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

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[3]Center for Applied Energy Research, University of Kentucky **(CAER)**

NETL CO_2 Capture Technology Project Review Meeting
Pittsburgh, PA
8/14/2018

Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture

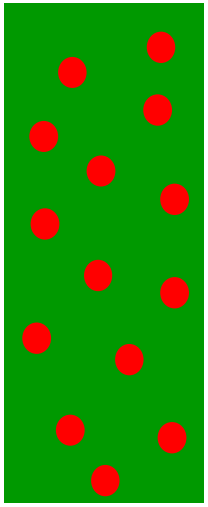
Award number:	DE-FE0026463
Project period:	10/1/15 to 12/31/18
Funding:	$1,485,099 DOE $ 376,837 UB and MTR contribution $1,861,936 total
Program manager:	Steve Mascaro
Participants:	University at Buffalo (**UB**); Membrane Technology and Research, Inc. (**MTR**); and University of Kentucky (**CAER**)
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 CAER.

Project Scope

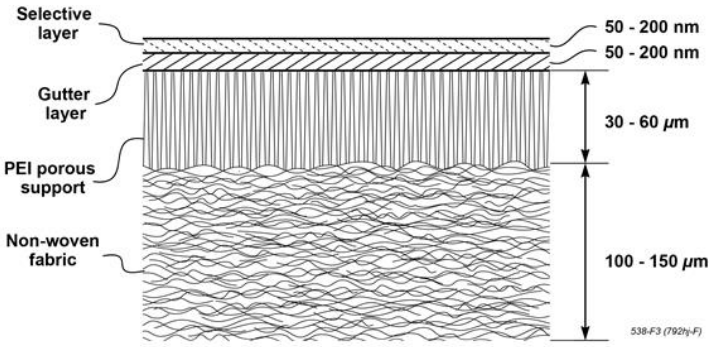
BP1: Prepare mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 **(Q1-Q4)**

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 20-day field test of membranes with real syngas at CAER **(Q11-Q13)**

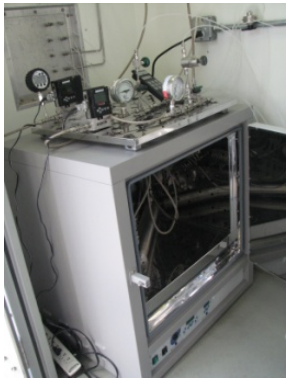


Nanostructured materials



Industrial membranes

Center for Applied Energy Research



Field test

Our Approach: H_2/CO_2 Solubility Selectivity

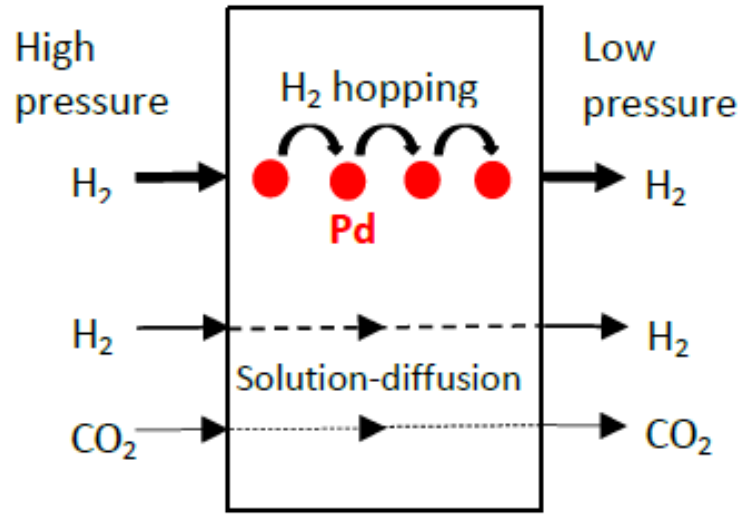
$$\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}$$

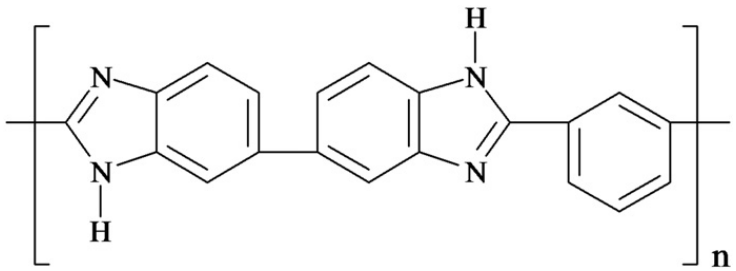
Materials	Temp. (°C)	H_2 solubility $cm^3(STP)/(cm^3 atm)$	H_2/CO_2 solubility selectivity
Poly(dimethyl siloxane)	35	0.10	0.078
Polysulfone	35	0.075	0.036
Matrimid®	35	0.12	0.035
Pd metal*	**25**	**38,000**	**> 1,000**

* Calculated at 0.02 bar H_2

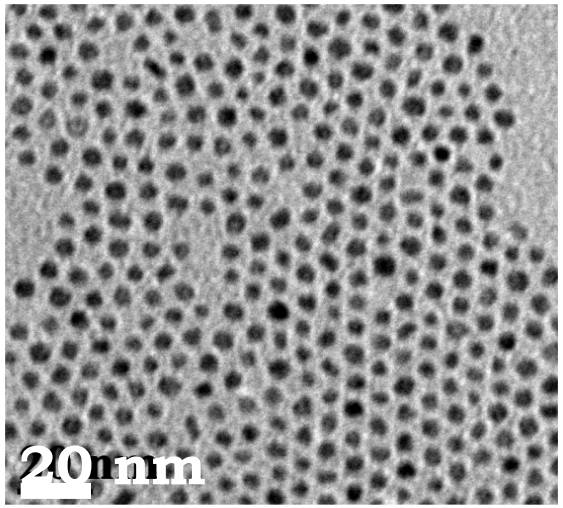
Adams and Chen, *Materials Today*, 14 (2011) 282-289

Our Approach: Sorption Enhanced Mixed Matrix Materials



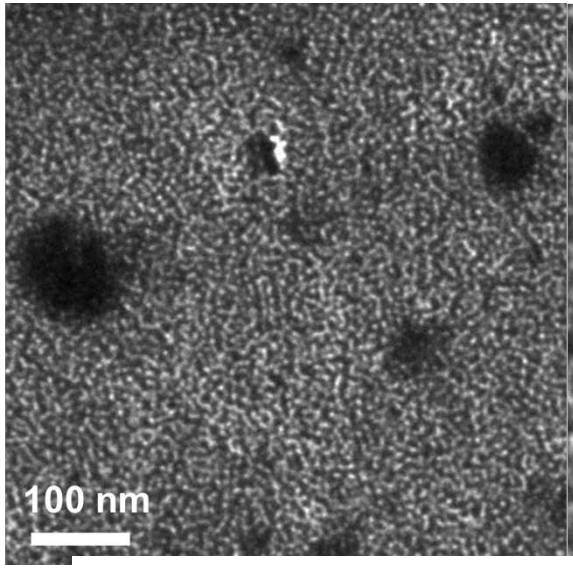


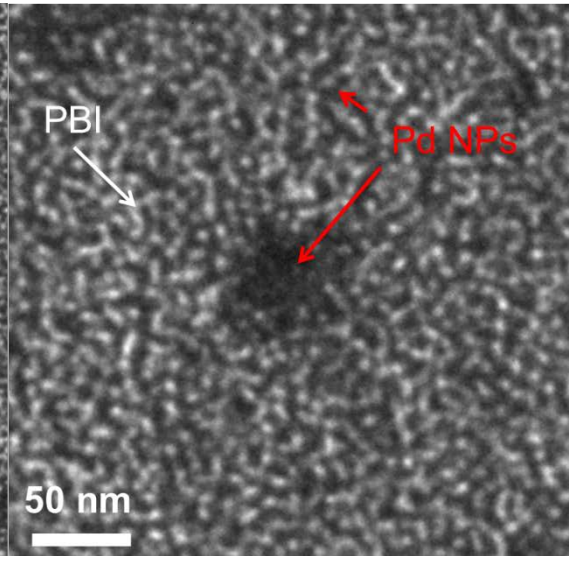
Polybenzimidazole
(PBI)



