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

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[3]National Carbon Capture Center, Wilsonville, AL **(NCCC)**

NETL CO_2 Capture Technology Project Review Meeting
Pittsburgh, PA
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Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture

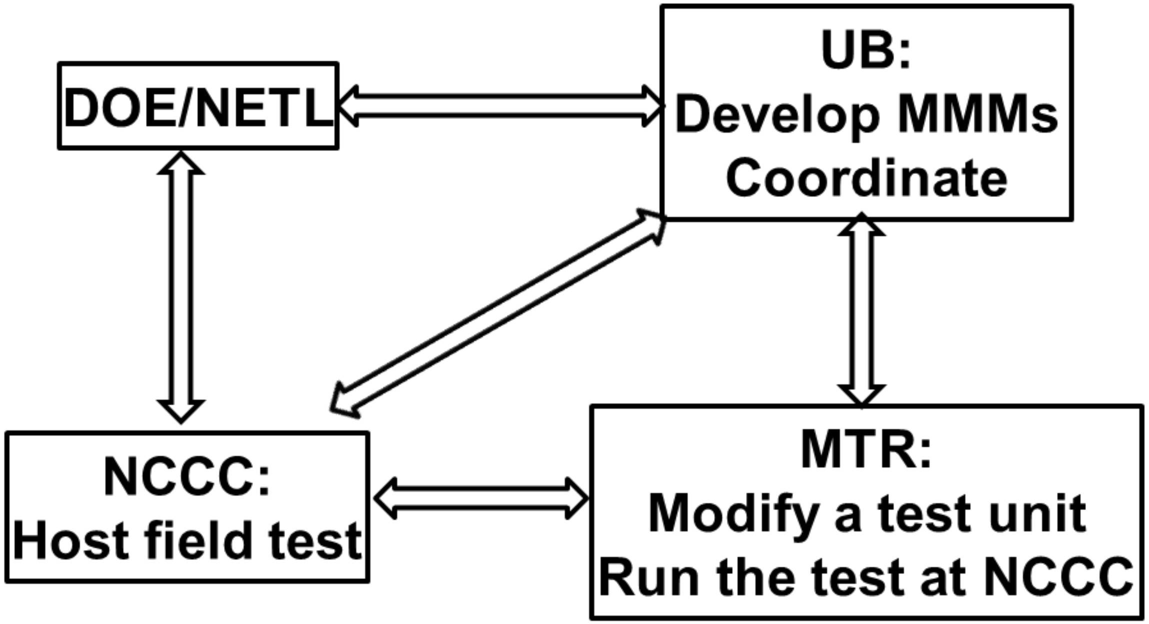
Award number:	DE-FE0026463
Project period:	10/1/15 to 9/30/18
Funding:	$1,470,099 DOE $ 373,004 UB and MTR contribution $1,843,103 total
Program manager:	Steve Mascaro (previously Elaine Everitt)
Participants:	University at Buffalo (**UB**) Membrane Technology and Research, Inc. (**MTR**), and National Carbon Capture Center (**NCCC**)
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 at NCCC.

Project Scope and Partners

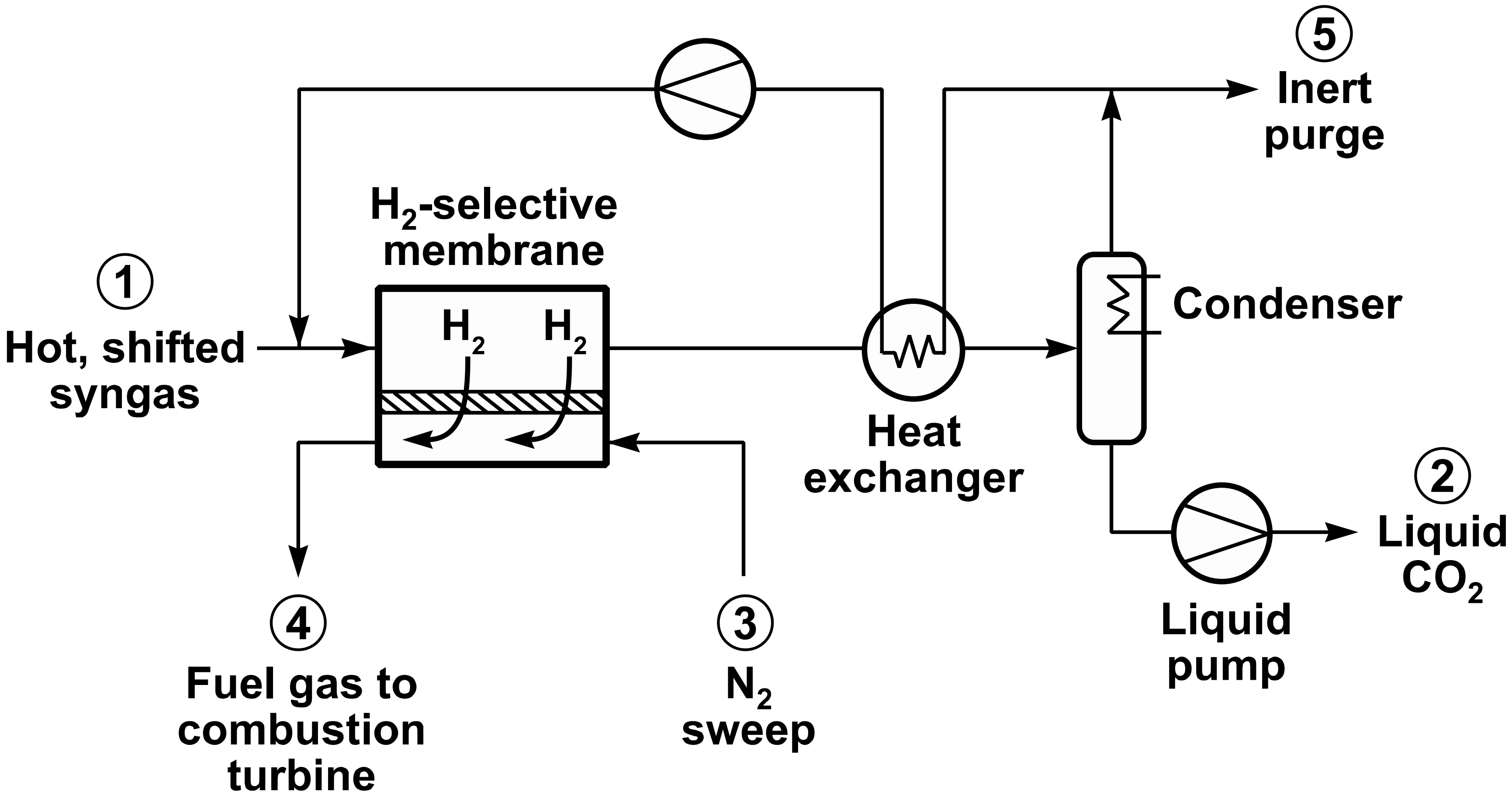
BP1: Prepare mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 **(Q1-Q4)**

