Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture (DE-FE0026463)

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NETL CO_2 Capture Technology Project Review Meeting
Pittsburgh, PA
8/22/2017

Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture

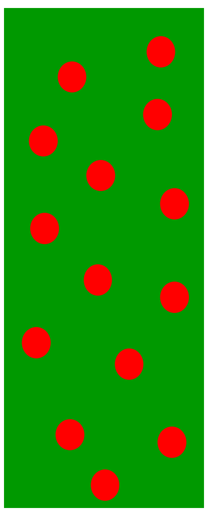
Award number:	DE-FE0026463
Project period:	10/1/15 to 9/30/18
Funding:	\$1,470,099 DOE \$ 373,004 UB and MTR contribution \$1,843,103 total
Program manager:	Steve Mascaro (previously Elaine Everitt)
Participants:	University at Buffalo (**UB**) Membrane Technology and Research, Inc. (**MTR**), and a site host
Project Objectives:	Develop industrial membranes with H_2 permeance of 500 gpu and H_2/CO_2 selectivity of 30; and Conduct parametric tests with real syngas stream.

Project Scope

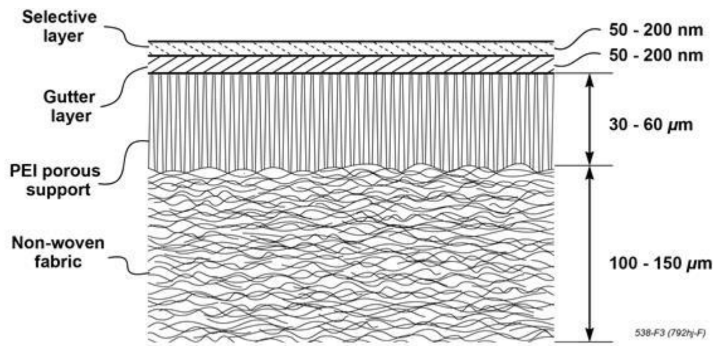
BP1: Prepare mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 **(Q1-Q4)**

BP2: Prepare thin film composite membranes with H_2 permeance of 500 gpu and H_2/CO_2 selectivity of 30 **(Q5-Q10)**

BP3: Conduct a 6-week field test of membranes with real syngas **(Q11-Q12)**



Nanostructured materials



Industrial membranes

Field test

Our Approach: H_2/CO_2 Solubility Selectivity

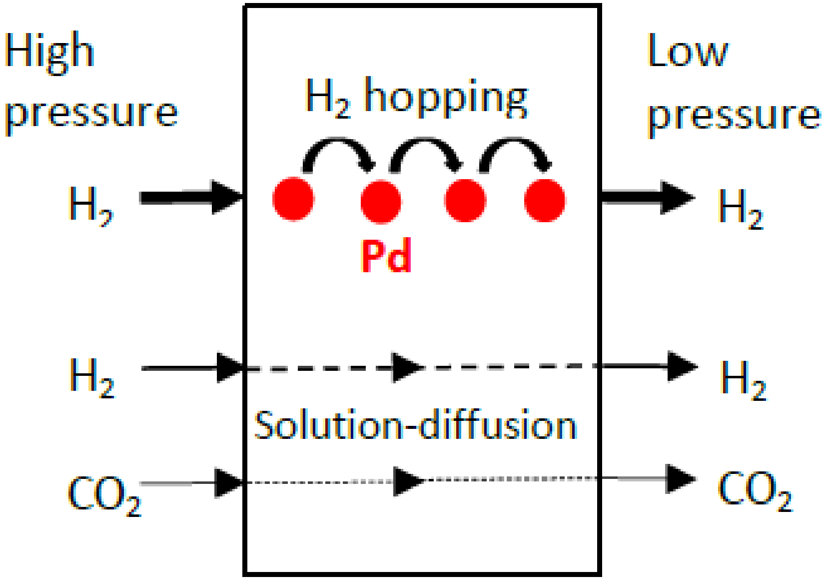
$$\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}$$

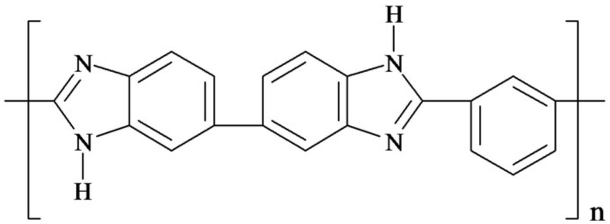
Materials	Temp. (°C)	H_2 solubility $cm^3(STP)/(cm^3\ atm)$	H_2/CO_2 solubility selectivity
Poly(dimethyl siloxane)	35	0.10	0.078
Polysulfone	35	0.075	0.036
Matrimid®	35	0.12	0.035
Pd metal*	**25**	**38,000**	**> 1,000**

