;
- Characterize H_2/CO_2 separation properties;
- Conduct parametric tests of membranes for H_2/CO_2 separation;

Organization Chart

Trimeric Corporation (Trimeric)

- Privately-owned consulting firm located in Buda (Austin), Texas

Team members

- Andrew Sexton
- Katherine Dombrowski

Project efforts:

- Perform Process Technical Analysis;
- Evaluate Economic Potential of Membrane Process Compared to Other Capture Technologies.

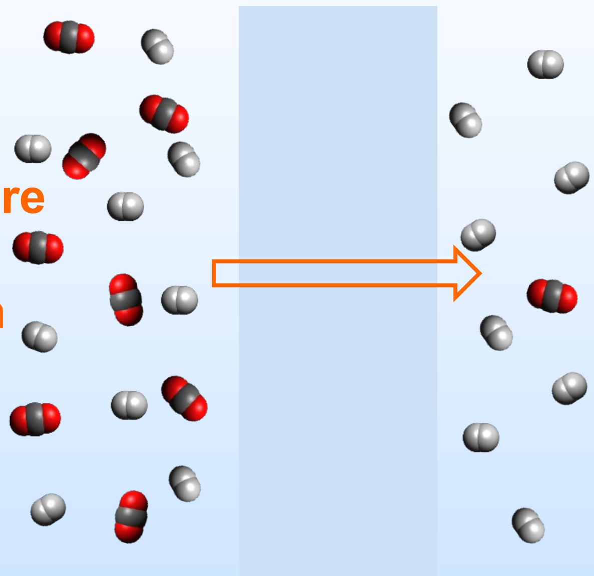
Project Timetable

Tasks	2018	2019				2020				2021		
	Oct - Dec	Jan - Mar	Apr - Jun	Jul - Sep	Oct - Dec	Jan - Mar	Apr - Jun	Jul - Sep	Oct - Dec	Jan - Mar	Apr - Jun	Jul - Sep
Project Management and Planning												95%
CMS films with an H_2 permeability of 200 Barrers and H_2/CO_2 selectivity of 40 ★					100%							
Hollow fiber membranes with H_2/CO_2 selectivity of 40						100%						
CMS hollow fiber membranes with an H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40 ★												100%
Database of H_2/CO_2 separation properties												90%
Performance data of membrane reactors for the WGS reaction												40%
Final Techno-Economic Analysis												25%

Membrane: Energy-efficient Separation

Solution-diffusion model

High pressure up-Stream (p_1)



Low pressure down-Stream (p_2)

(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

Productivity - Permeability

$$P_A = S_A \times D_A$$

Purity - Gas selectivity

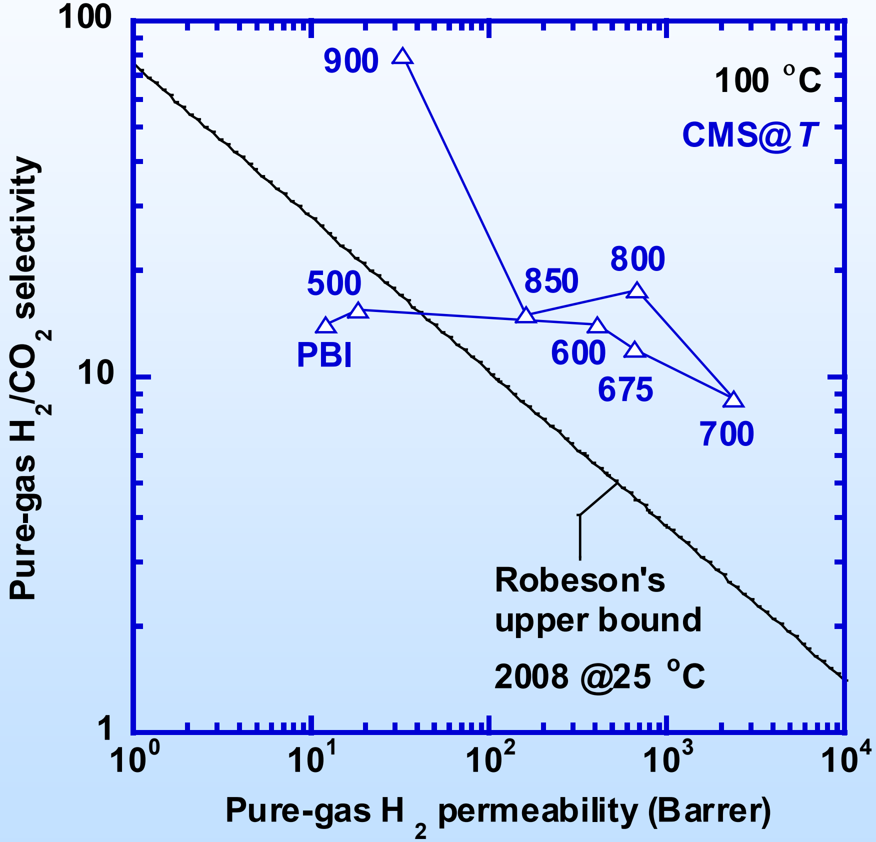
$$\alpha_{H_2/CO_2} = \frac{P_{H_2}}{P_{CO_2}} = \left(\frac{S_{H_2}}{S_{CO_2}}\right) \times \left(\frac{D_{H_2}}{D_{CO_2}}\right)$$

