High Temperature Polymer-Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture

LANL-FE-10-002

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NETL CO_2 Capture Technology Meeting
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High T_g Polymer for Carbon Capture Projects

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Outline

- **Project Overview**
- **Technology Background**
- **Technology Status**
- **Future Plans**

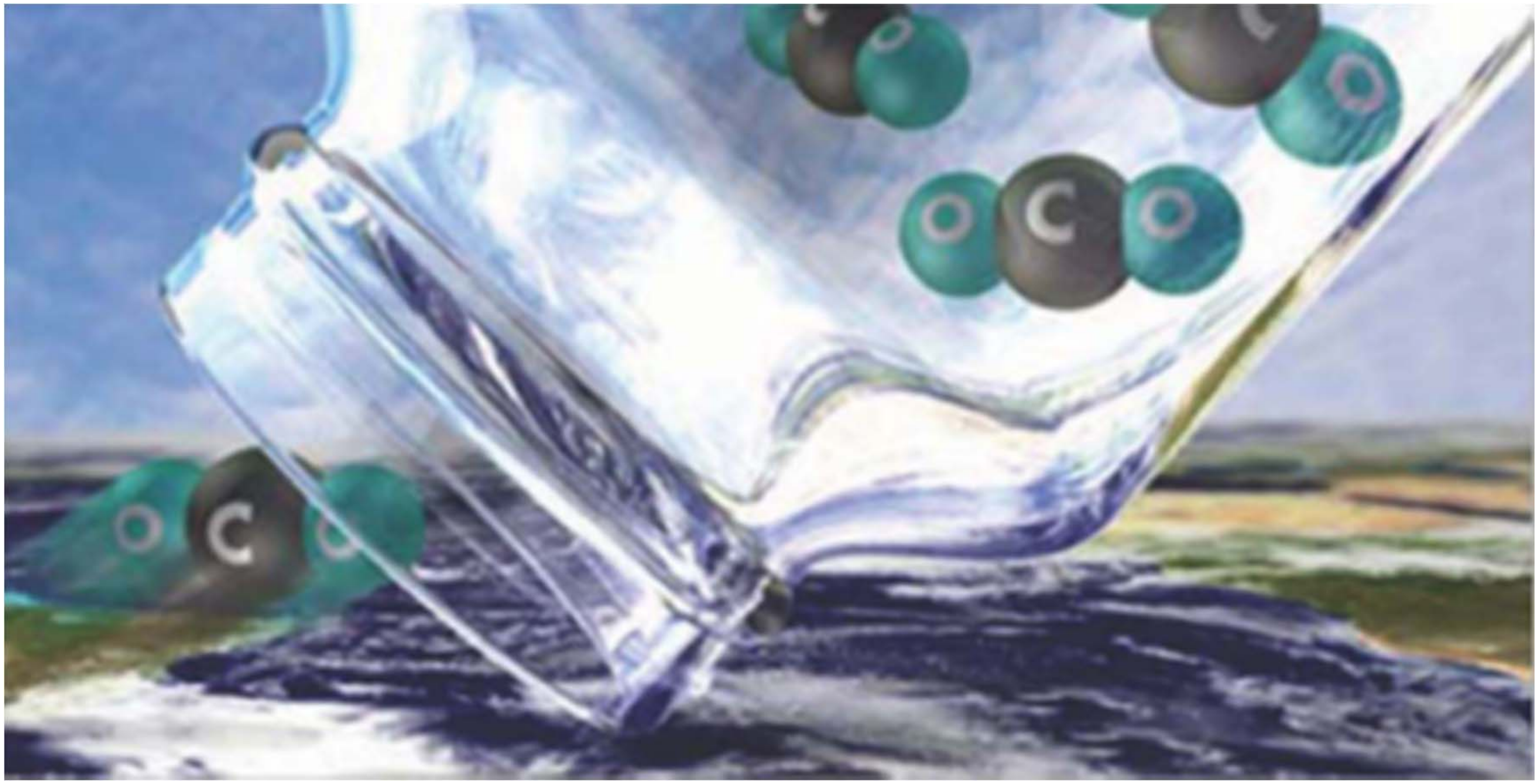
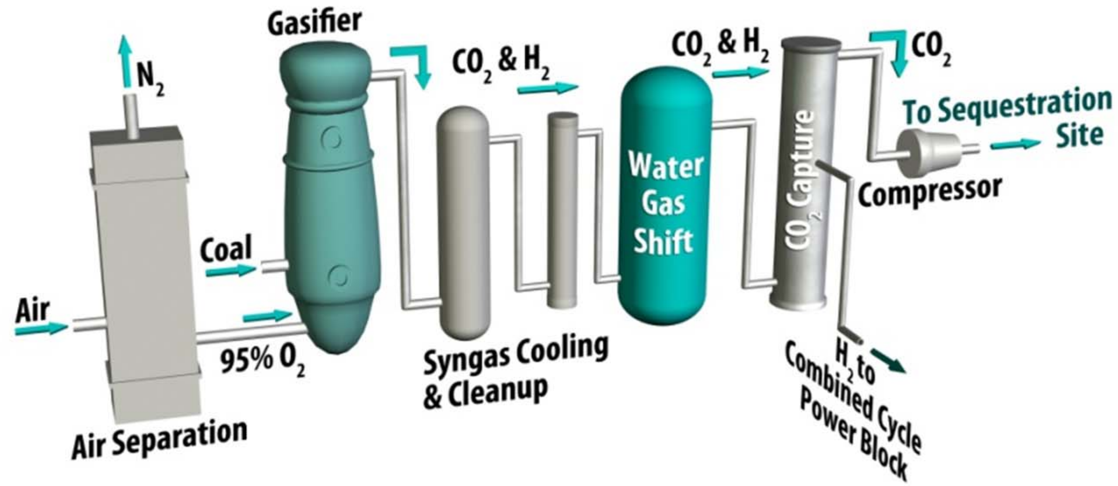