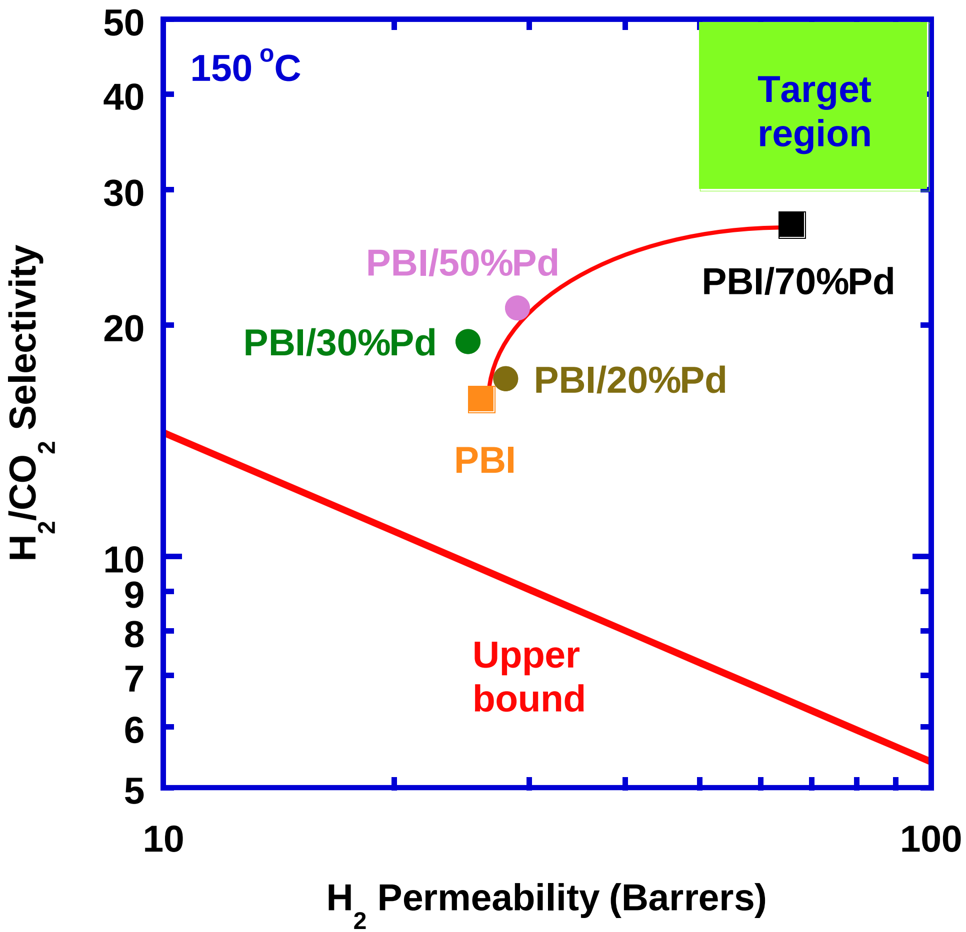
* Calculated at 0.02 bar H_2

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

Our Approach:
Mixed Matrix Materials

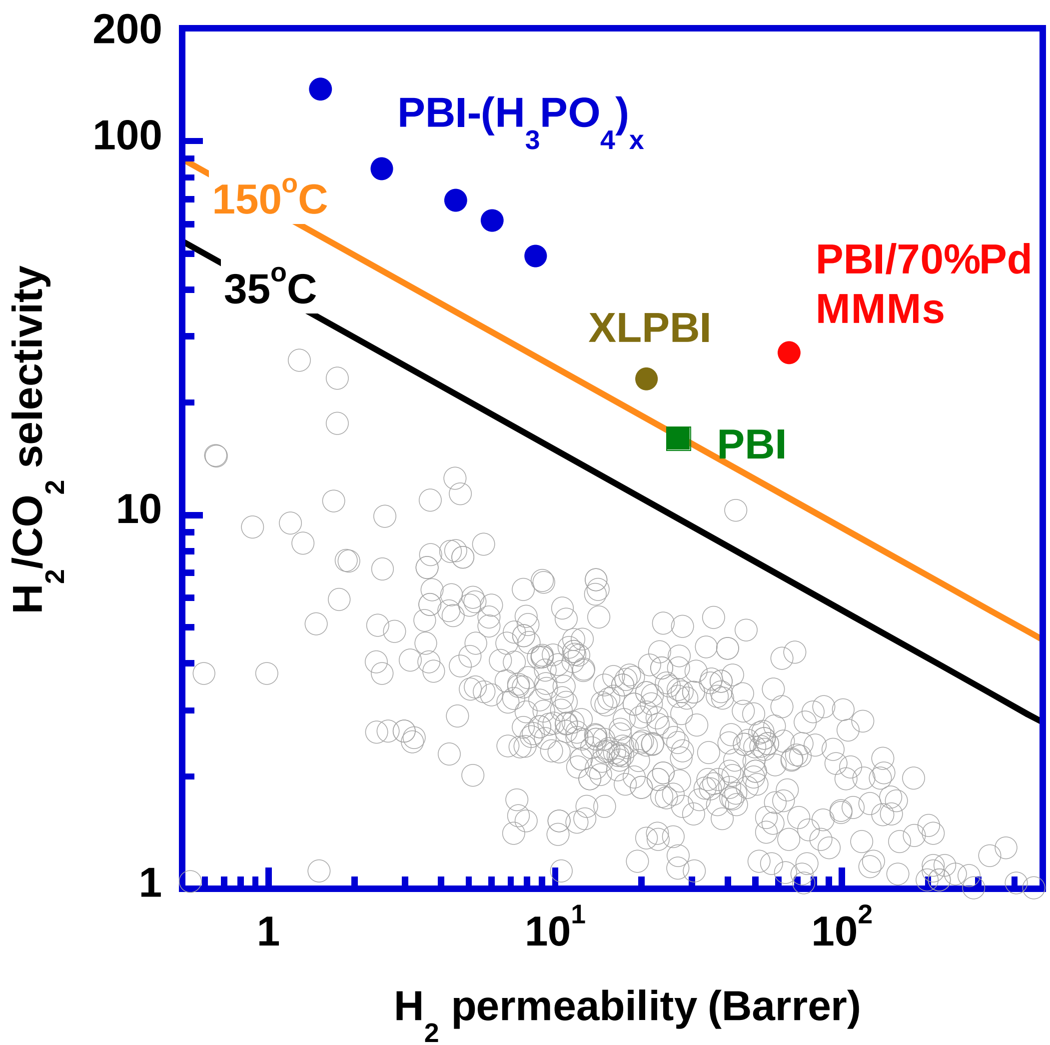






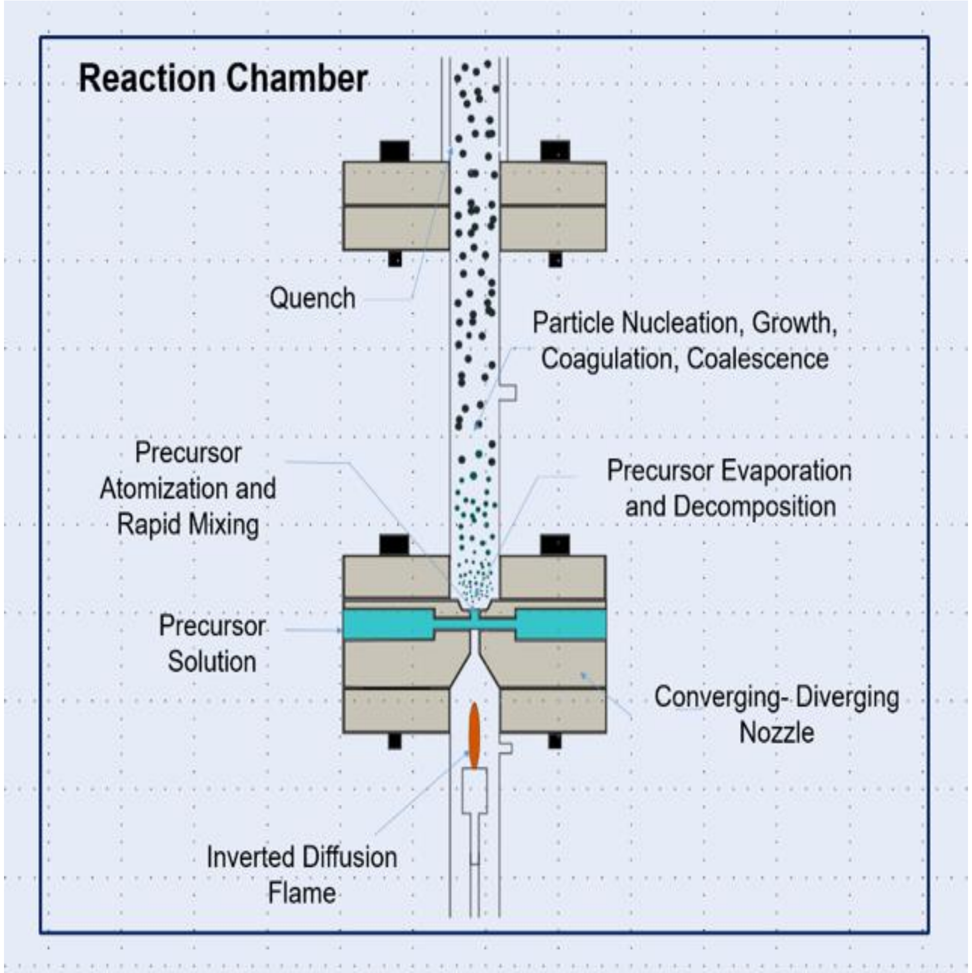
Tasks (BP2)	Start date	End date
Task 7 Scale up Polymer Synthesis	10/1/2016	3/31/2017
Task 8. Scale up Synthesis of Pd-based Nanomaterials	10/1/2016	3/31/2017
Task 9. Prepare Thin Film Composite Membranes	1/1/2017	12/31/2017
Task 10. Conduct Parametric Tests of Membranes for H_2/CO_2 Separation	1/1/2017	3/31/2018
Task 11. Design and Modify Membrane Stamp Test Unit for NCCC Field Test	6/1/2017	3/31/2018
Milestone f: Mixed matrix membranes with superior H_2/CO_2 separation properties prepared		
Task 13. Run One-Month Field Test at NCCC	4/1/2018	6/30/2018
Task 14. Analyze Field Test Results / Membrane Post-analysis	6/1/2018	9/30/2018
Milestone h: Successful field test completed		

Polymer Development and Scale-up



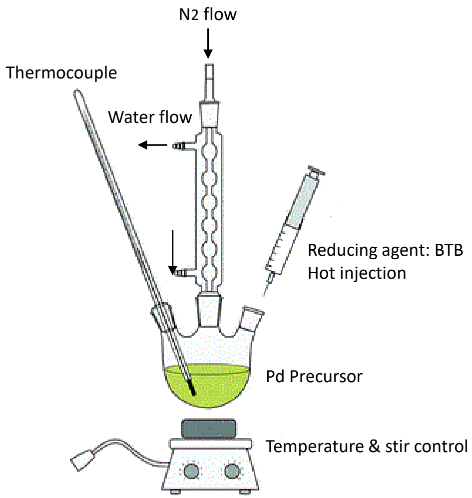
- Commercial PBIs are identified
- Modification of PBIs has been demonstrated to improve performance

Nanoparticle Synthesis Scale-up: Gas Phase Synthesis

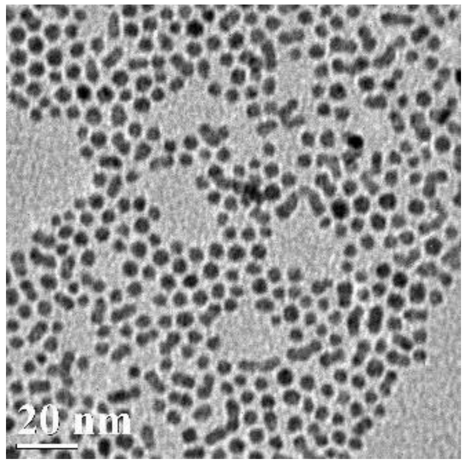


- ❑ Scaled up the size of the nozzle by 10 times
- ❑ Plugging free production
- ❑ 2g in 8 hrs of reaction time

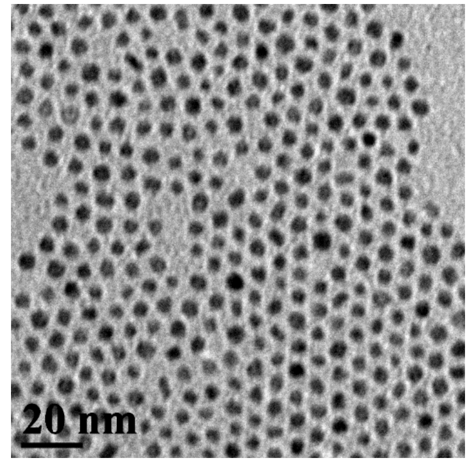
Nanoparticle Synthesis Scale-up: Solution Synthesis