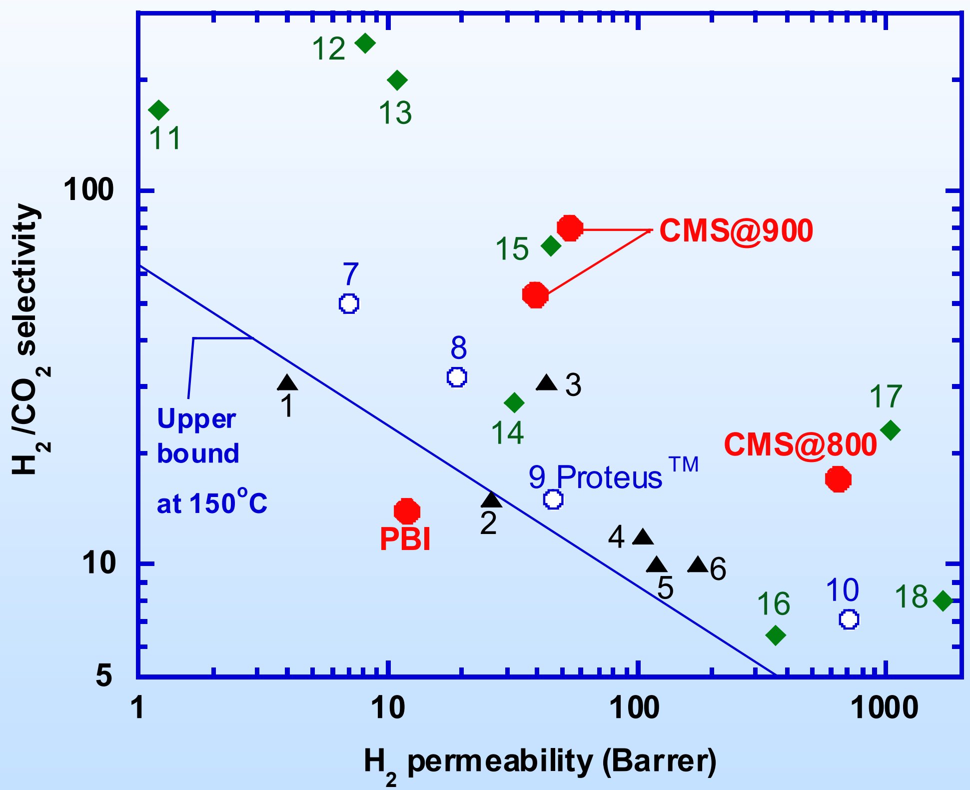
solubility selectivity

diffusivity selectivity

Wijmans and Baker, *J. Membr. Sci.* **107**, 1 (1995)