Pd nanoparticles

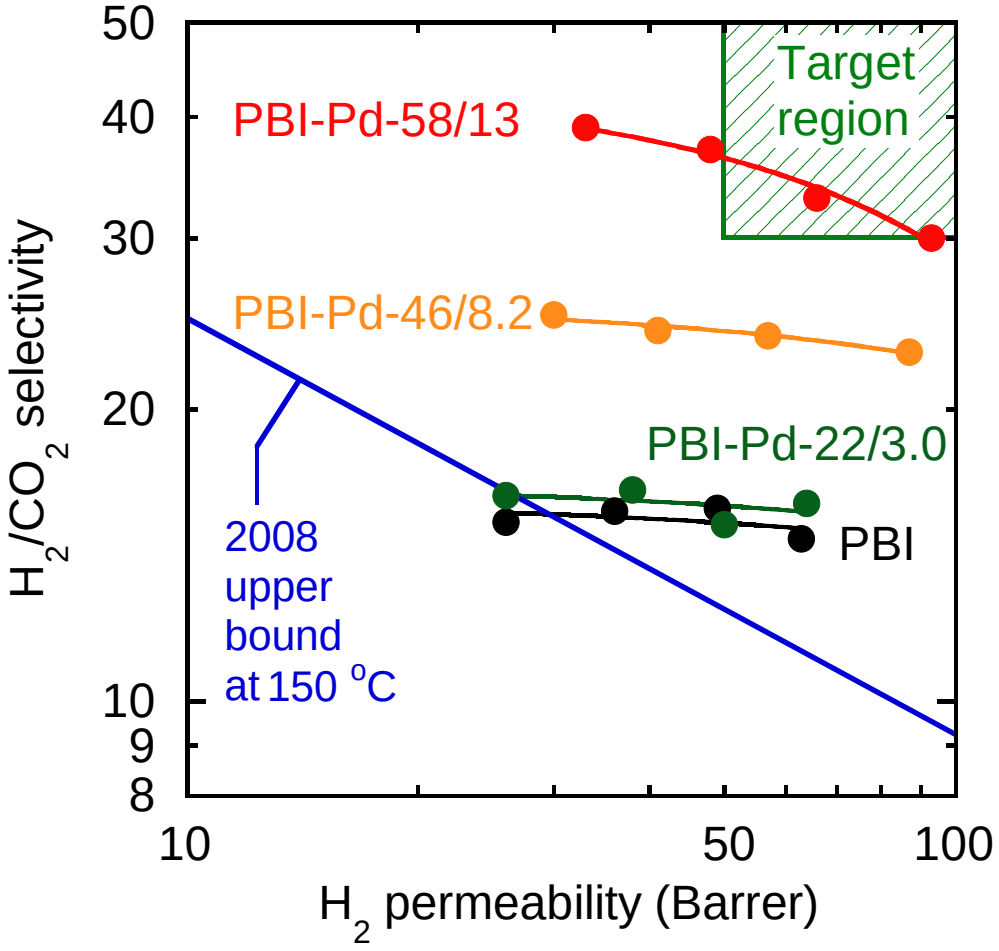
Konda, Lin, Swihart, et al., *AIChE J.*, in press





Mixed matrix materials (MMMs)

Membrane Materials Meeting the BP1 Target



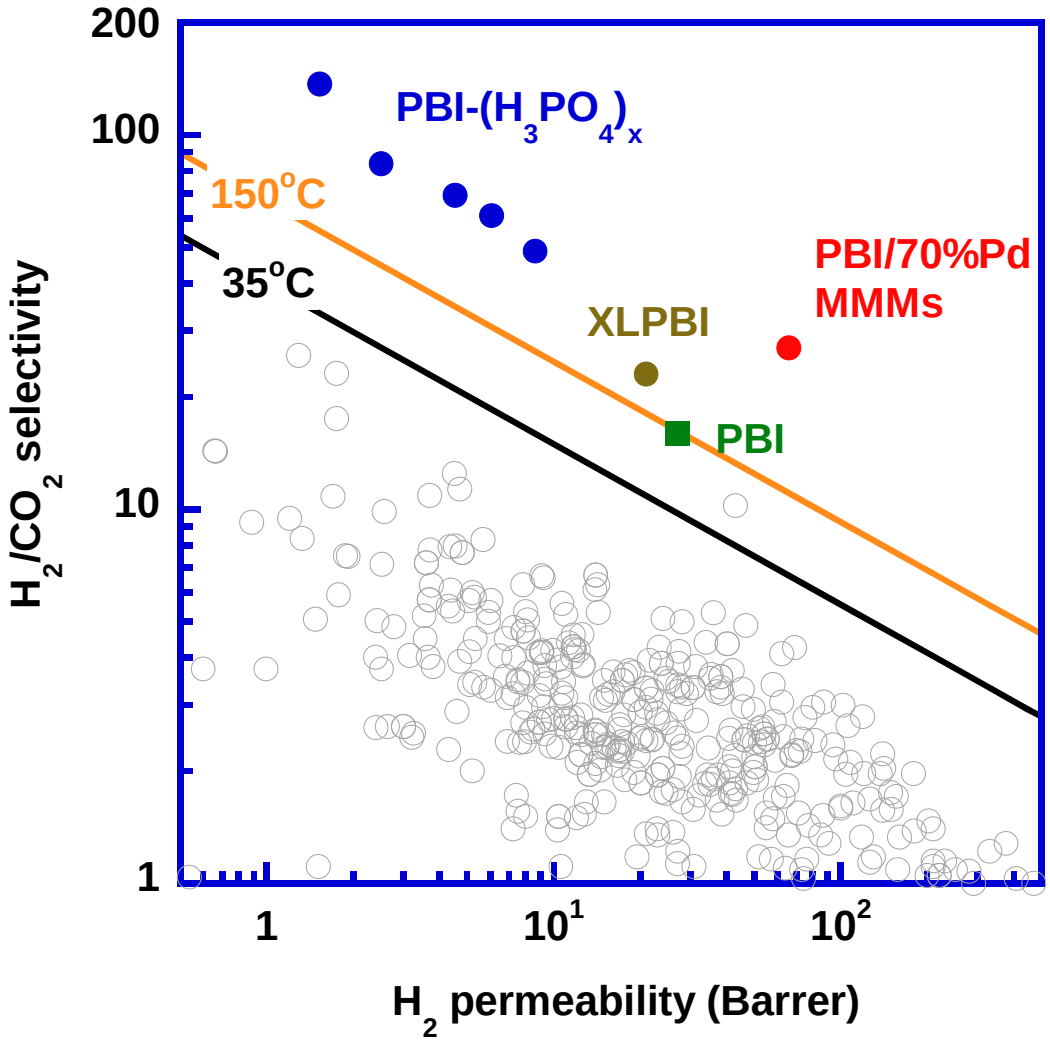
Mixed-gas:
50% H_2/50% CO_2

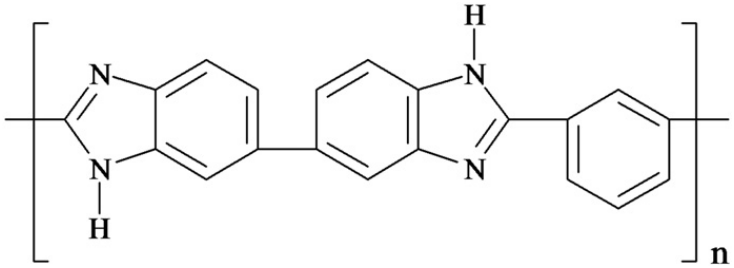
Temperatures:
150-175-200-225 °C from left to right.