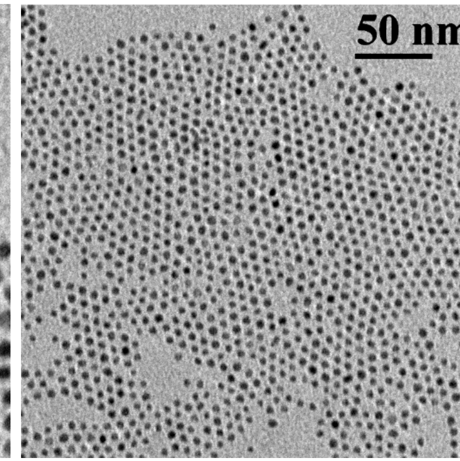


25 mg

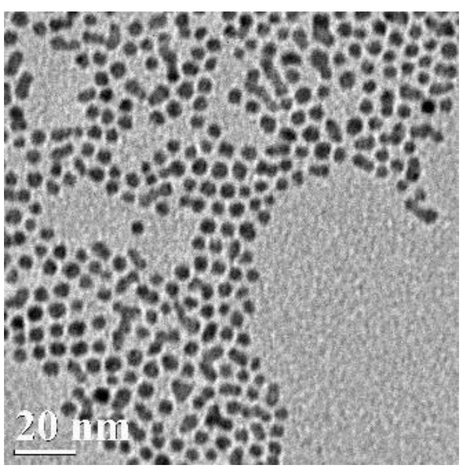


50 mg

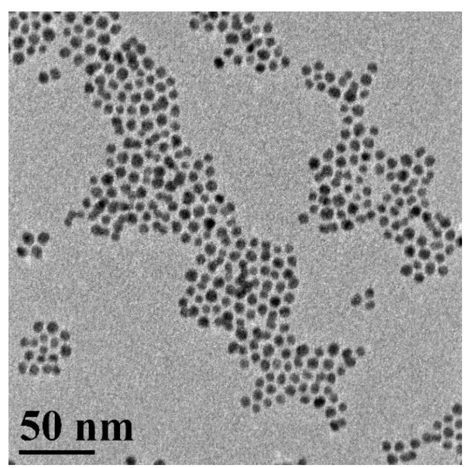


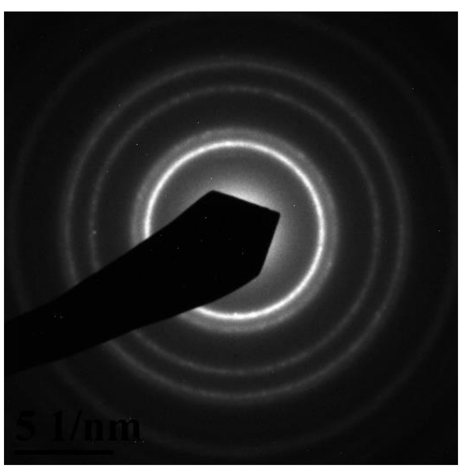


100 mg

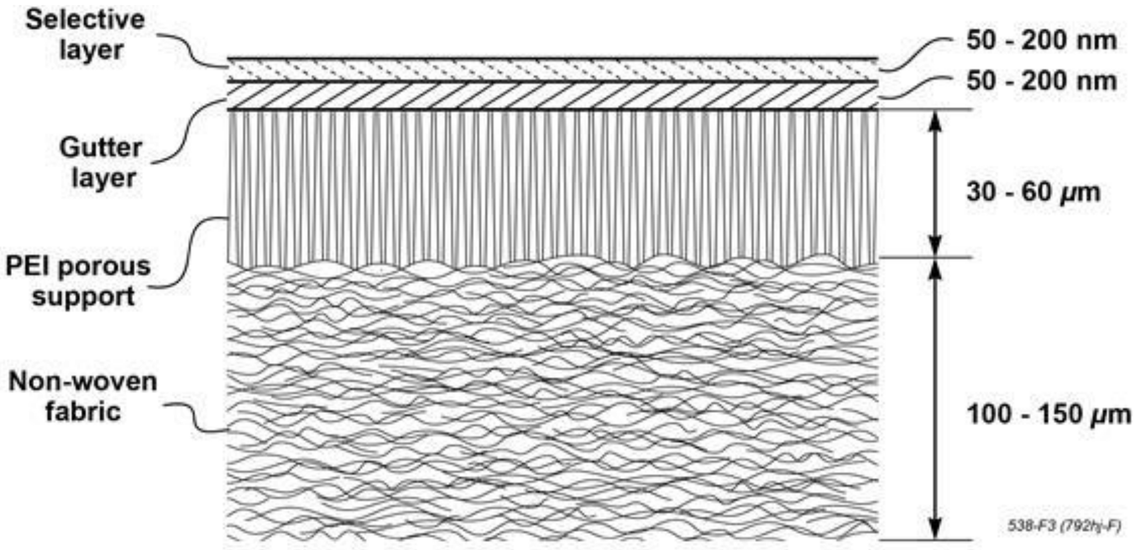


200 mg

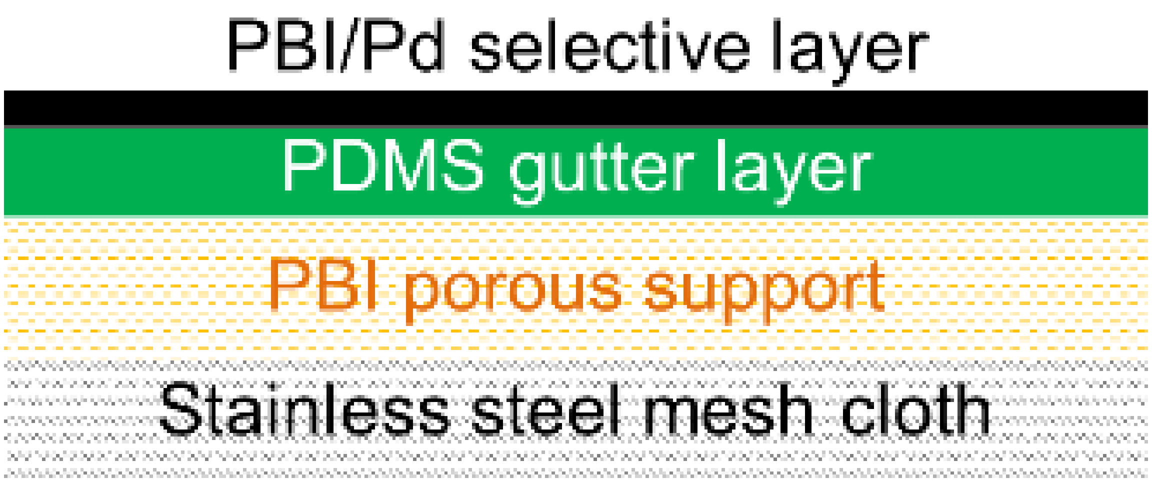




Thin Film Composite (TFC) Membranes



Conventional TFC membranes



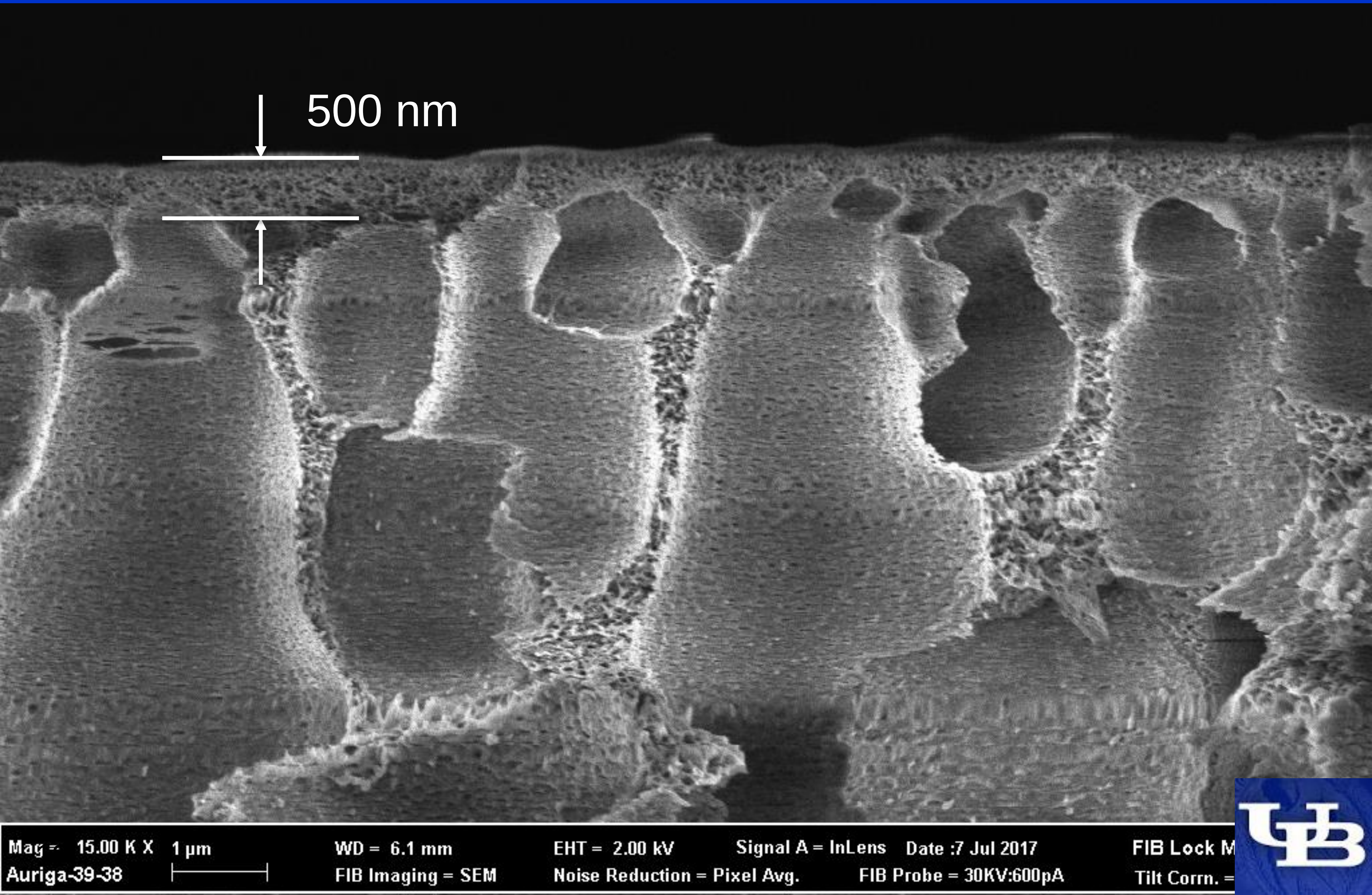
TFC membranes to be developed

Surface of PBI-supports: SEM Characterization