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 at NCCC **(Q11-Q12)**

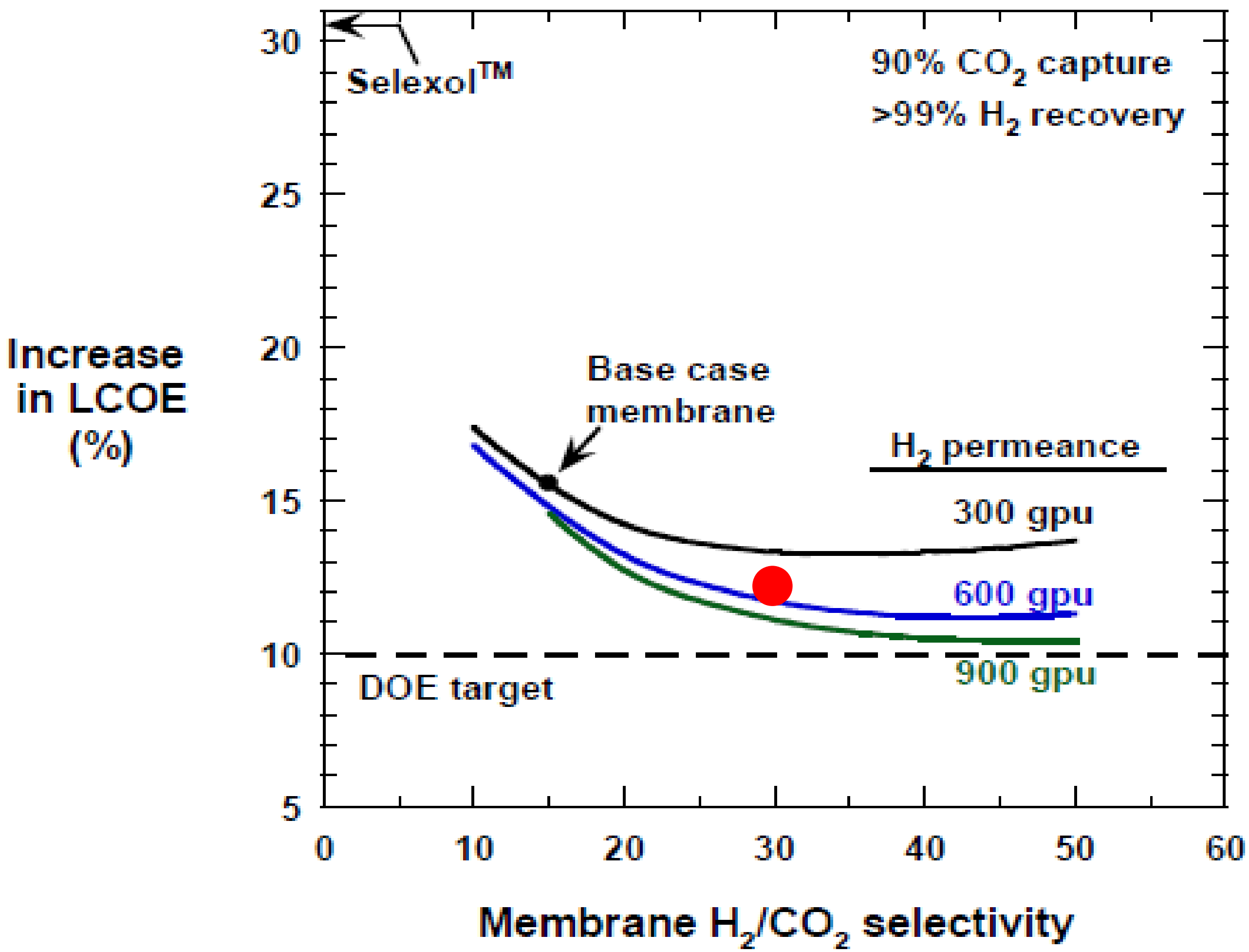


MTR's Exampled Membrane Process for Precombustion CO_2 Capture



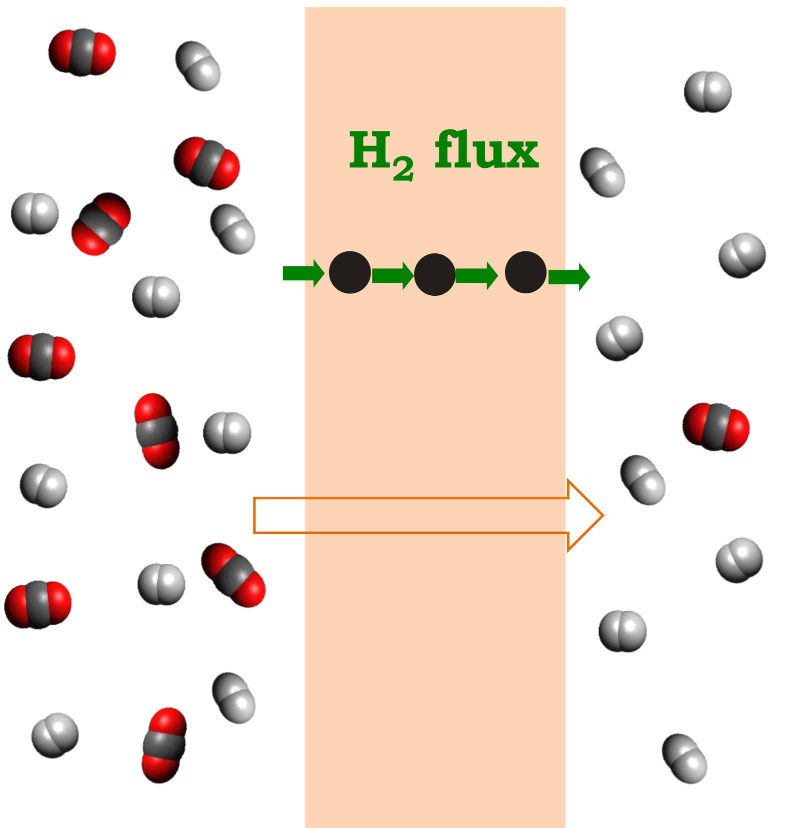
Merkel, Zhou and Baker, J. Membr. Sci., 389, 442 (2012)
Merkel, et al., NETL CO_2 Capture Technology Review Meeting, 2011.

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.

Membrane: Energy Efficient Separation



$$P_A = S_A \times D_A$$

Materials with high H_2 sorption

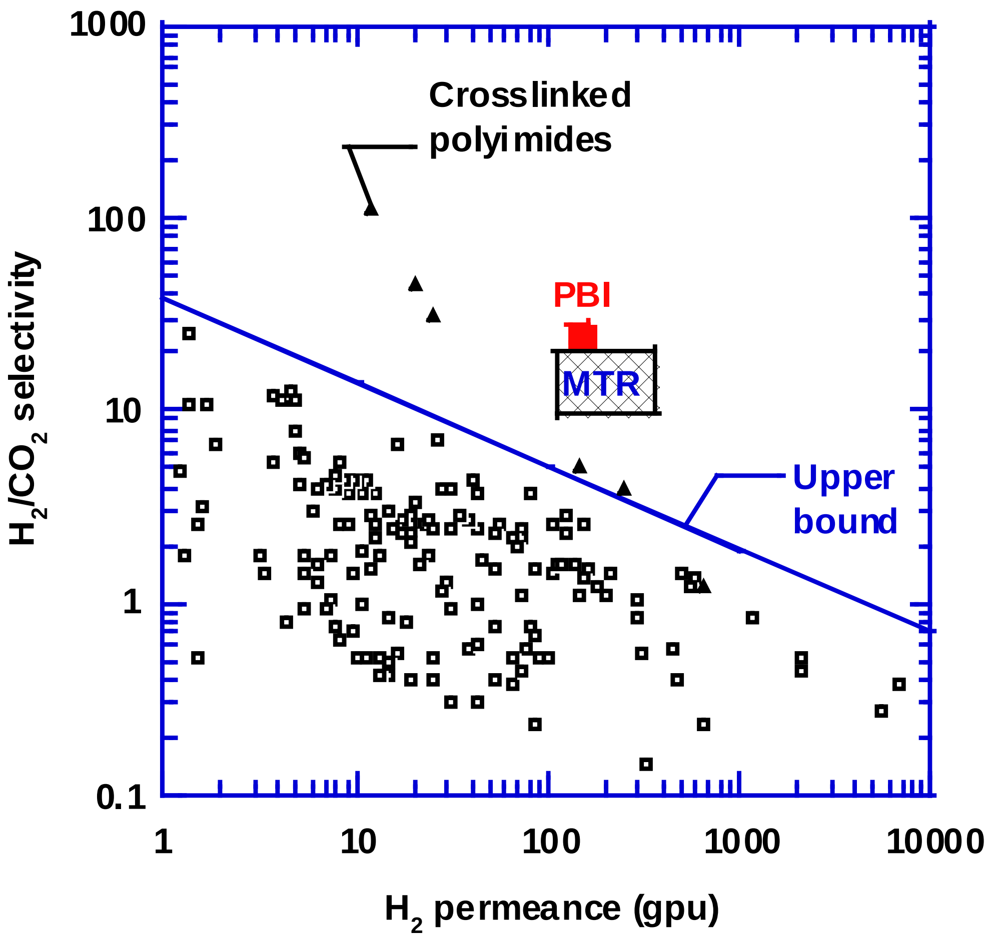
solubility selectivity

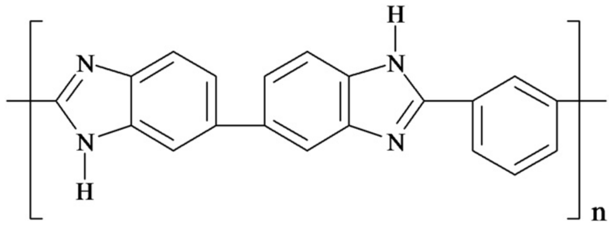
$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right) \times \left(\frac{D_A}{D_B}\right)$$

diffusivity selectivity

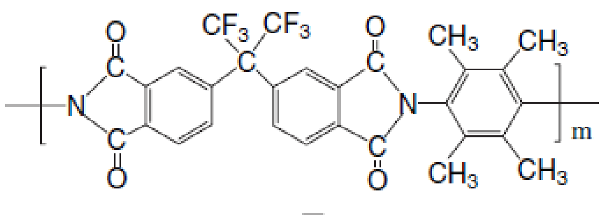
Materials with good size-sieving ability

State-of-Art Membrane Materials





Berchtold, et al., NETL CO_2 Capture Technology Meeting, 2015.
Jayaweera, et al., NETL CO_2 Capture Technology Meeting, 2015.