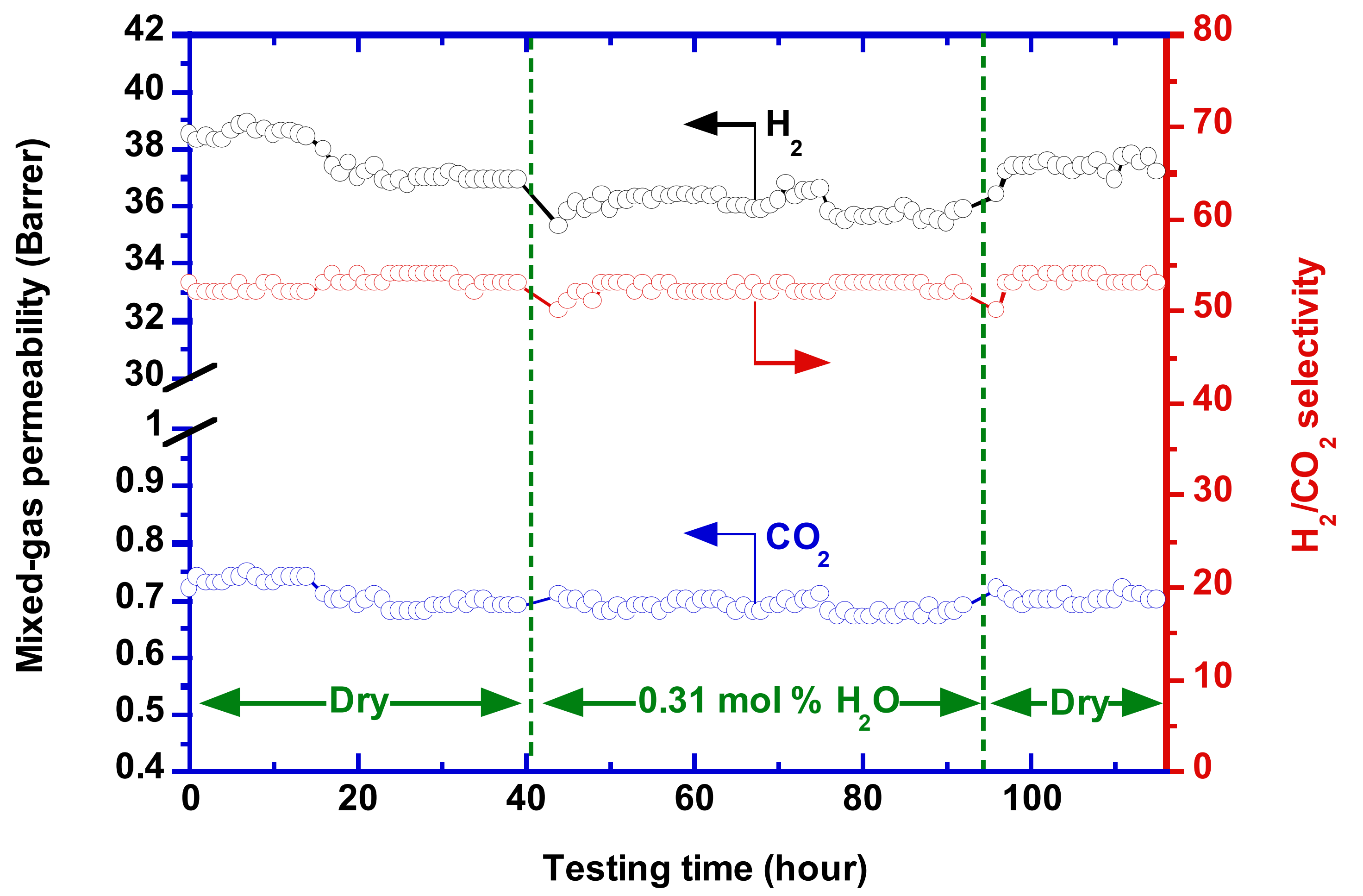
Super H_2/CO_2 Separation Performance of PBI CMS membranes





Omidvar, et al, ACS appl. mater. interfaces 2019, 11(50), 47365-47372.

Stable H_2/CO_2 Separation Performance of PBI-CMS@900 at 100 °C



Omidvar, et al, ACS appl. mater. interfaces 2019, 11(50), 47365-47372.