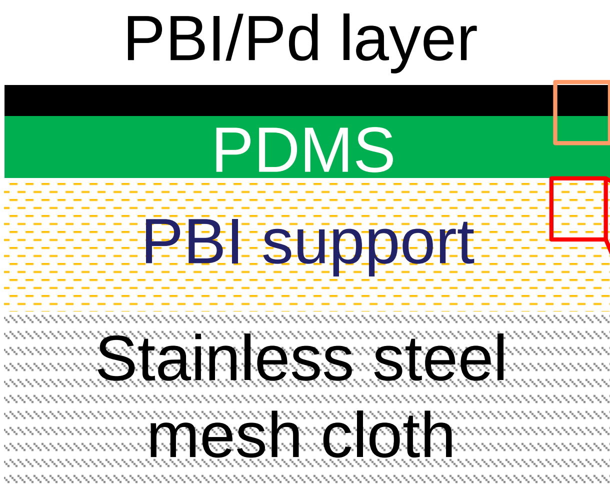
Aver. pore size: 14 nm

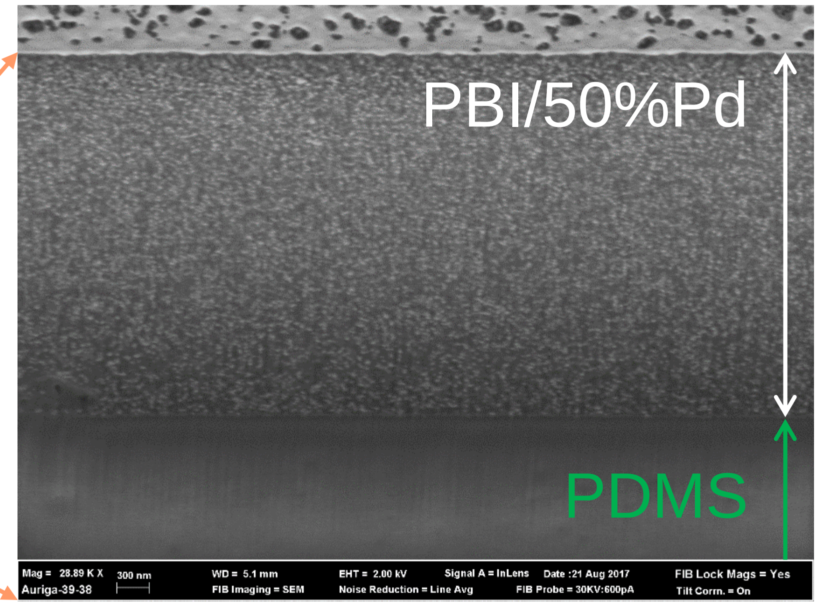
Surface porosity: ~15%

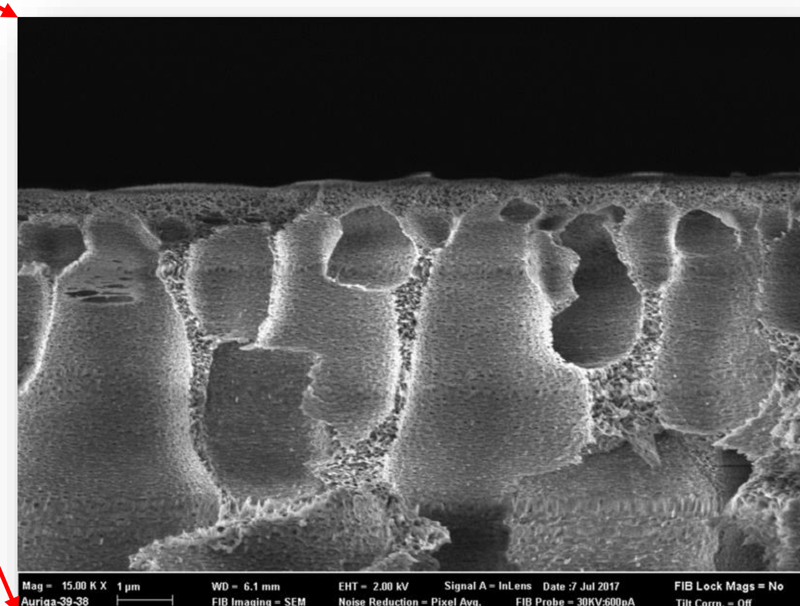
Cross-section of PBI-supports: SEM Characterization



Cross-sectional SEM of TFC Membranes



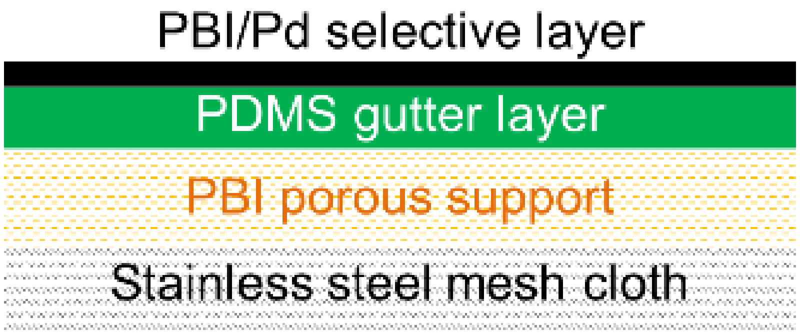




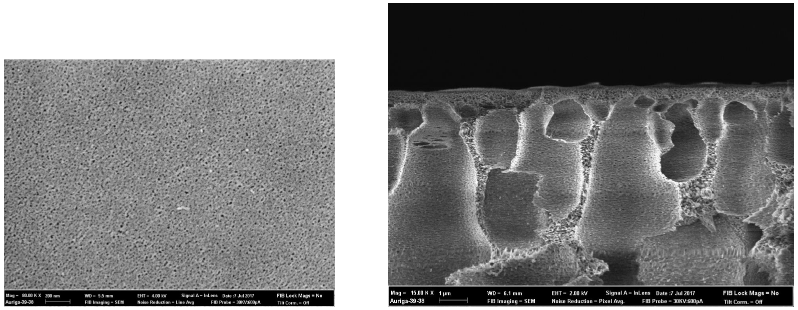
- 3-micro PBI/Pd selective layer
- Good compatibility between PDMS and PBI/Pd MMMs