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

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	9/30/2017
Task 10. Conduct Parametric Tests of Membranes for H_2/CO_2 Separation	1/1/2017	12/31/2017
Task 11. Design and Modify Membrane Stamp Test Unit for CAER Field Test	6/1/2017	12/31/2017
Milestone f: Mixed matrix membranes with superior H_2/CO_2 separation properties prepared		
Task 13. Run 20-Day Field Test at CAER	6/1/2018	11/30/2018
Task 14. Analyze Field Test Results / Membrane Post-analysis	10/1/2018	12/31/2018
Milestone h: Successful field test completed		

Polymer Development and Scale-up

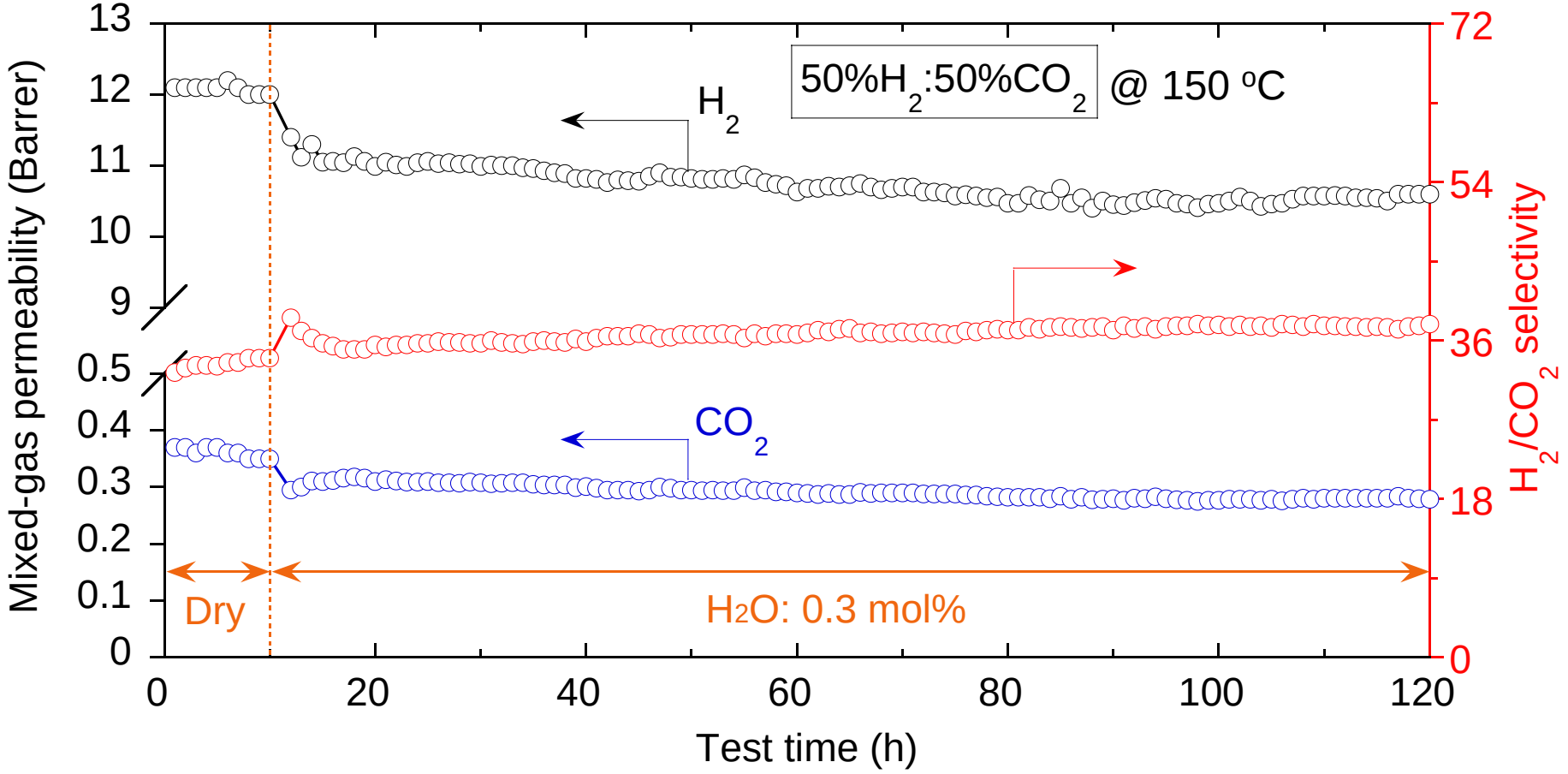




- Commercial PBIs are identified
- Modification of PBIs has been demonstrated to improve performance

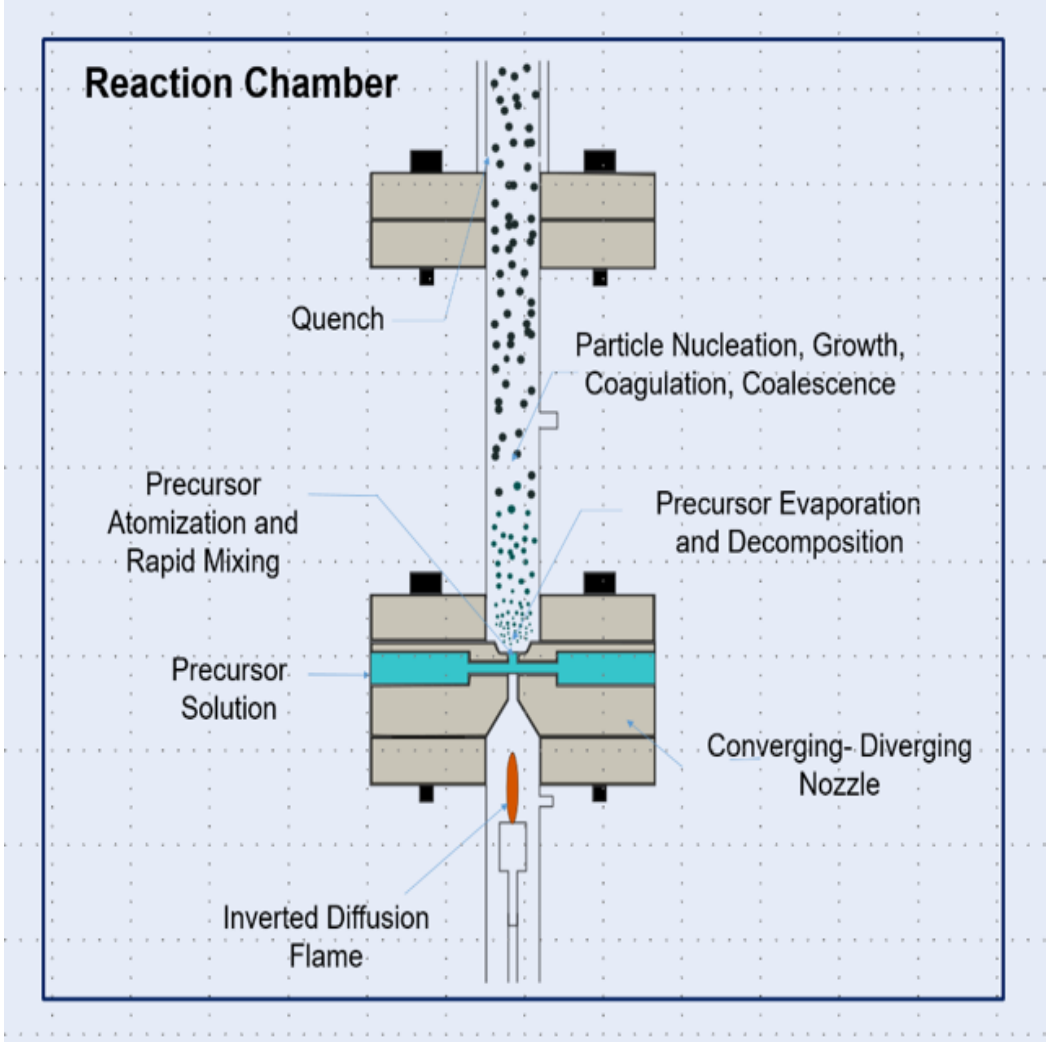
Zhu, Swihart and Lin, *J. Mater. Chem. A*, 5(37), 19914-23, 2017