L. Shao, et al., J. Membr. Sci., 256 (2005) 46-56.

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

Our Approach: H_2/CO_2 Solubility Selectivity

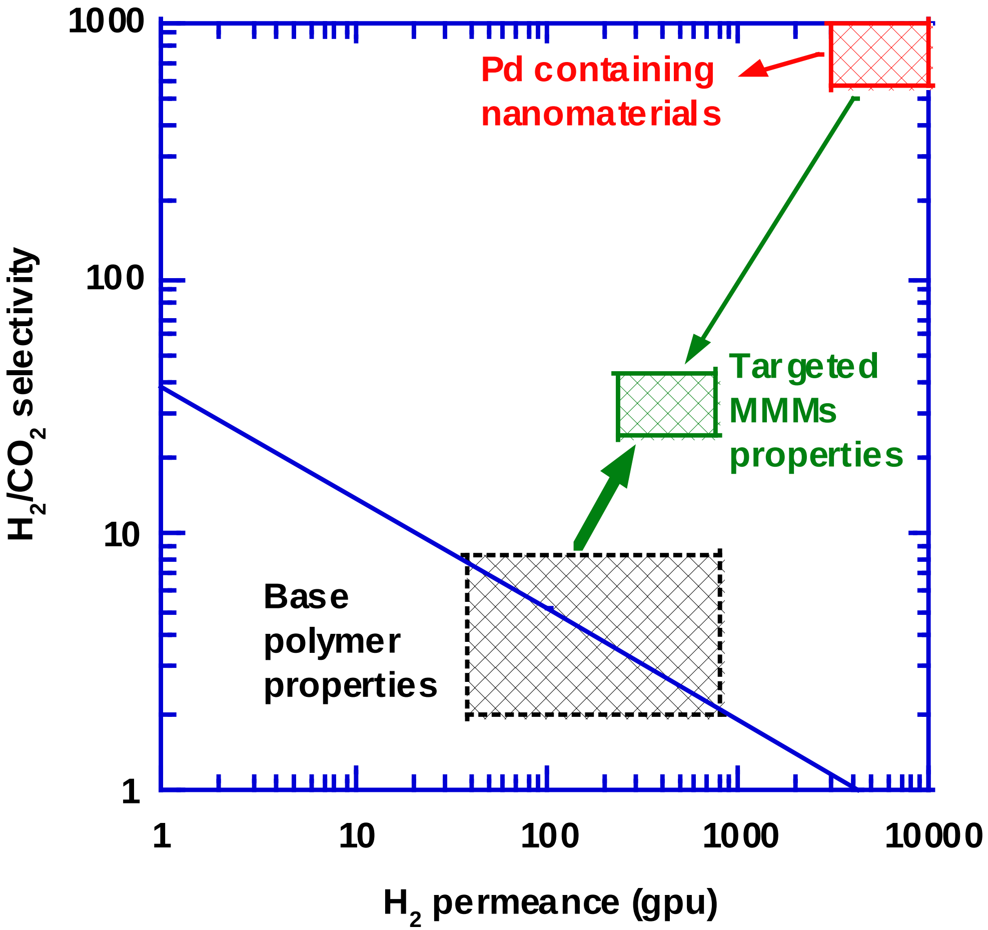
$$\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}$$

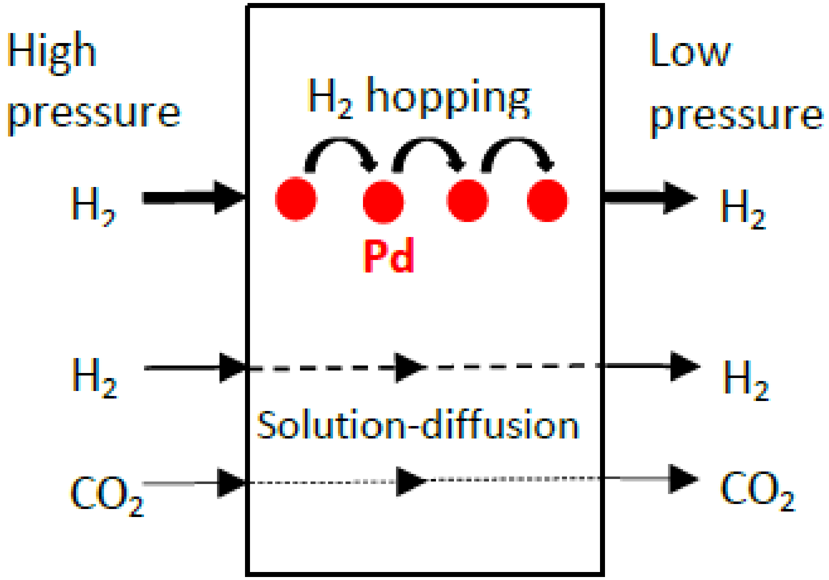
Materials	Temp. (°C)	H_2 solubility $cm^3(STP)/(cm^3\ atm)$	H_2/CO_2 solubility selectivity
Poly(dimethyl siloxane)	35	0.10	0.078
Polysulfone	35	0.075	0.036
Matrimid®	35	0.12	0.035
Pd metal*	**25**	**38,000**	**> 1,000**

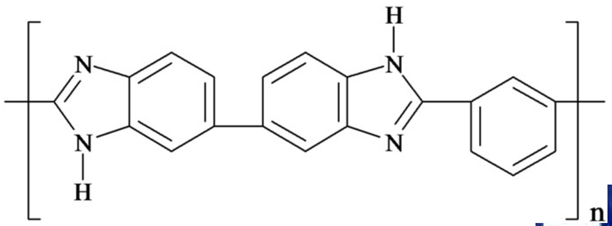
* Calculated at 0.02 bar H_2

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

Our Approach:
Mixed Matrix Materials







Project Plan and Milestones

10/15 **10/16** **4/18**

High performance materials development → **(1)**

Thin film composite membranes developed → **(2)**

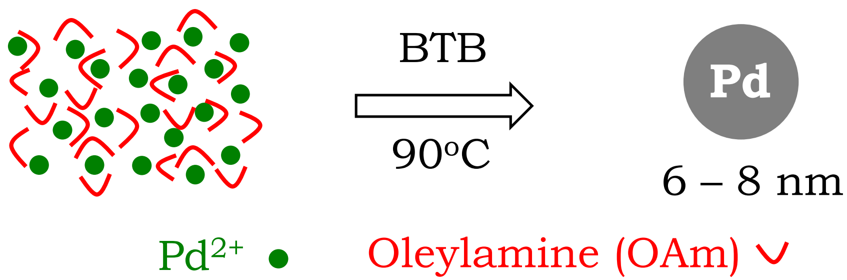
Modify a testing unit at NCCC →

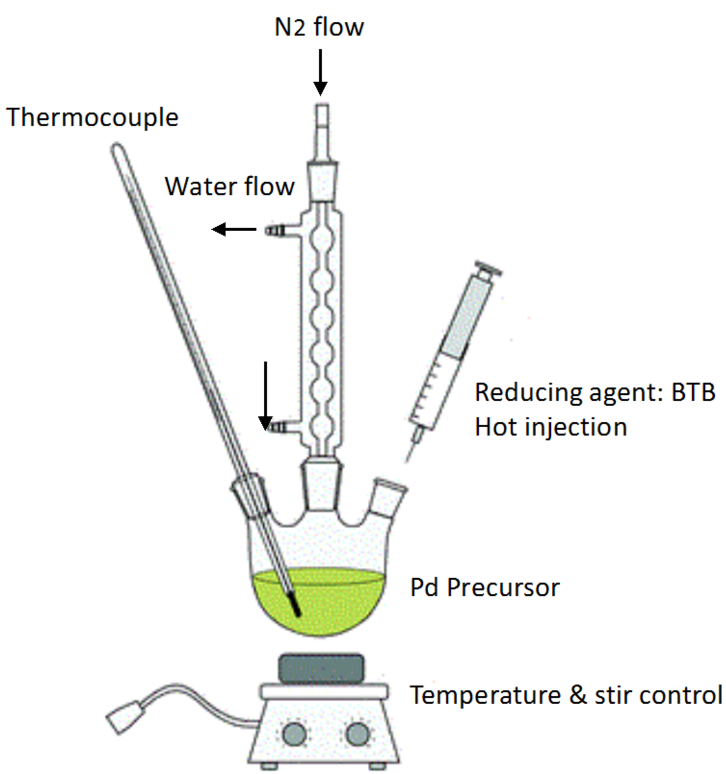
6 weeks testing → **(3)**

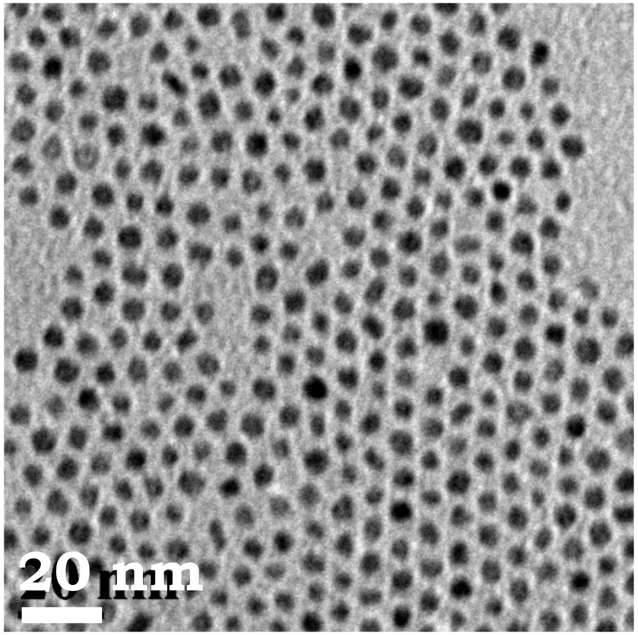
(1) High performance mixed matrix materials identified;
(2) High performance thin film composite membranes prepared;
Testing skid modified at NCCC;
(3) Parametric testing of membranes