Thin Film Composite (TFC) Membranes

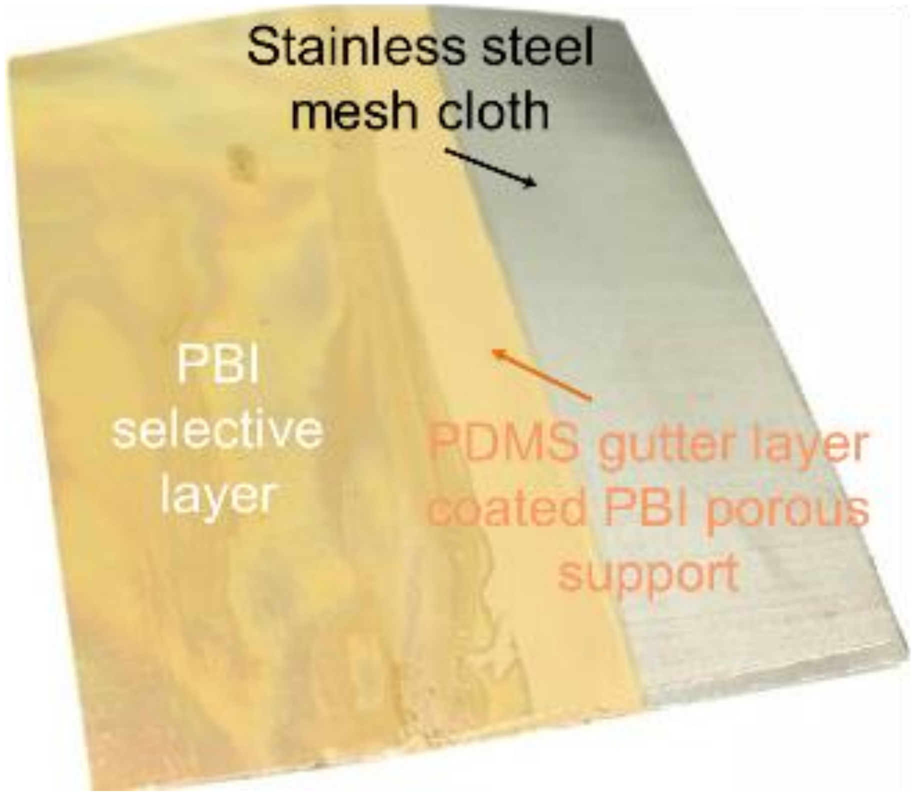
Schematic of TFC membranes



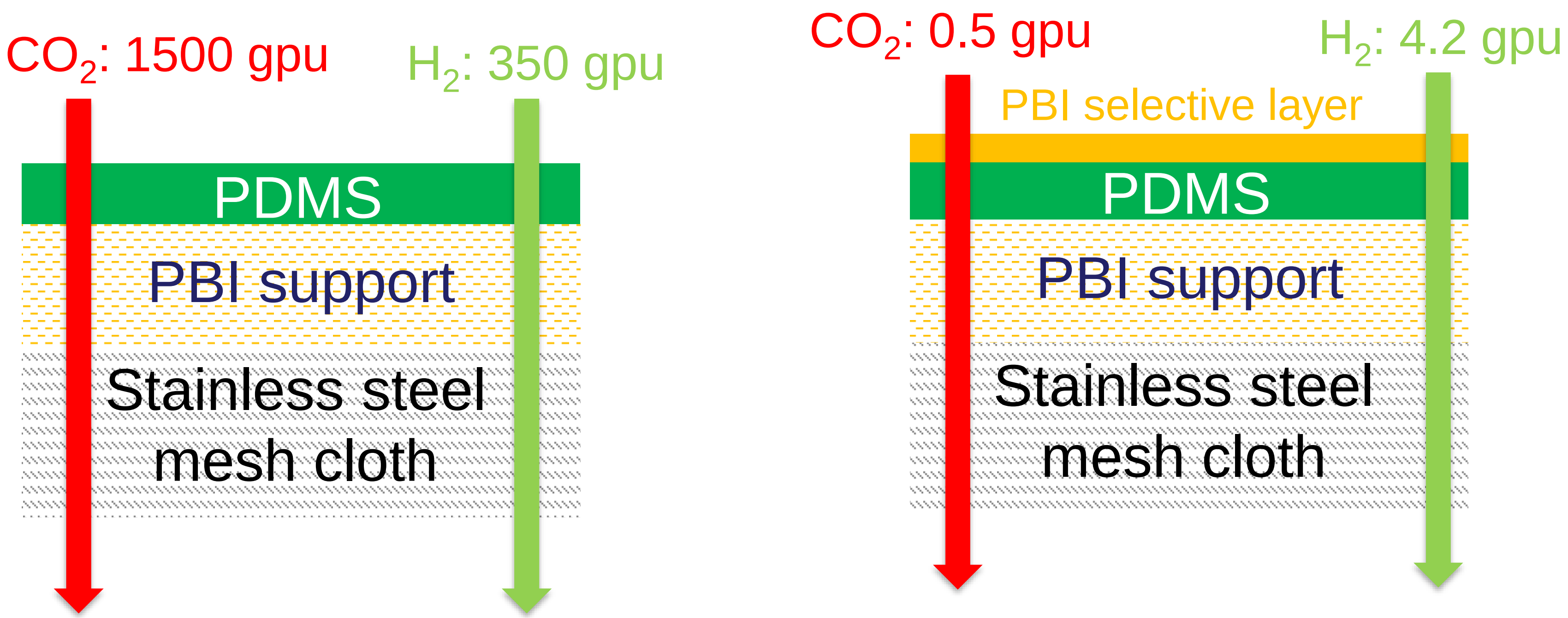
PBI porous support



PBI based TFC membranes



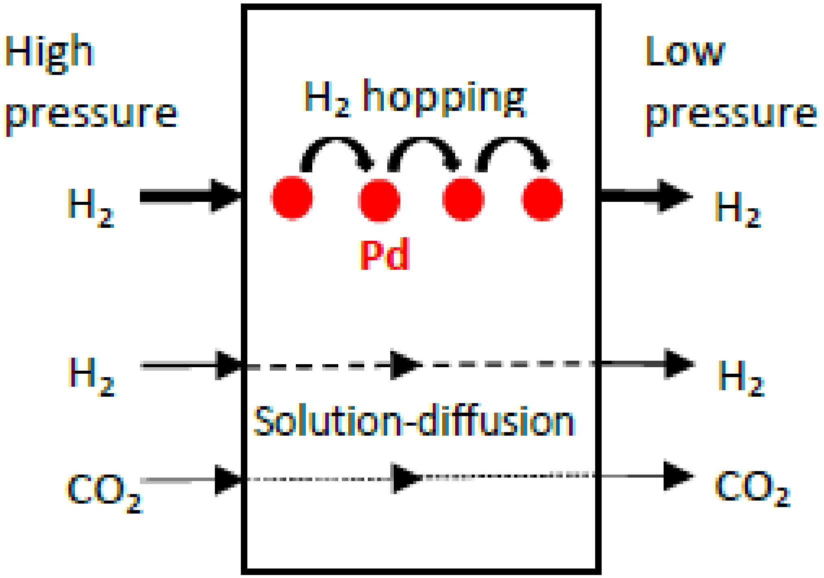
Gas Permeance in TFC Membranes

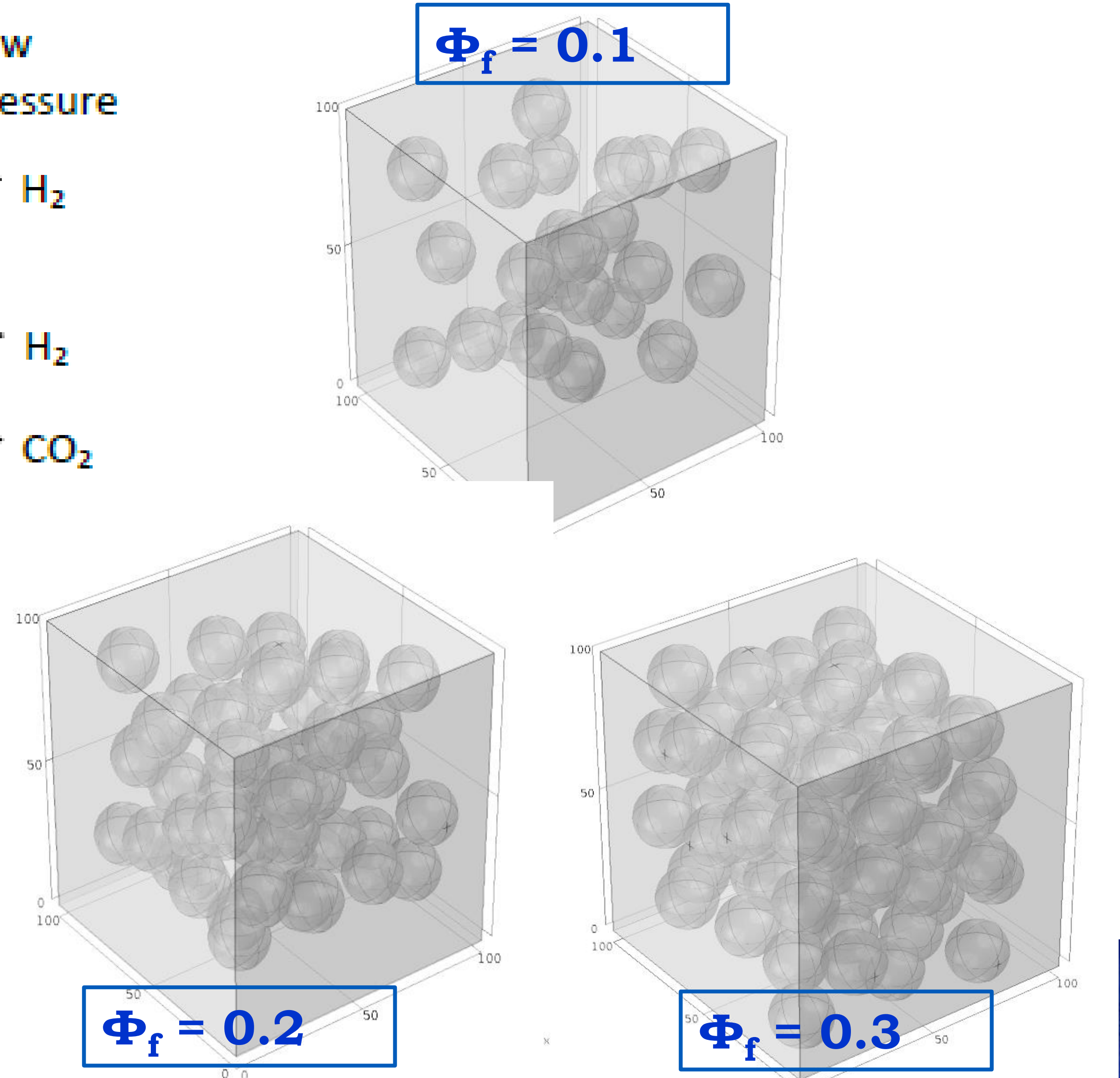


After O_2 plasma etching, we are able to apply PBI based coating solutions on the PDMS gutter layer.

Note: Gas permeance measured at 23 °C.