Long-term Stability of a PBI-$(H_3PO_4)_{0.16}$ Film in Simulated Syngas (H_2, CO_2 and H_2O)



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

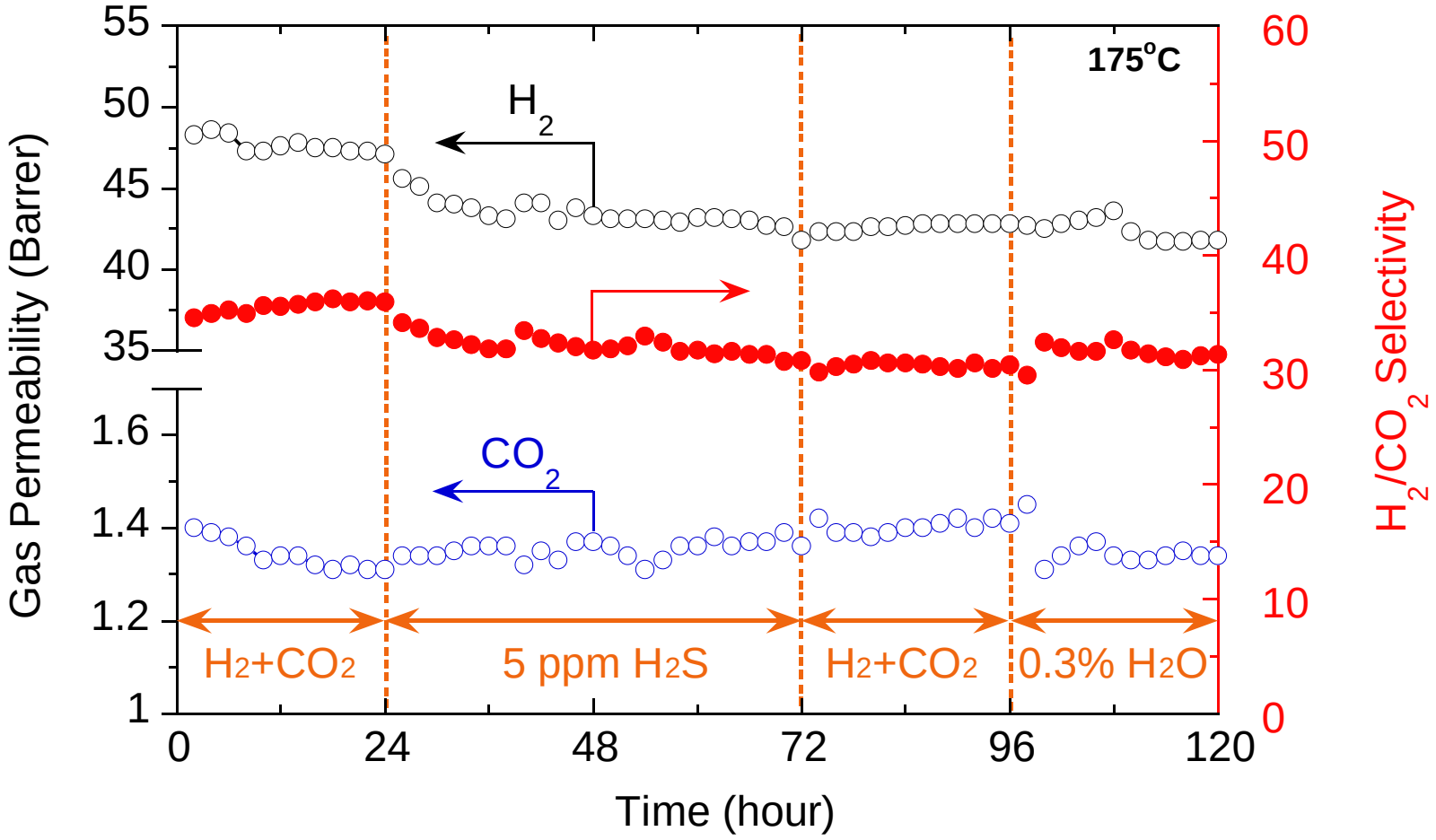
Nanoparticle Synthesis Scale-up: Gas Phase Synthesis



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

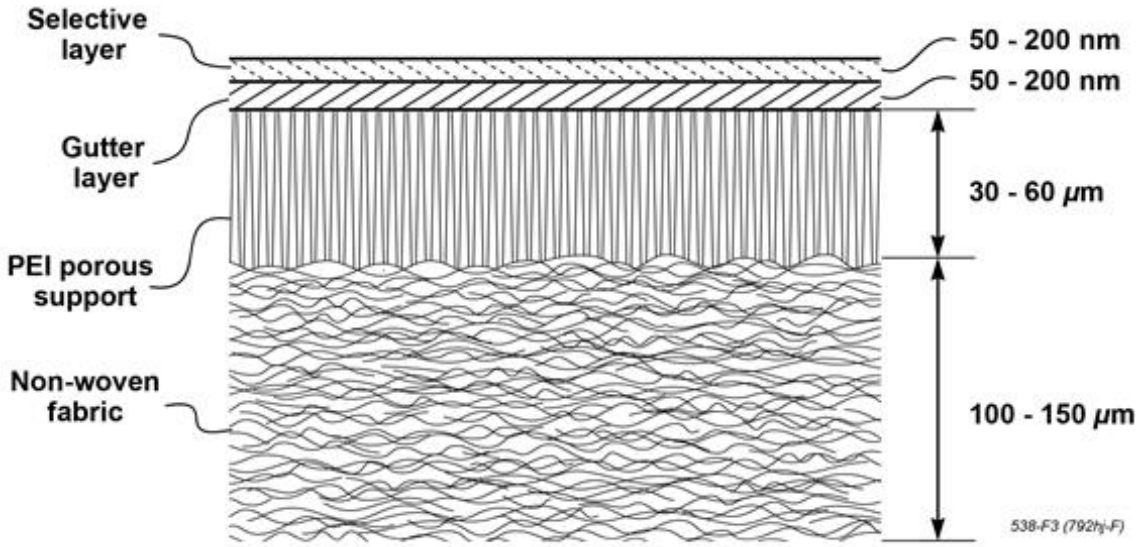
Konda, Lin, Swihart, et al., Flame-based synthesis and in situ functionalization of palladium alloy nanoparticles, *AIChE J.*, in press