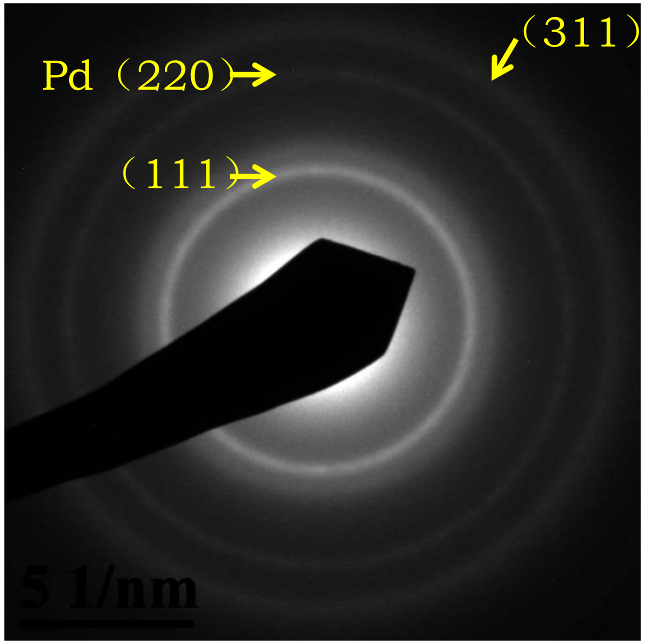
Preparation and Characterization of Pd Nanoparticles