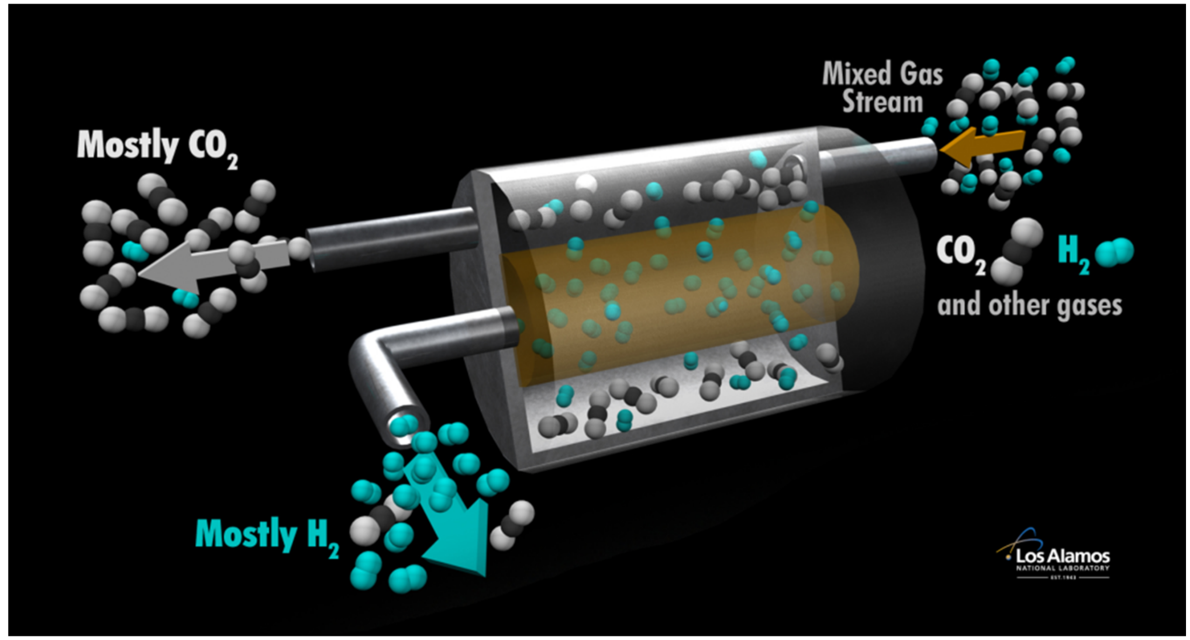
Photo Courtesy of EPRI Journal, Spring 2007

Project Overview

- Award Name:
  - High Temperature Polymer-Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture
- Award Number:
  - FE-10-002
- Project Start:
  - 10/2009
- Project Cost (DOE):
  - \$1.8 million (10/2009 – 9/2012)
- DOE NETL Project Manager:
  - C. Elaine Everitt