CFD Simulations of MMMs





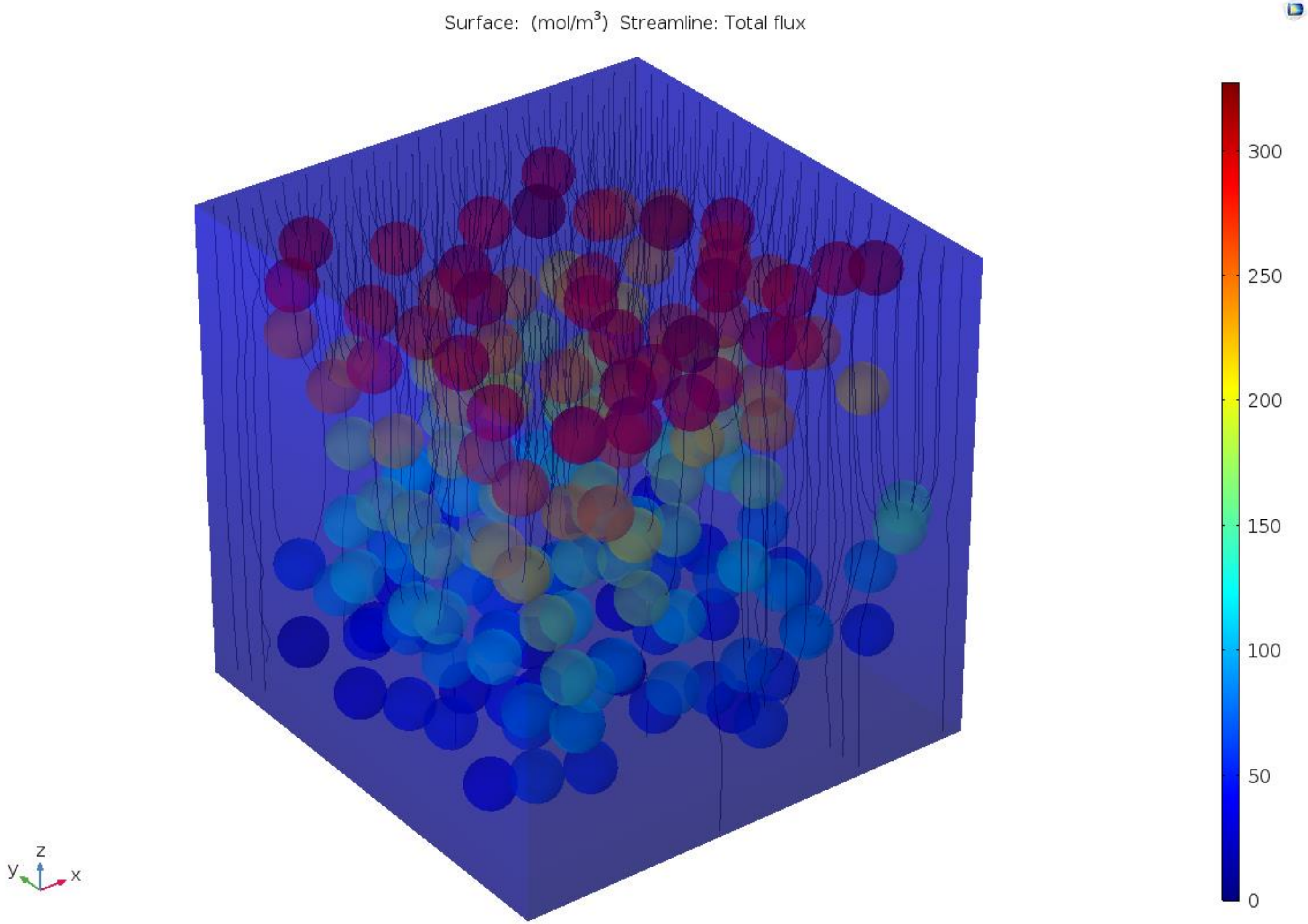
Simulation Parameters at 150 ºC

Parameters	PBI	Pd NPs
CO_2 solubility (cm^3 (STP)/(cm^3 atm)	0.46	**0**
CO_2 diffusivity (m^2/s)	3.1×10^{-12}	**0**
H_2 Solubility (cm^3 (STP)/(cm^3 atm)	0.12	**K_S = 500**
H_2 diffusivity (m^2/s)	1.7×10^{-10}	**5.1×10^{-10}**

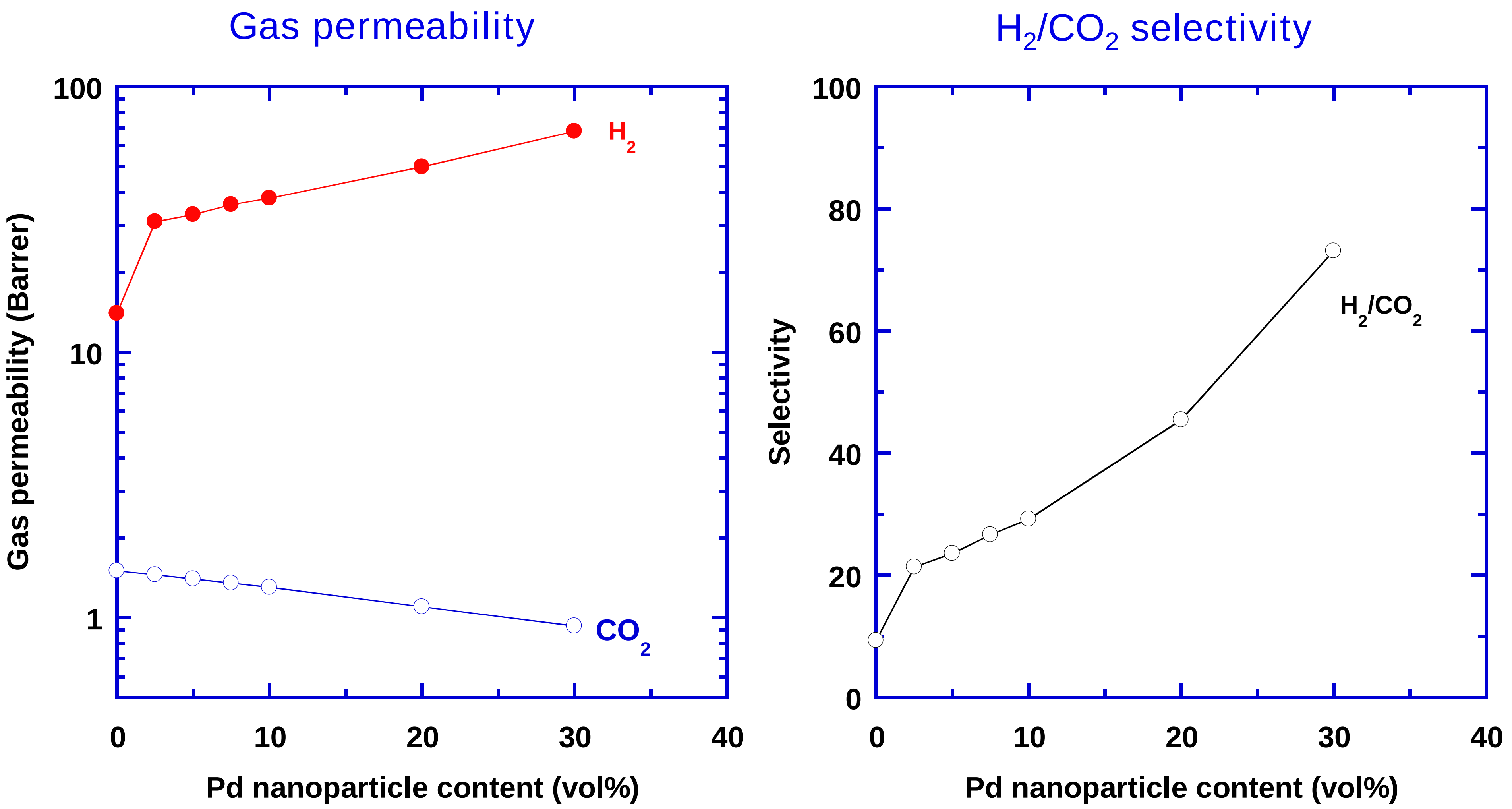
H_2 sorption in Pd:

$$C_{H_2,Pd} = K_S\sqrt{p_{H_2}}$$

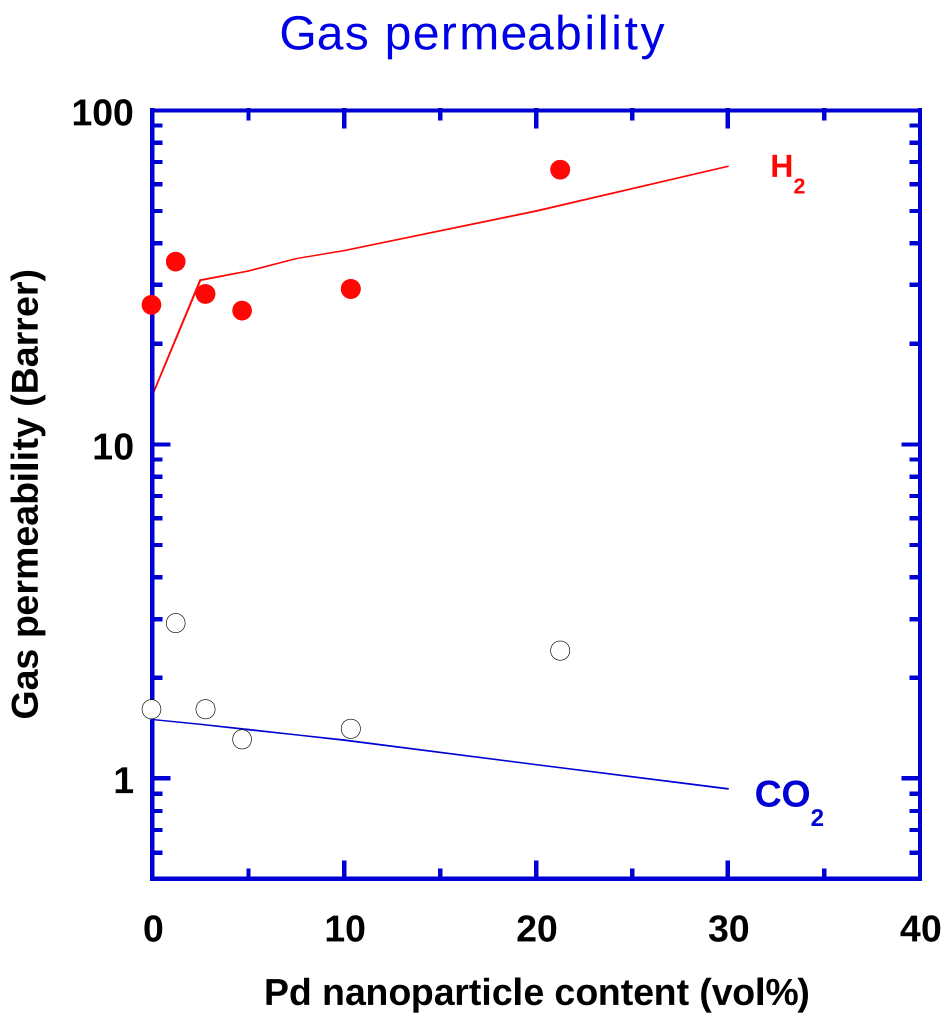
Modeling the Effect of Pd Nanoparticles on H_2 Permeability