Hot-injection method

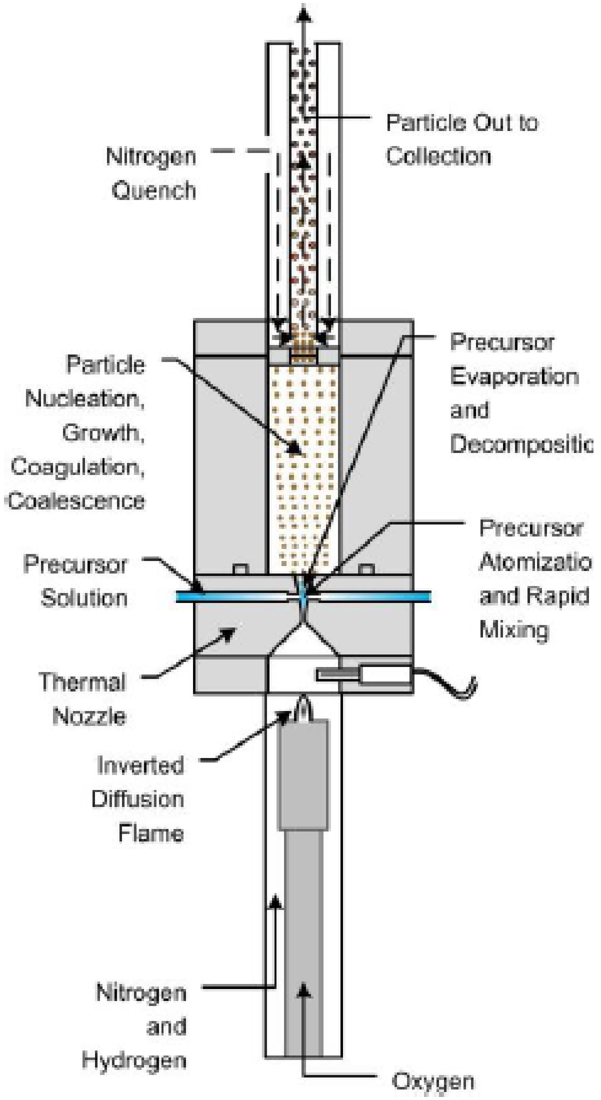




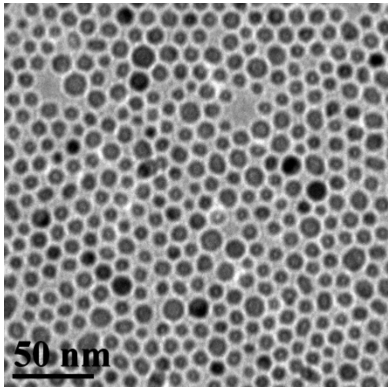


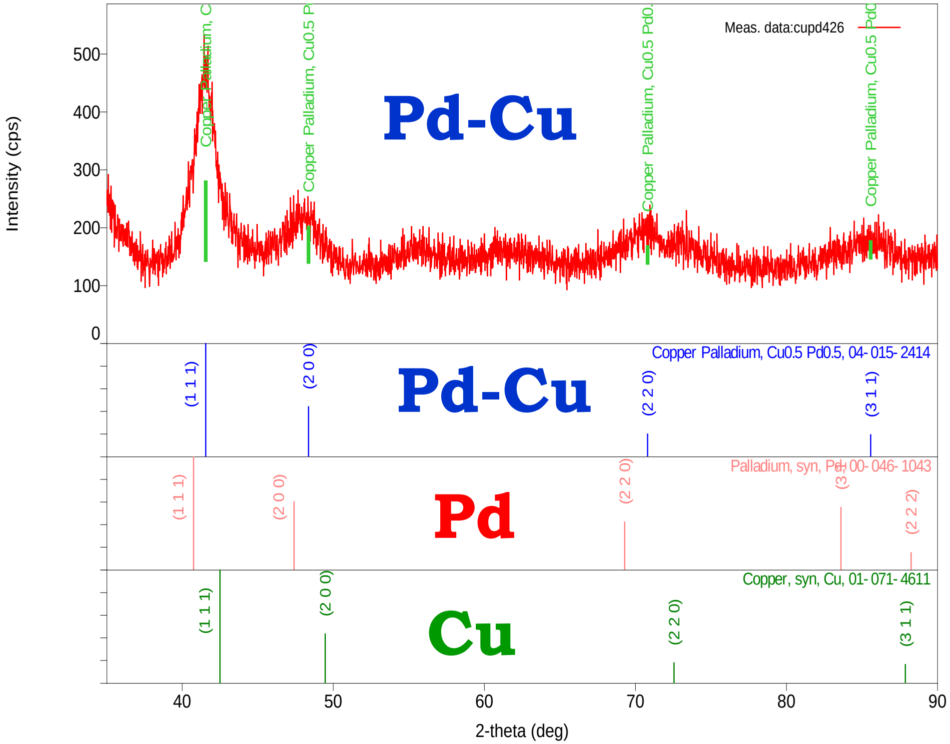


Preparation and Characterization of Pd-Cu (60/40) Alloy Nanoparticles



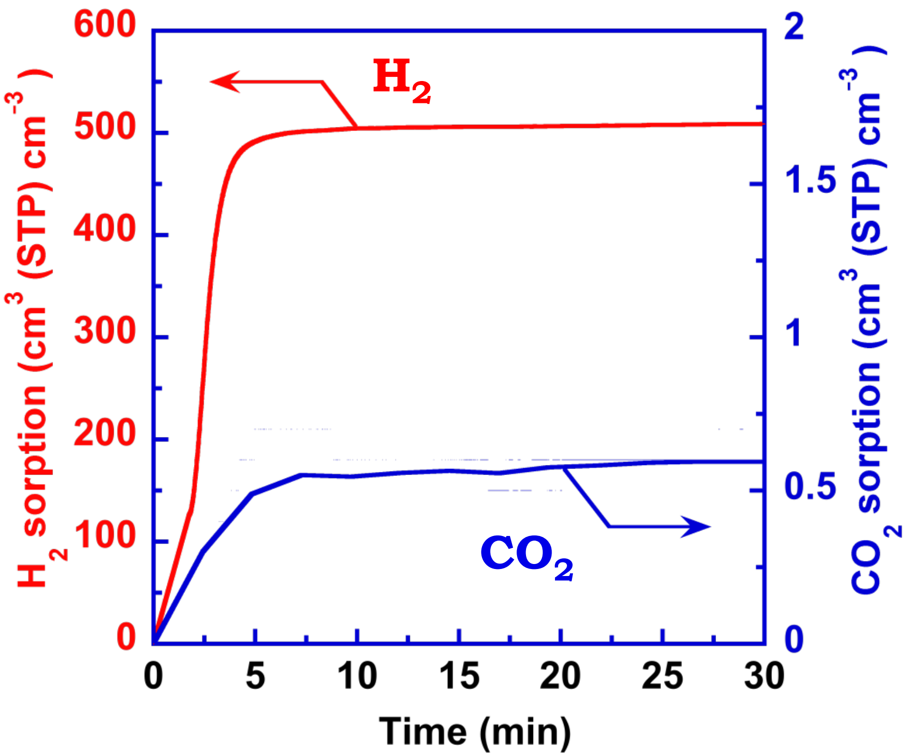
High Temperature Reactor Jet system



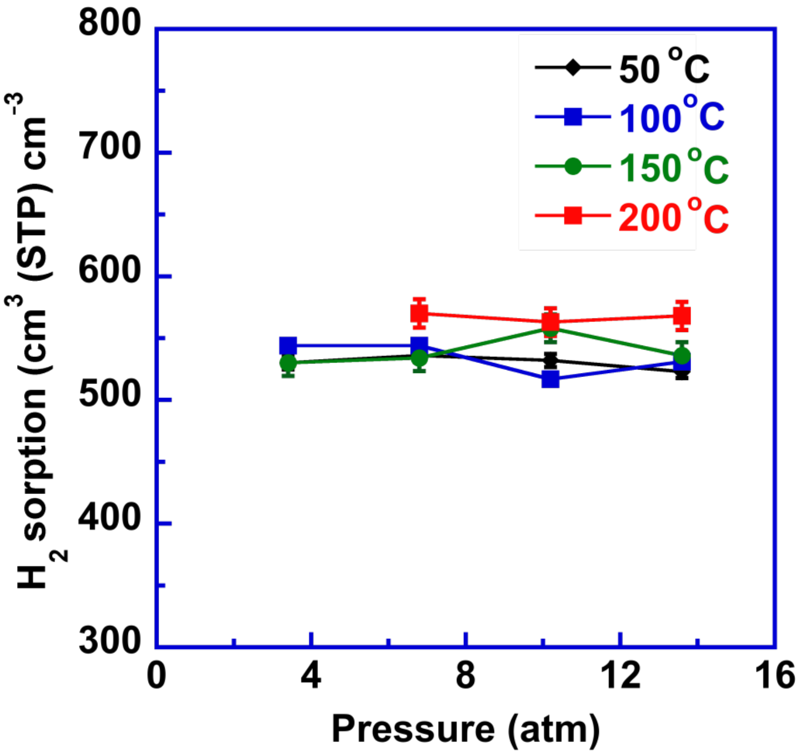


Gas Sorption in Pd Nanoparticles

Gas sorption vs. time at 1 atm/50°C

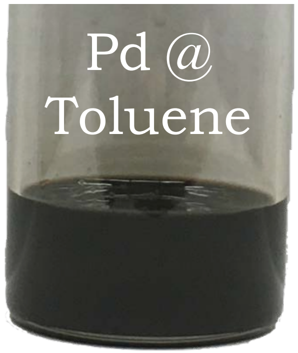


H_2 sorption at different temperatures

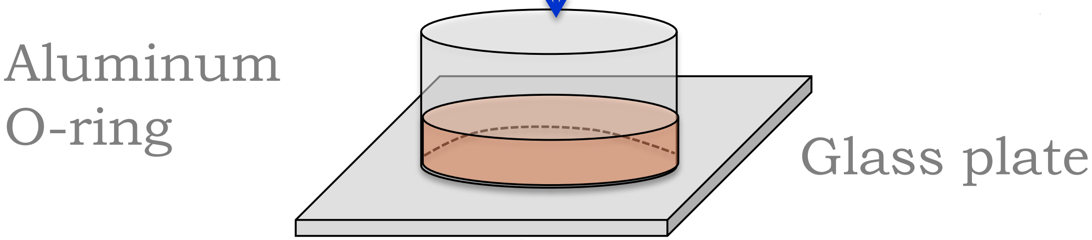


- **Extremely high H_2/CO_2 solubility selectivity (~ 840)**
- **H_2 chemisorption: independent of gas pressure**

Preparation of PBI/Pd Mixed Matrix Materials



Mixing & Sonication
(Toluene/DMAc co-solvent system)