Stability of Mixed Matrix Materials against H_2S



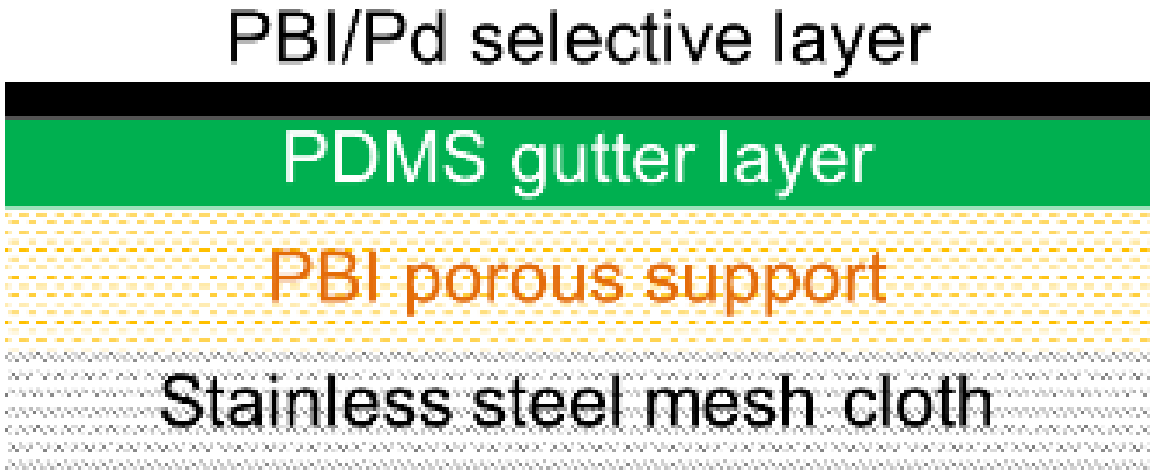
PBI-Pd-58/13: 58 wt% or 13 vol% Pd nanoparticles

Thin Film Composite (TFC) Membranes



Conventional TFC membranes

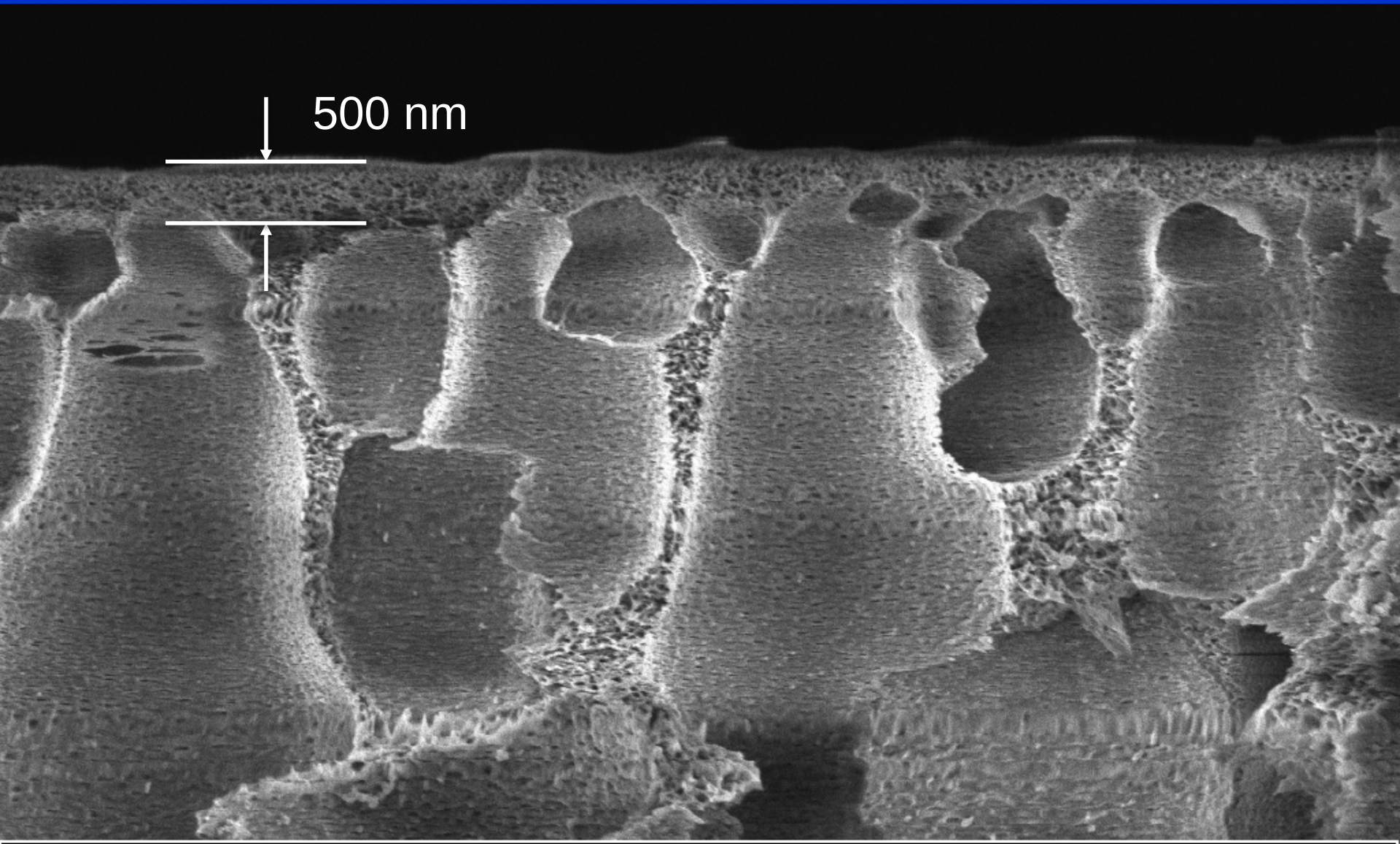
Baker and Low, *Macromolecules*, 47 (2014) 6999-7013.