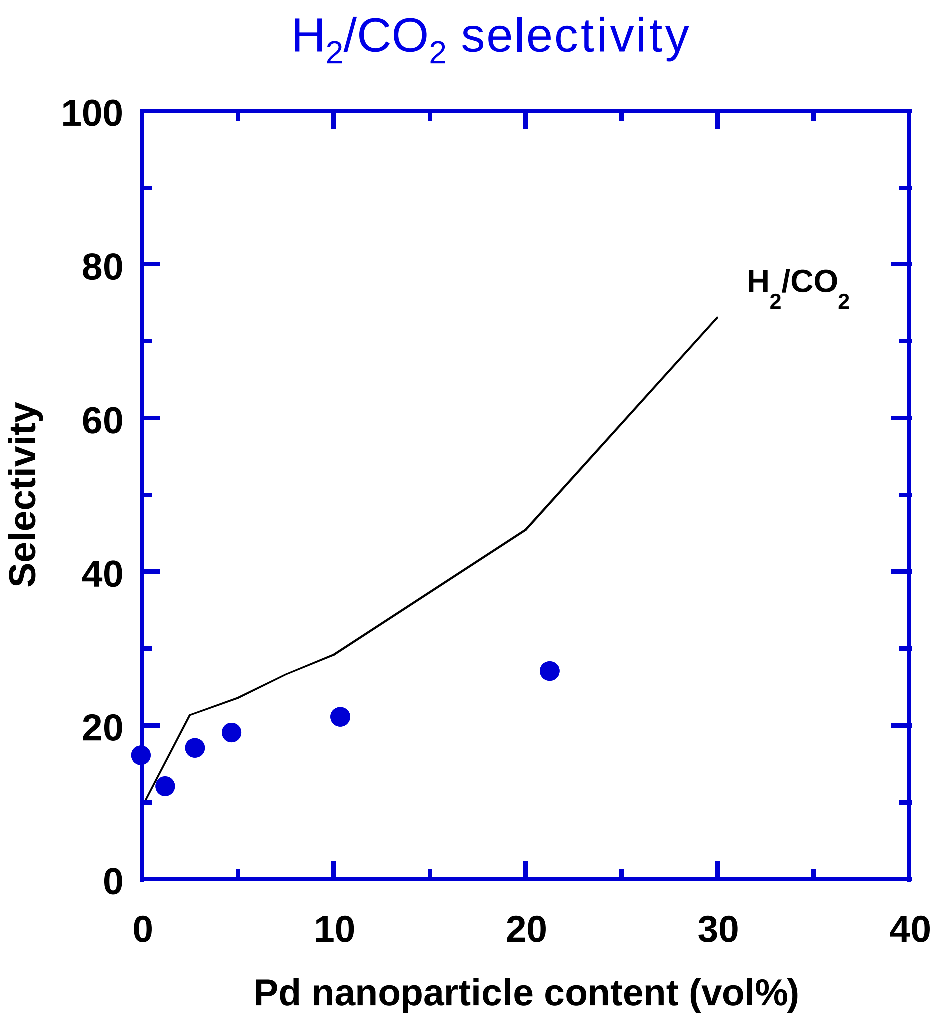


CFD Simulation of the Effect of Pd Loading on H_2/CO_2 Separation Properties



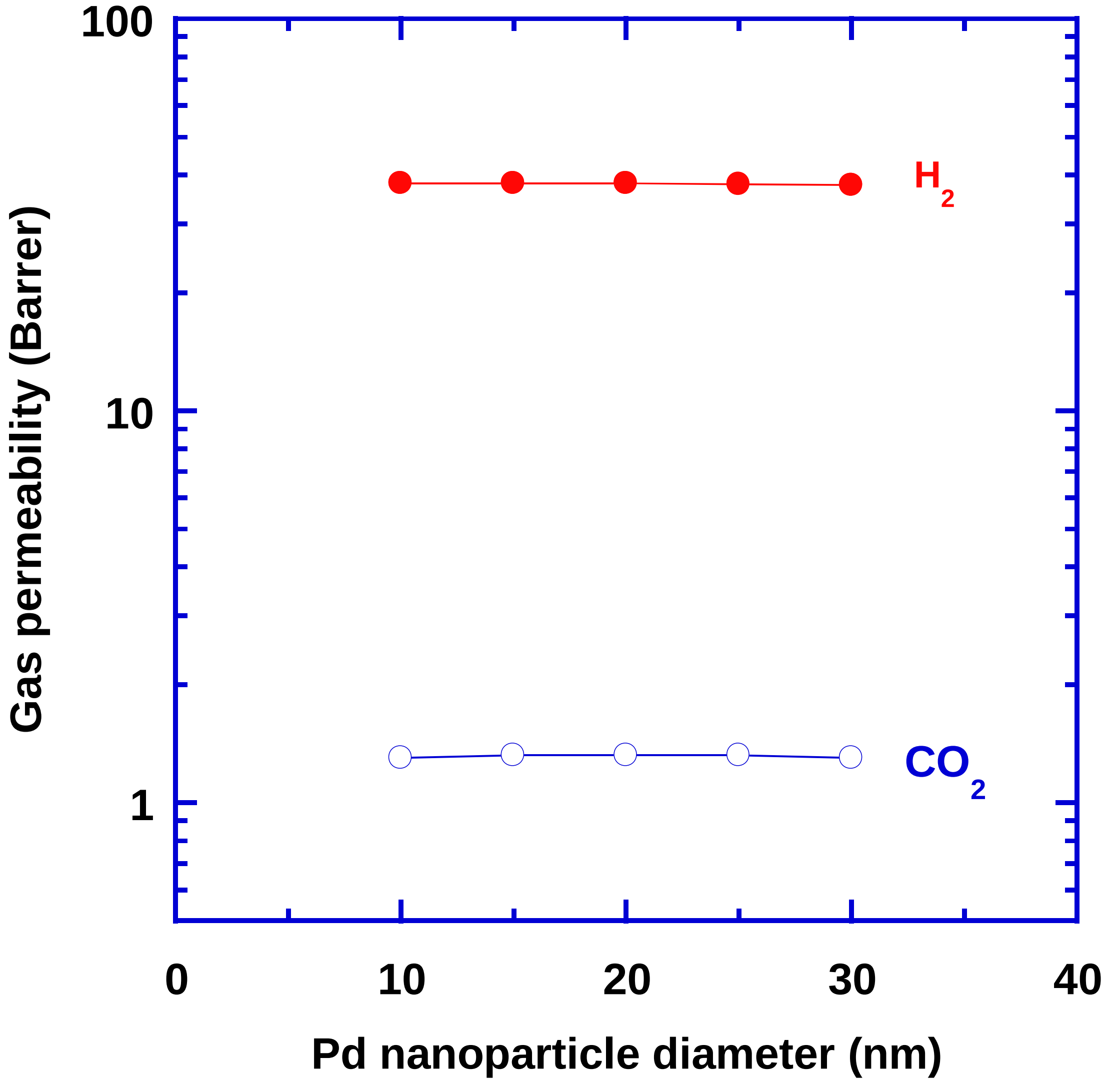
Comparison of Simulated and Experimental Results