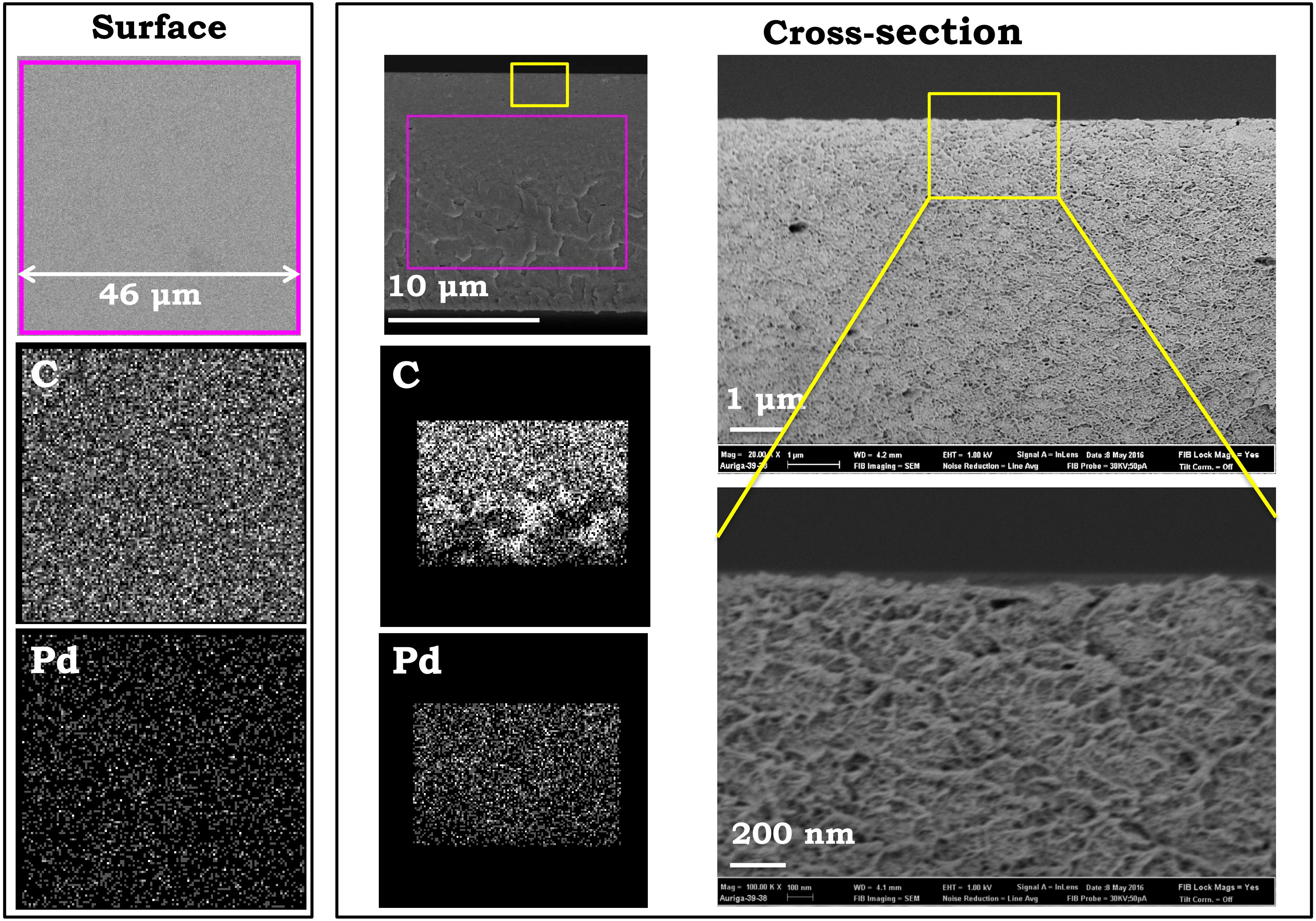


a. 60 ^{o}C/24 h
b. Vacuum at 120 ^{o}C/12 h

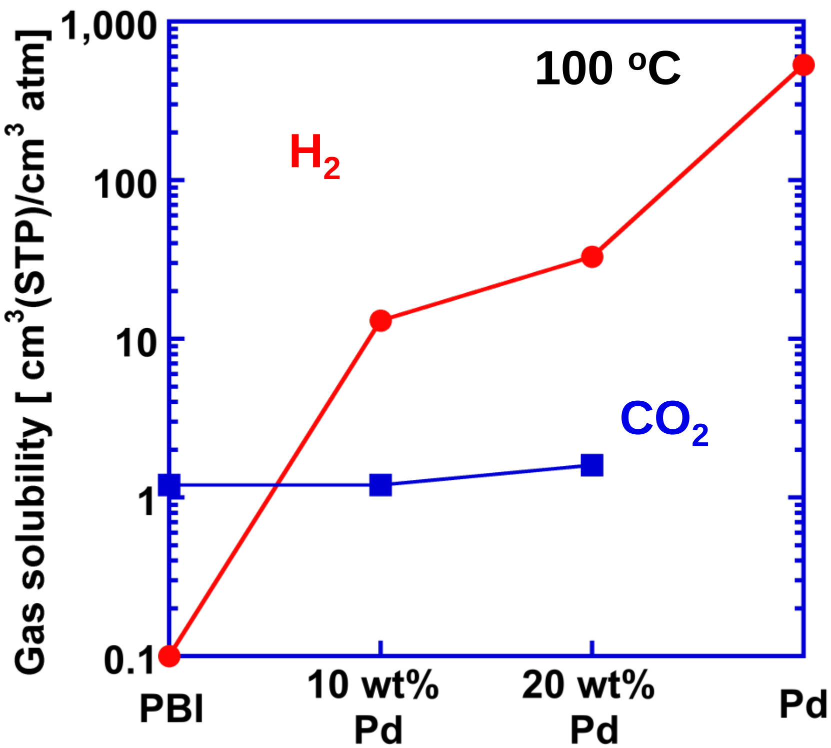
PBI/Pd (10 – 70 wt%) MMMs

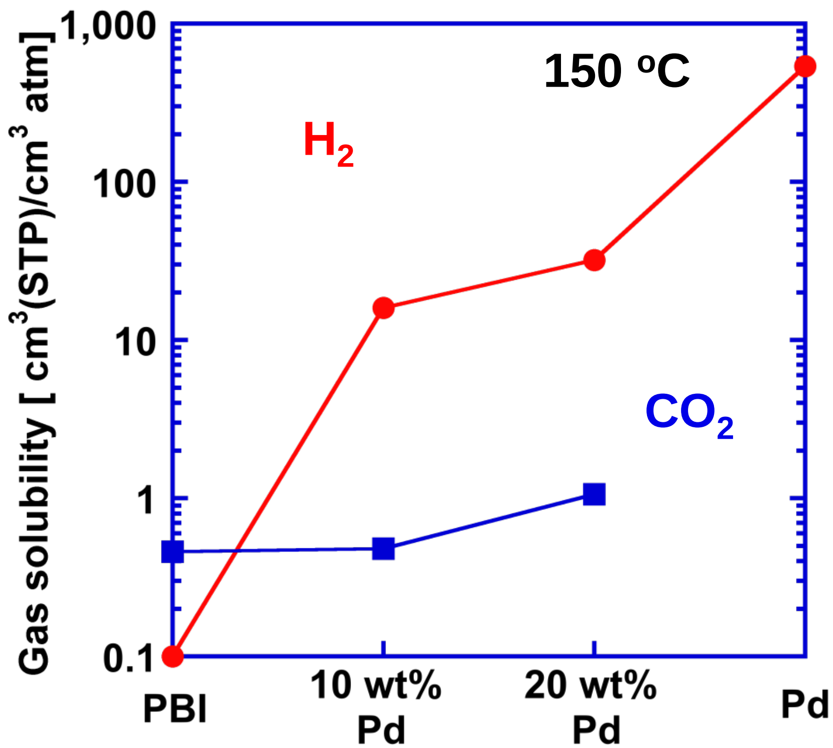
Pure PBI

SEM - EDS Mapping of PBI/30%Pd



Adding Pd increases H_2/CO_2 solubility selectivity

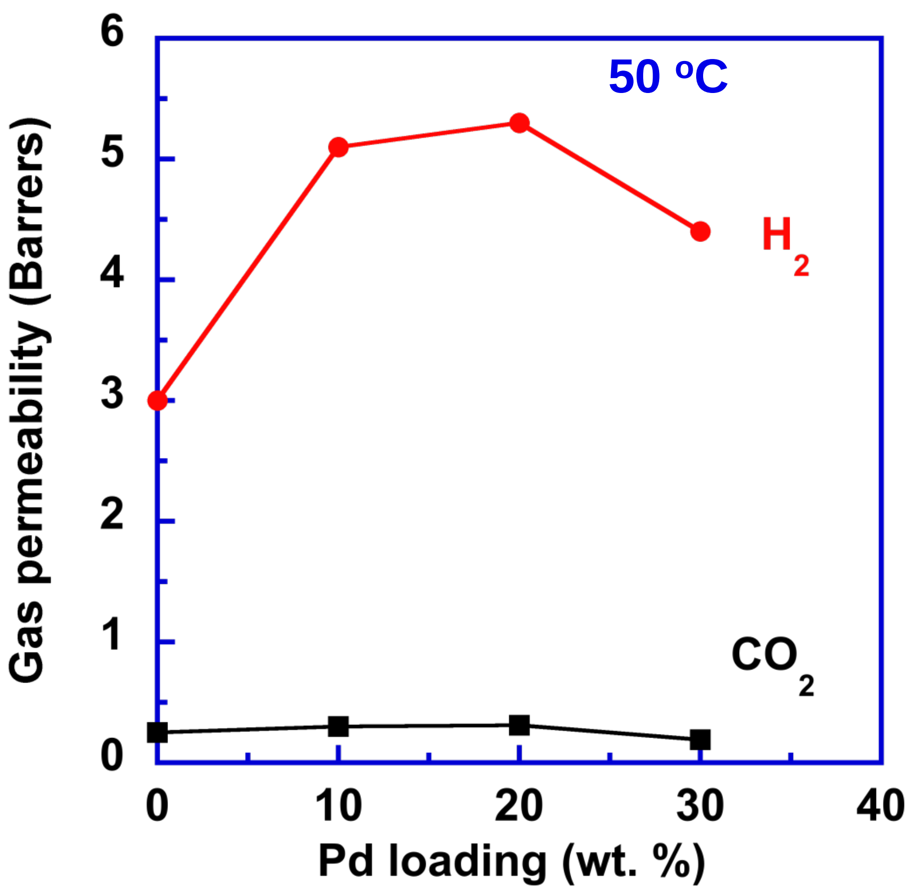




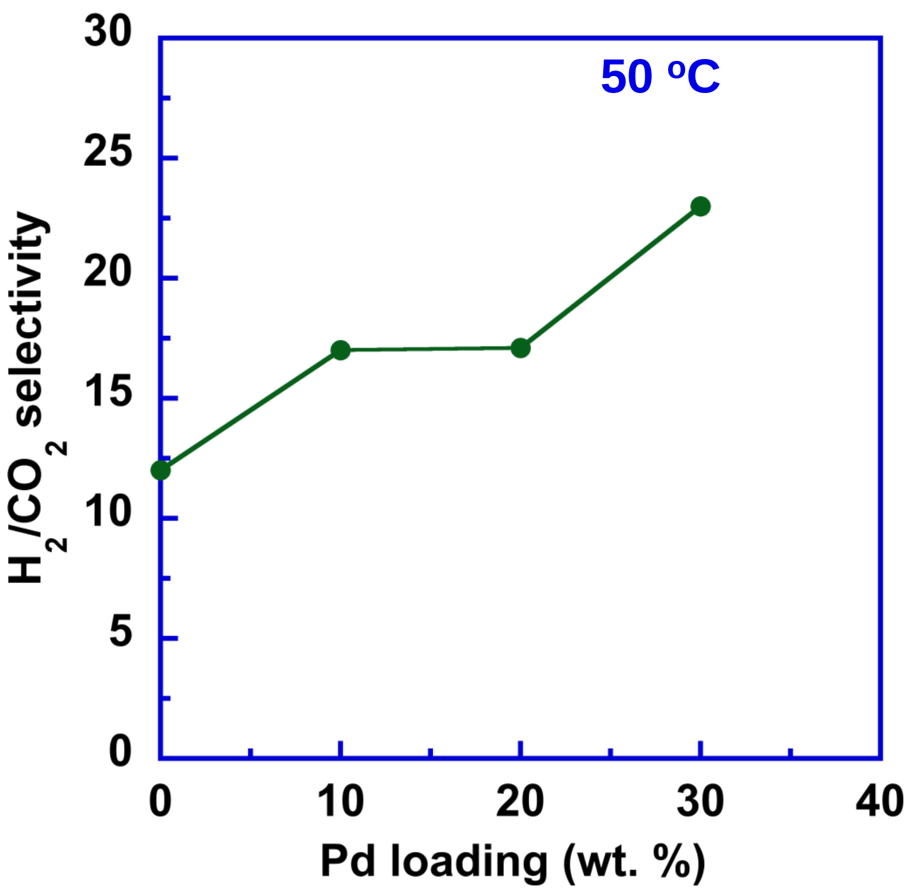
Materials	T(°C)	H_2 solubility cm^3(STP)/(cm^3 atm)	H_2/CO_2 solubility selectivity
Matrimid®	35	0.12	0.035
PBI	**150**	**< 0.10**	**< 0.20**
PBI/ 10wt% Pd	**150**	**16**	**33**
PBI/ 20wt% Pd	**150**	**32**	**32**