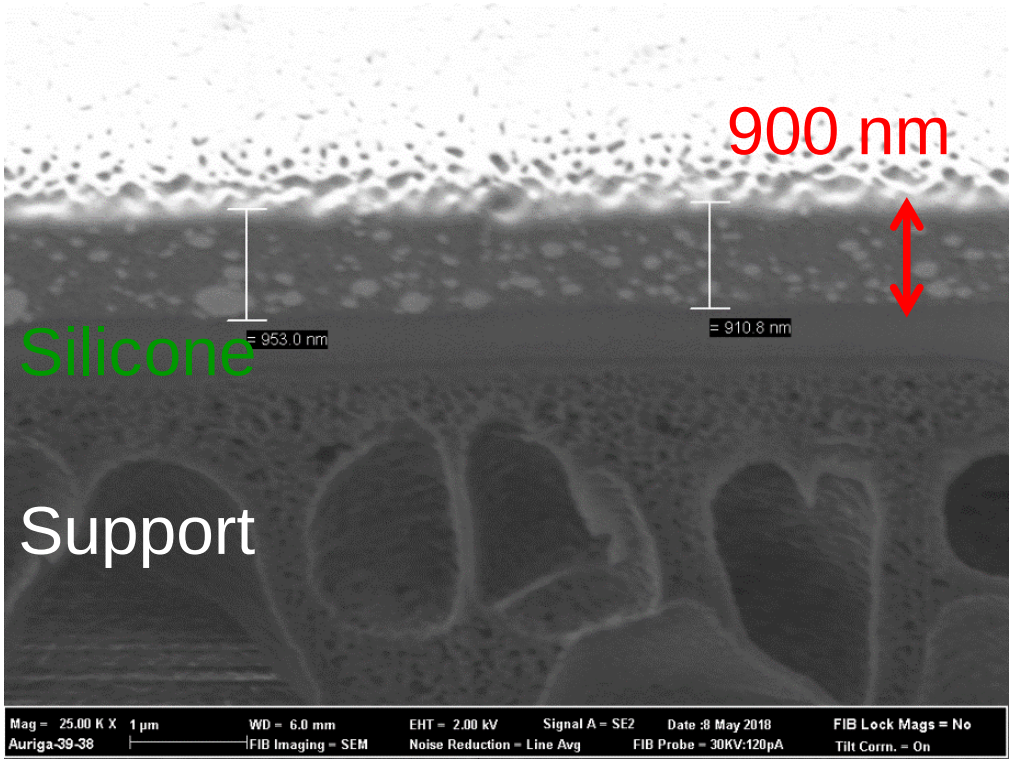
Thermally stable TFC membranes

Surface of PBI-supports: SEM Characterization

Cross-section of PBI-supports: SEM Characterization



Reduce PBI/Pd Selective Layer Thickness to below 900 nm



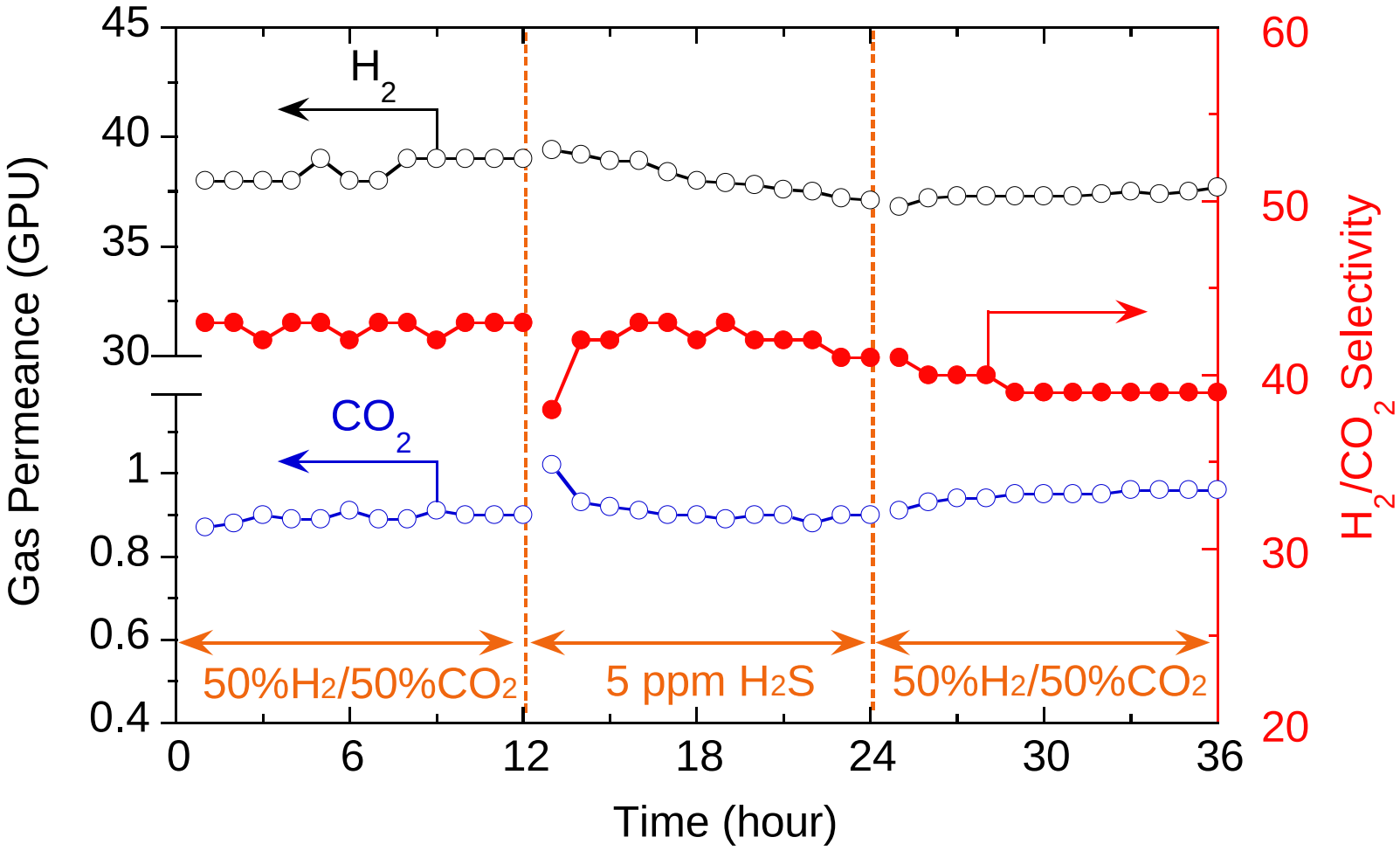
PBI-Pd-58/13

H_2 permeance: ca. 40 GPU
H_2/CO_2 selectivity: 40

Note: The PDMS gutter layer has an H_2 permeance of ~400 GPU

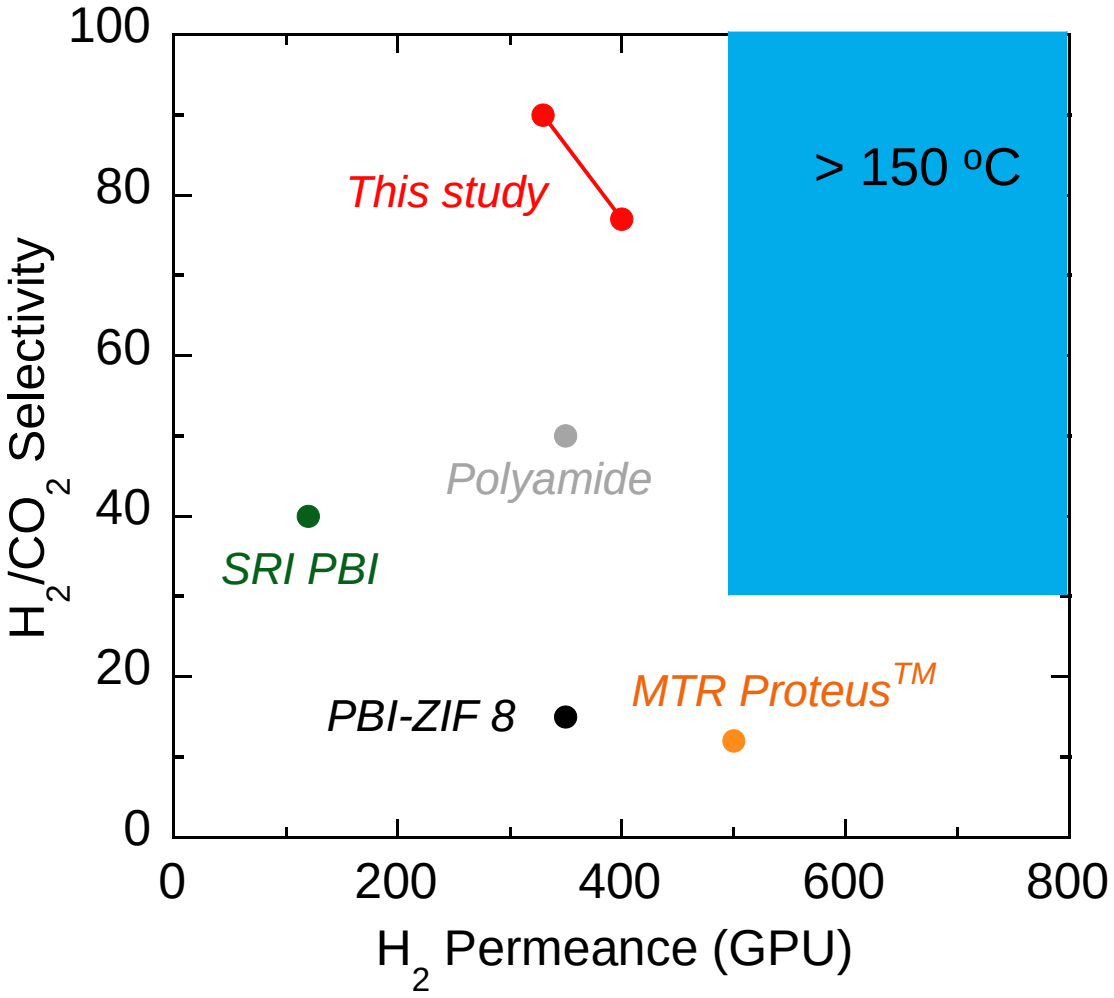
Measurement condition: 150 °C, 150 psig; 50% H_2/50% CO_2