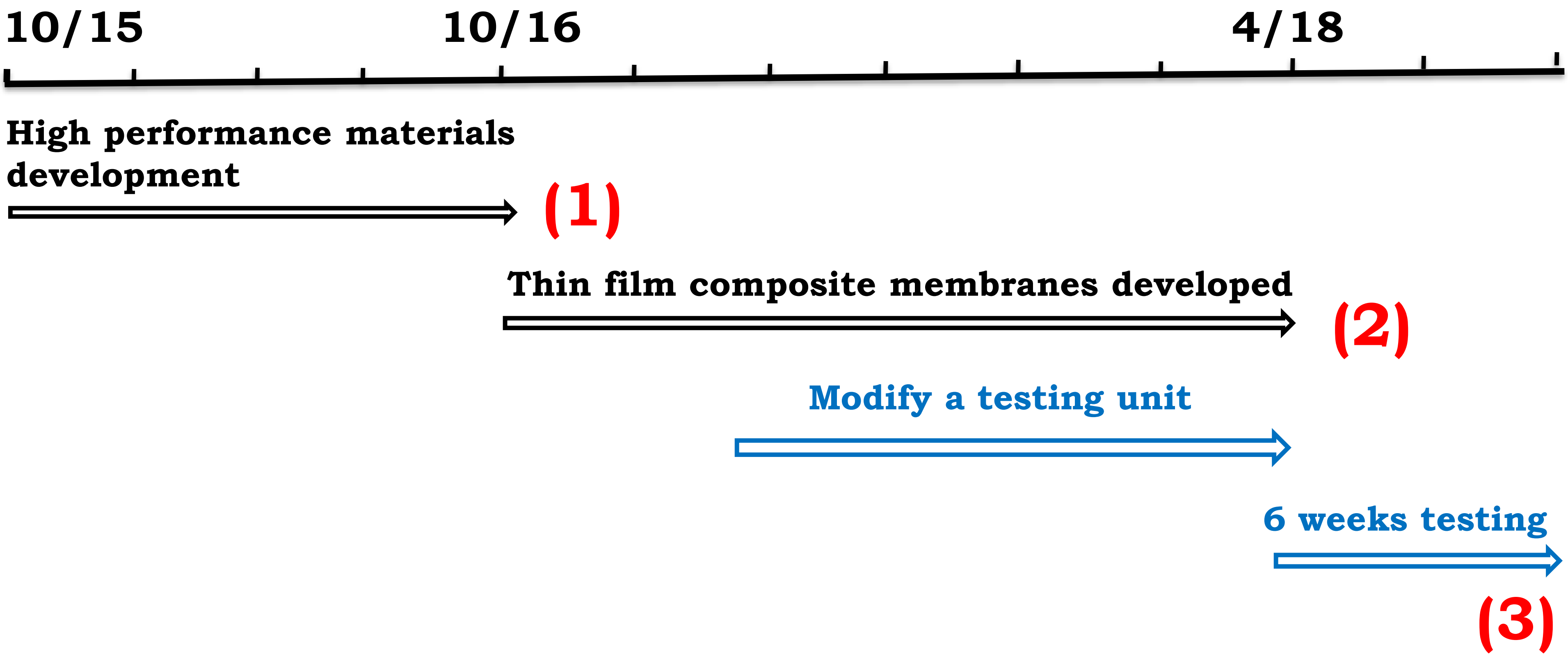
Symbol: experimental data
Curves: simulation data

Effect of Particle Size on Permeability



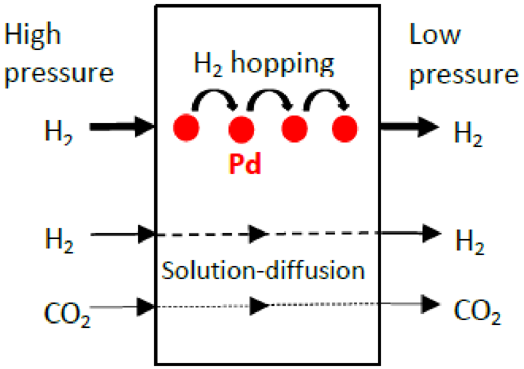
Volume fraction = 0.1

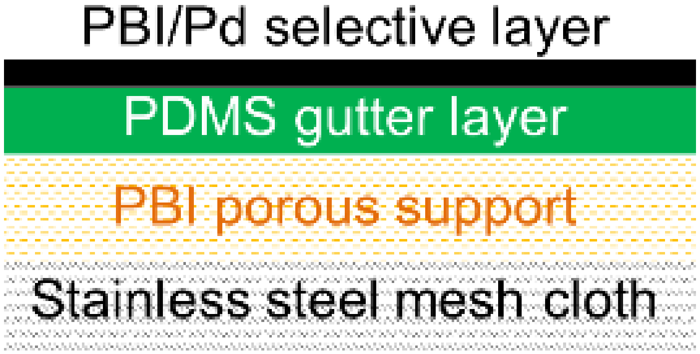
Project Plan and Milestones

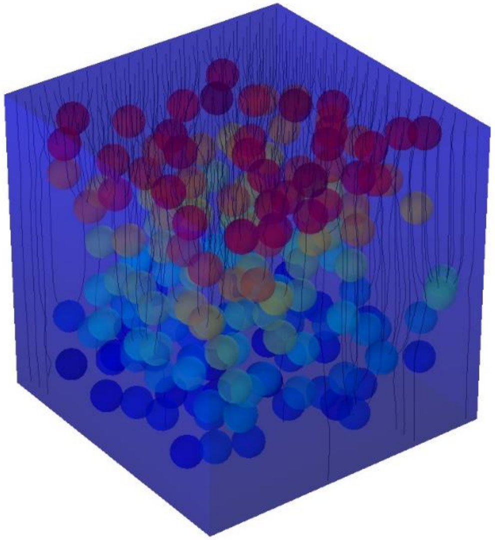


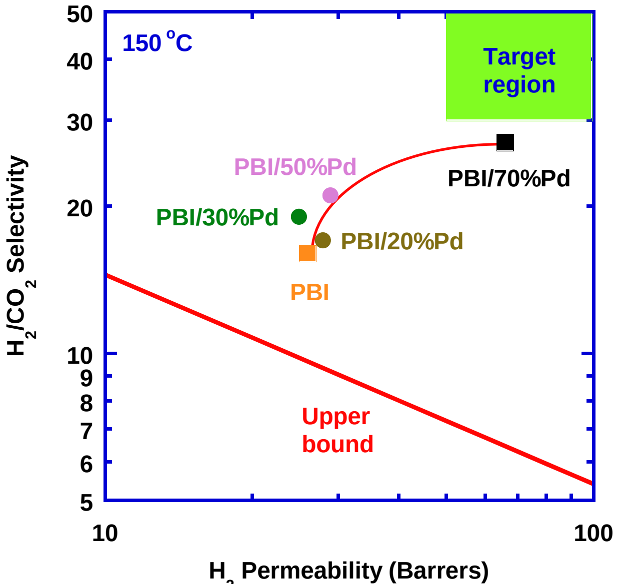
(1) High performance mixed matrix materials identified;
(2) High performance thin film composite membranes prepared; Testing skid modified;
(3) Parametric testing of membranes using real syngas

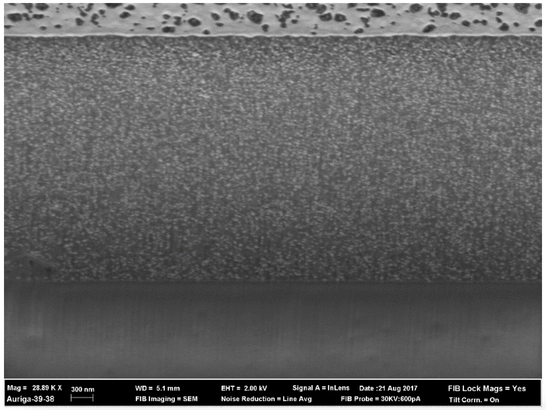
Summary

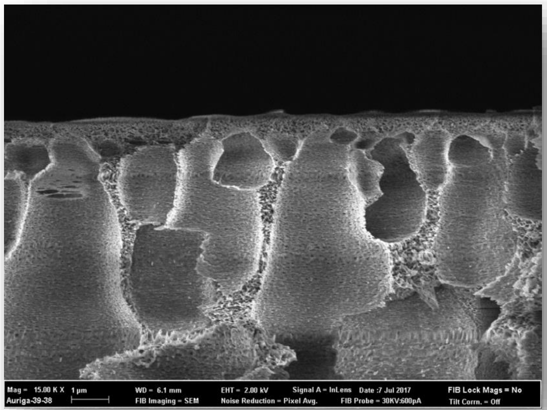

High pressure
Low pressure
H_2 hopping
H_2
Pd
H_2
H_2
H_2
Solution-diffusion
CO_2
CO_2

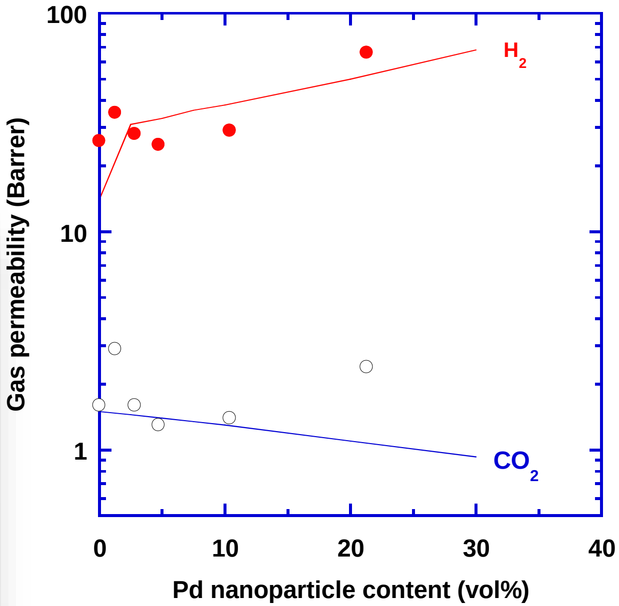

PBI/Pd selective layer
PDMS gutter layer
PBI porous support
Stainless steel mesh cloth




150 °C
Target region
PBI/50%Pd
PBI/70%Pd
PBI/30%Pd
PBI/20%Pd
PBI
Upper bound
H_2/CO_2 Selectivity
H_2 Permeability (Barrers)
50
40
30
20
10
9
8
7
6
5
10
100






H_2
CO_2
Gas permeability (Barrer)
Pd nanoparticle content (vol%)
100
10
1
0
10
20
30
40

Acknowledgments

Steve Mascaro
Elaine Everitt

Mark Swihart's research group

Tim Merkel
Jay Kniep