Effect of Pd Loading on H_2/CO_2 Separation Properties

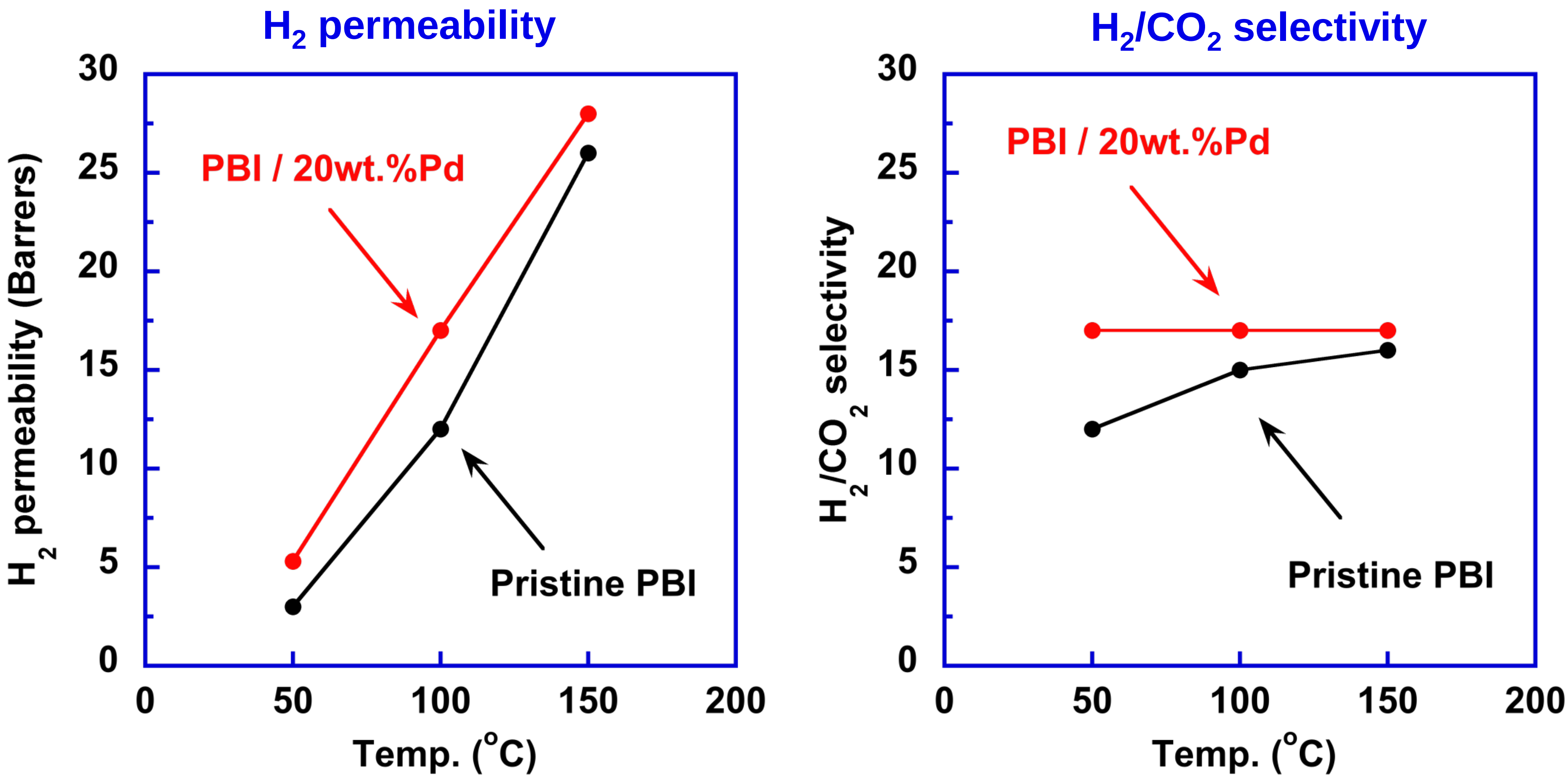
Gas permeability



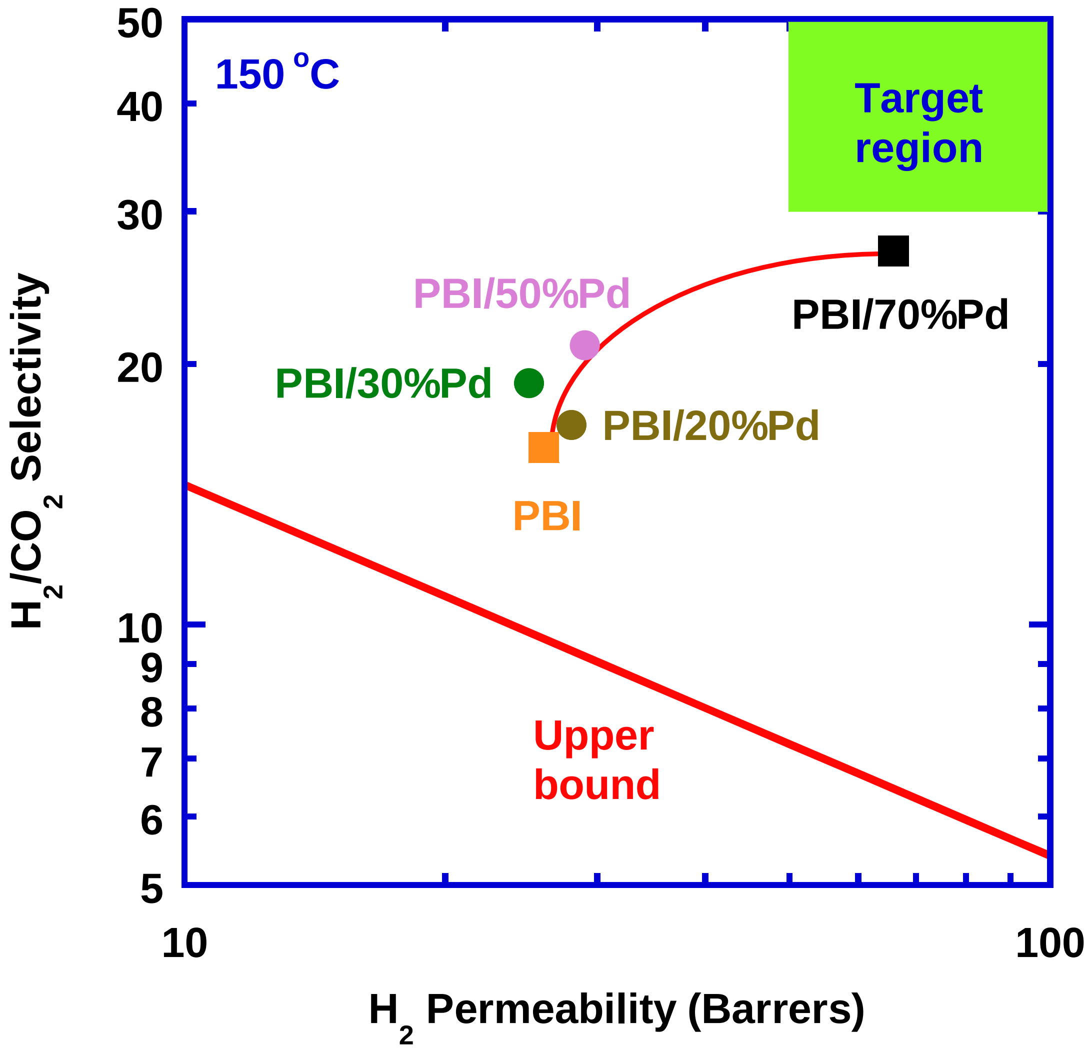
H_2/CO_2 selectivity



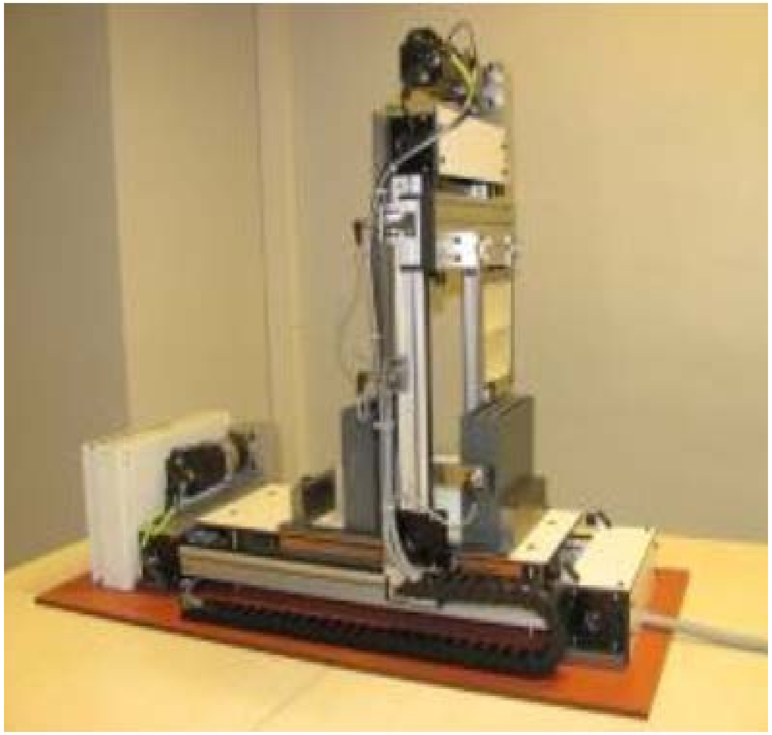
Effect of Temperature on H_2/CO_2 Separation Properties



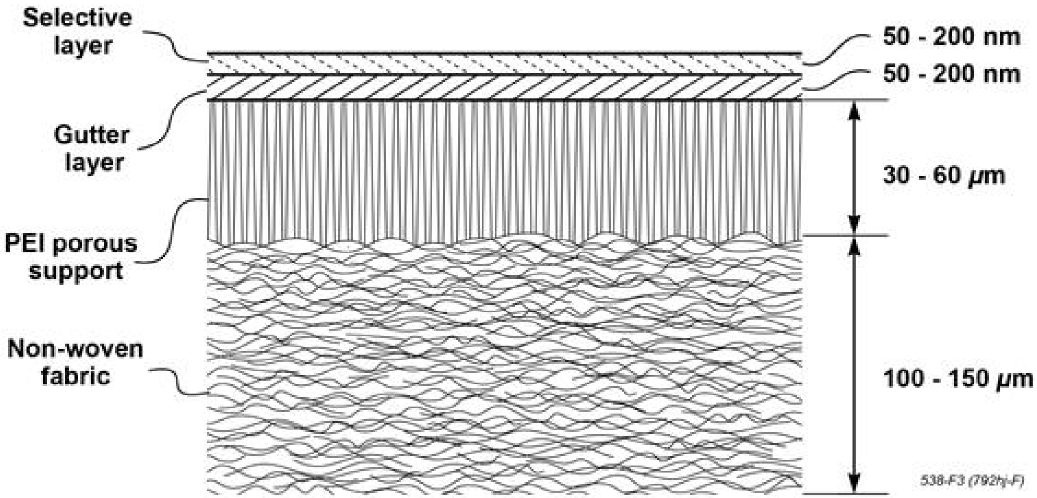
Gas Separation Properties of Mixed Matrix Materials