Stability with H_2S for PBI-Pd-58/13-based TFC Membrane



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

Benchmarking Our TFC Membranes



- Thin film (70 nm)
- 230 °C

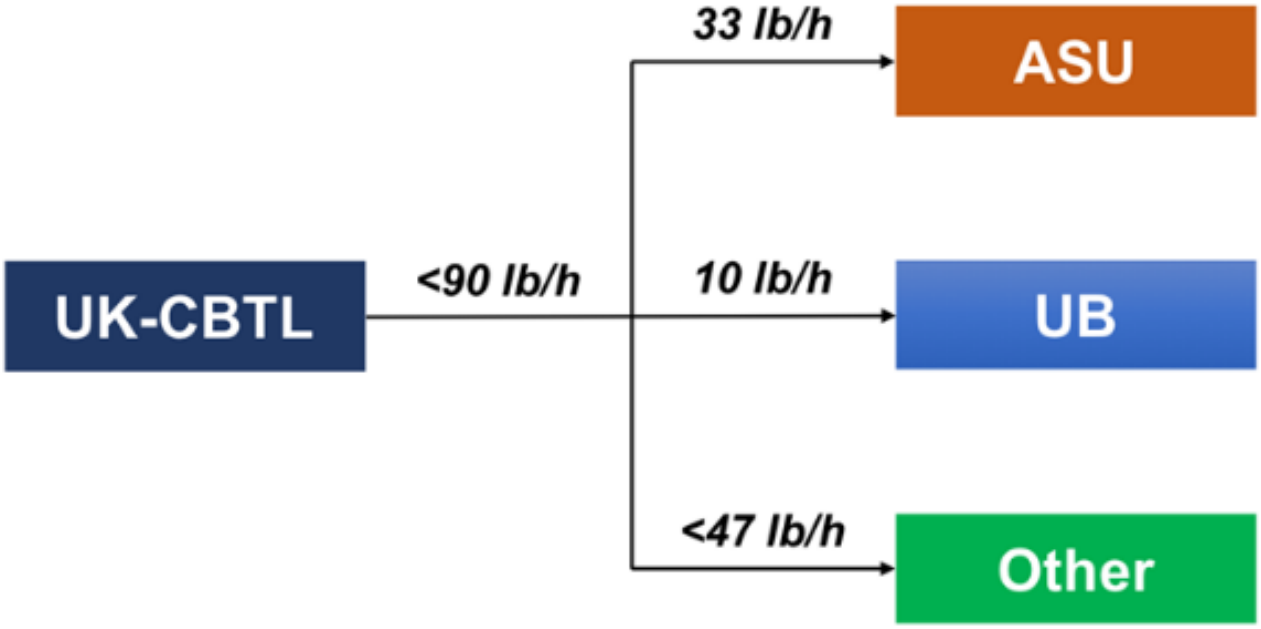
Ali, Pacheco, Litwiller, Wang, Han, and Pinnau, *J. Mater. Chem. A* (2018) 6, 30-35

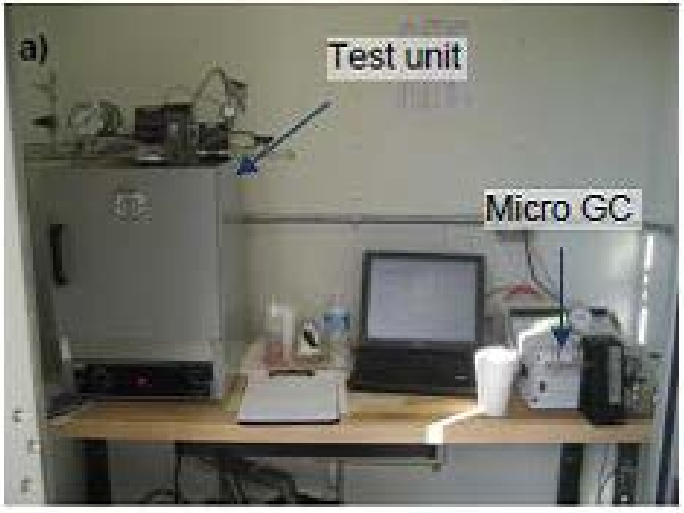
Gasifier at University of Kentucky Center for Applied Energy Research (CAER)