Future Work: Thin Film Composite Membranes (BP2)



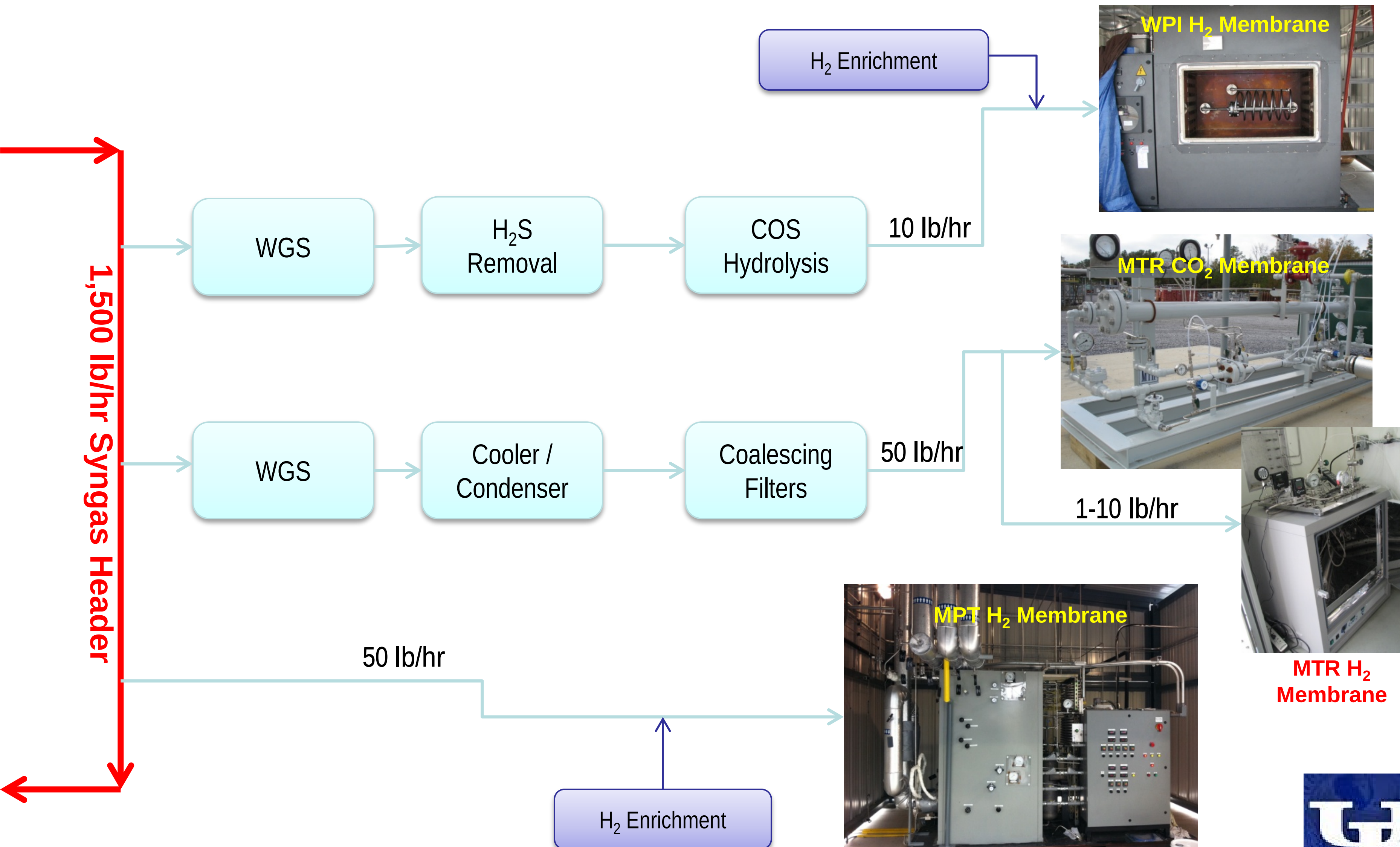
Automatic dip coater



Thin film composite membranes

H. Lin *et al.*, *J. Membr. Sci.* 457, 149-161 (2014).

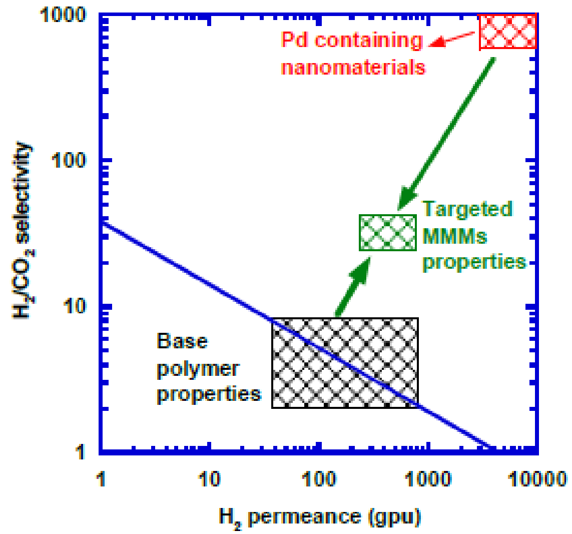
Future Work: Membrane Test at NCCC



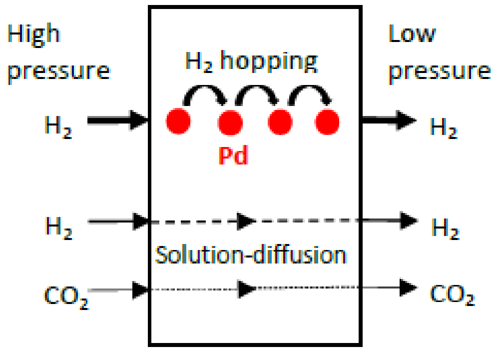
Provided by Tony Wu at NCCC

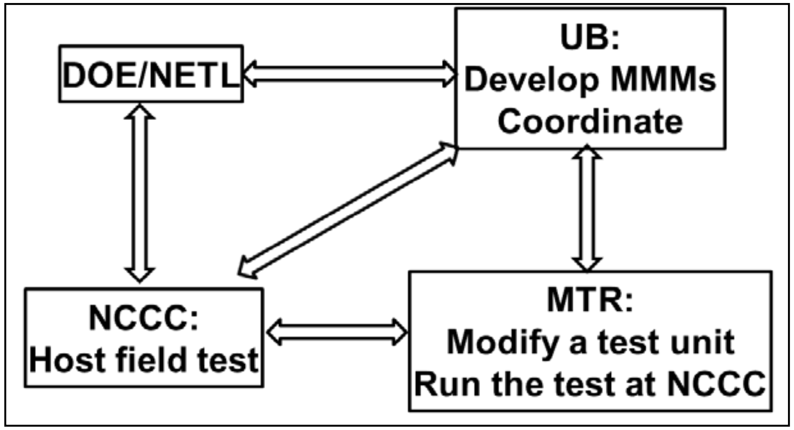
Summary

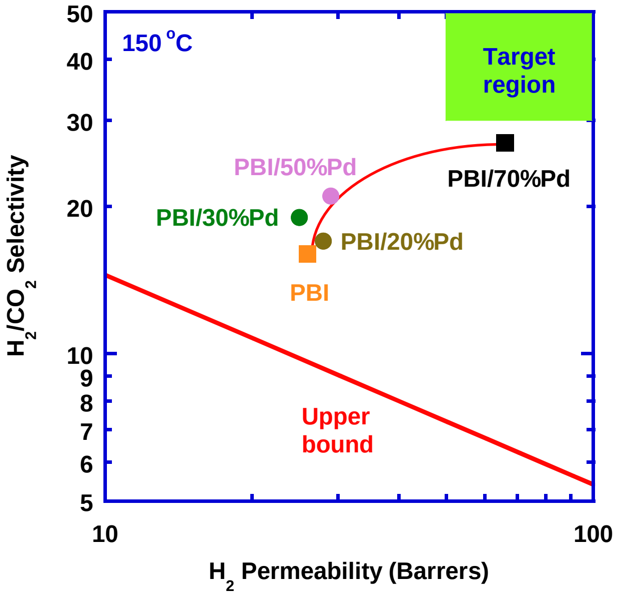
(a) Extraodinary separation property in Pd



(b) Tailoring Pd-based nanomaterials for H_2 sorption and diffusion







Acknowledgments

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