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

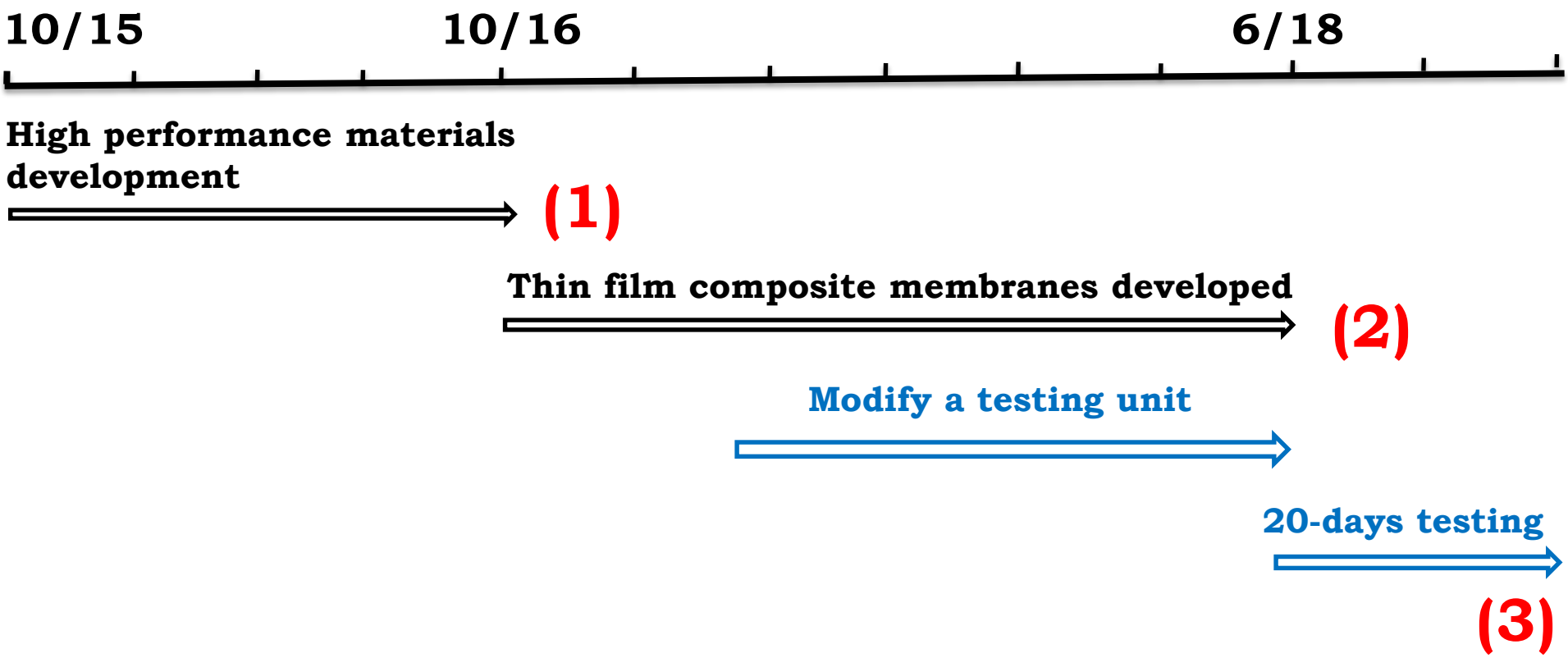
Photos provided by Andy Placido of CAER

Membrane Testing Apparatus





Project Plan and Milestones

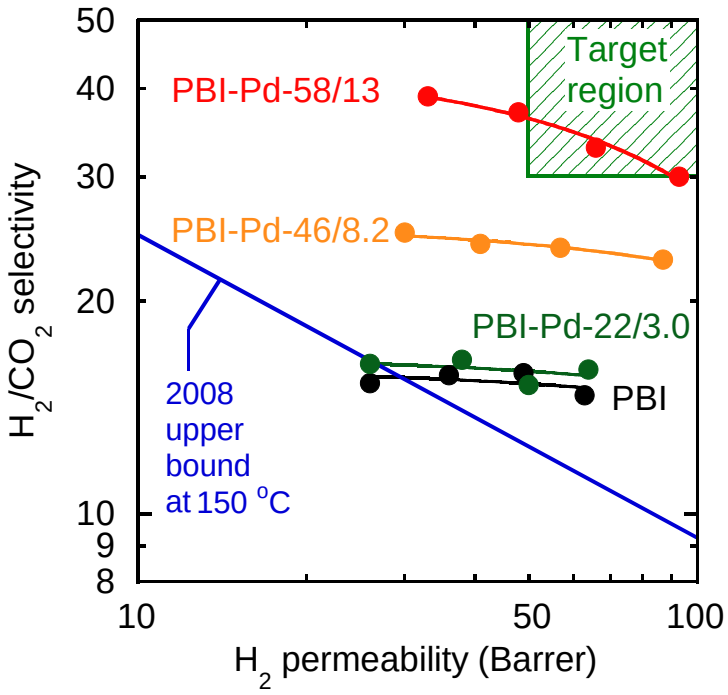


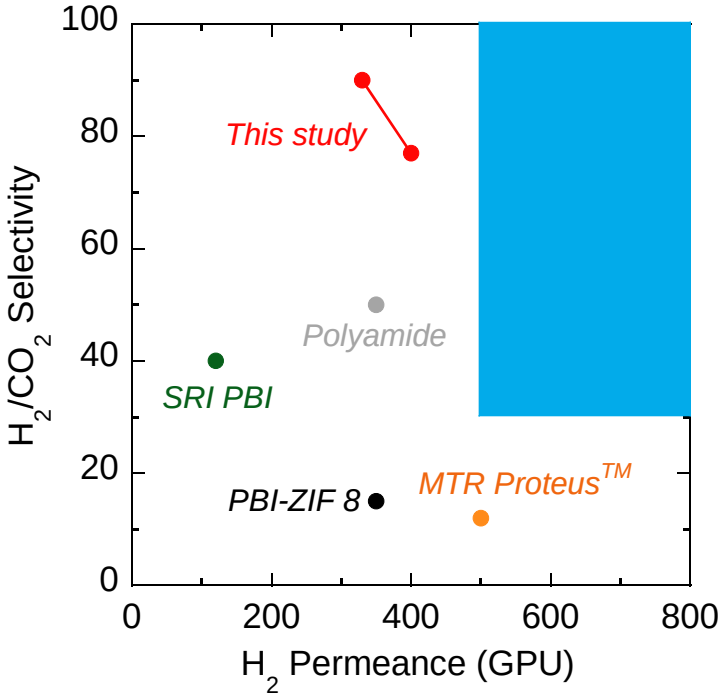
(1) High performance mixed matrix materials identified;
(2) High performance thin film composite membranes prepared;
Testing skid modified;
(3) Parametric testing of membranes using real syngas

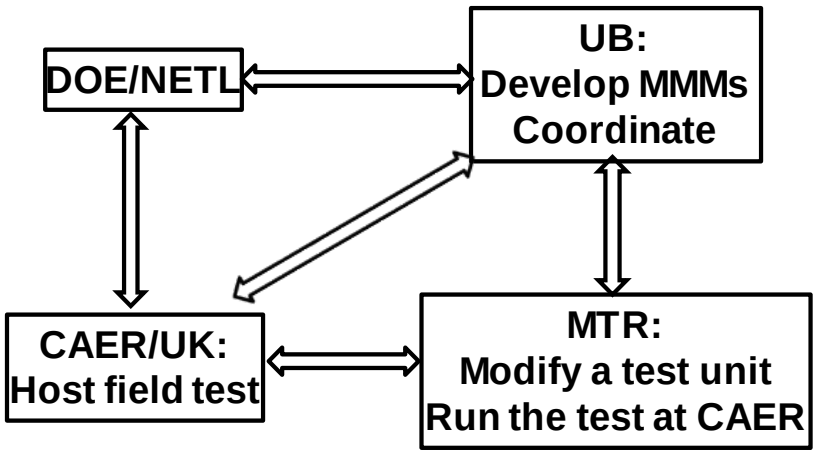
Project Milestones

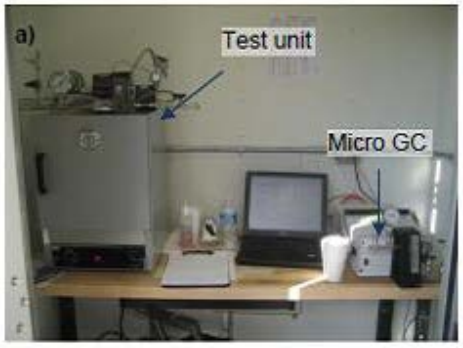
Budget Period	ID	Description	(Planned) Completion Date
1	a	Updated Project Management Plan	11/30/15
1	b	Kickoff Meeting	12/31/15
3	**c**	**Final report**	**12/31/18**
1	d	Polymers and nanomaterials with promising H_2/CO_2 separation properties identified and prepared	6/30/16
1	e	Mixed matrix materials with superior H_2/CO_2 separation properties prepared	9/30/16
2	**f**	**Mixed matrix membranes with superior H_2/CO_2 separation properties**	**3/31/18**
2	**g**	**Field test unit modified**	**3/31/18**
3	**h**	**Successful field test**	**11/30/18**

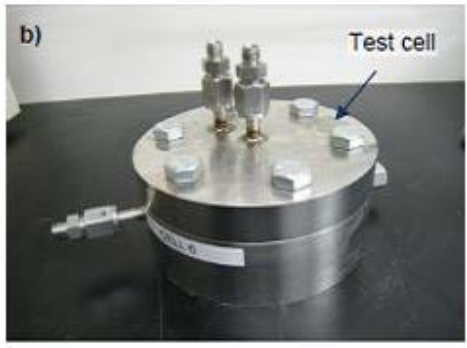
Summary


50
40
30
20
10
9
8
10
50
100
H2/CO2 selectivity
H2 permeability (Barrer)
Target region
PBI-Pd-58/13
PBI-Pd-46/8.2
PBI-Pd-22/3.0
PBI
2008 upper bound at 150 °C


100
80
60
40
20
0
0
200
400
600
800
H2/CO2 Selectivity
H2 Permeance (GPU)
This study
Polyamide
SRI PBI
PBI-ZIF 8
MTR Proteus™


DOE/NETL
UB:
Develop MMMs
Coordinate
CAER/UK:
Host field test
MTR:
Modify a test unit
Run the test at CAER


a)
Test unit
Micro GC


b)
Test cell

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Kunlei Liu