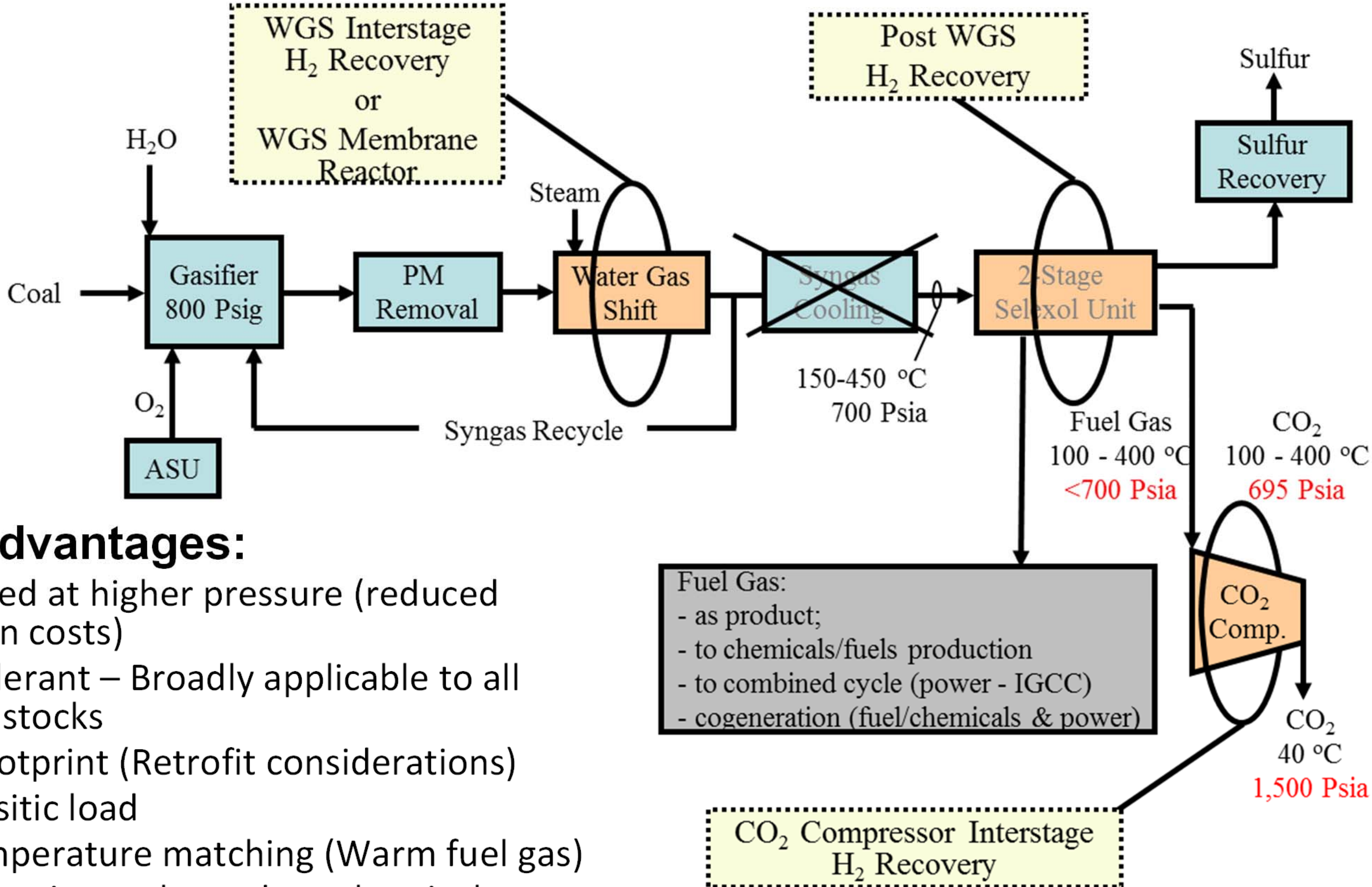


Overarching Objective



Development and Demonstration of an innovative polymer-based membrane separation technology aimed at improving the economics and performance of hydrogen separation and carbon capture from synthesis (syn) gas, enabling more-efficient and cleaner energy production from coal.

Process Areas Targeted: Membrane Separations



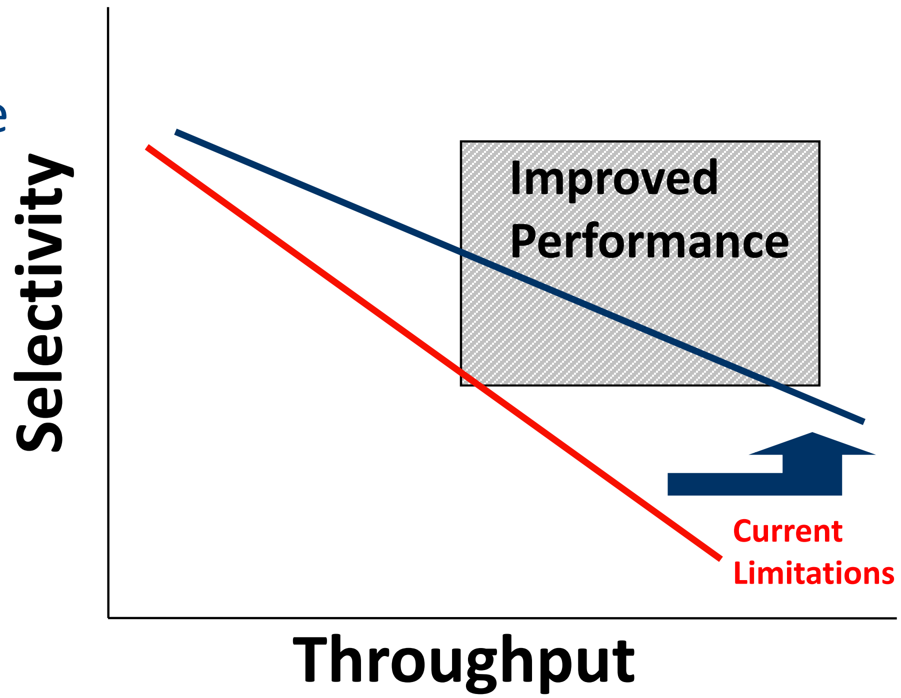
Membrane Advantages:

- CO_2 produced at higher pressure (reduced compression costs)
- Impurity tolerant – Broadly applicable to all syngas feedstocks
- Reduced footprint (Retrofit considerations)
- Lower parasitic load
- Process temperature matching (Warm fuel gas)
- Emission free, i.e. no hazardous chemical use
- Decreased capital costs
- Continuous facile operation (passive process)
- Low maintenance

Separation and Capture – National Needs/Membrane Opportunities

High Temperature Membranes are in Great Demand…
But in short supply – Materials

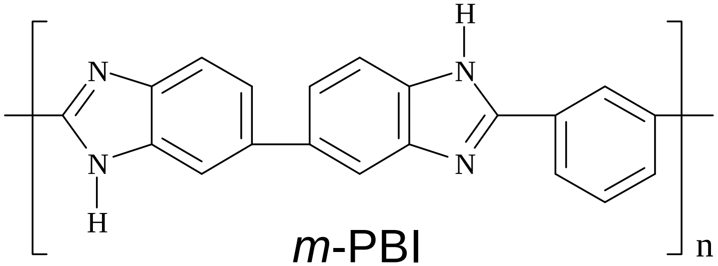
- **Commercially available polymer membranes and module manufacture/sealing technologies are limited to 150 °C operating temperature**
  - Economic advantages of membrane separations are strongly tied to process/separation temperature
- **Membrane materials and systems capable to withstand syngas operating conditions are required**
  - Hydrothermal, chemical & mechanical stability and durability are often elusive
- **Tradeoff between selectivity and productivity has proven difficult to overcome**
  - Key DOE Program Goals
    - >90% CO_2 Capture, <10% increase in COE
- **Commercial Viability Driven by Combination**



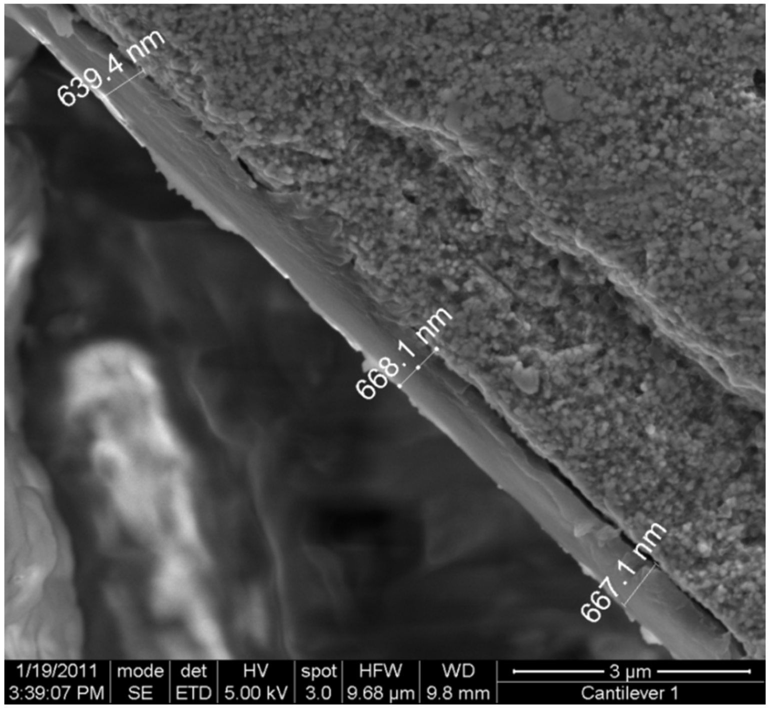
Overview/Background

Efforts Focused on High T_g Polymer Selective Layers

- Development of high T_g (Polybenzimidazole (PBI)- based) materials & membranes with tailored chemistry, morphology, and permselectivity character
  - Thermally stable (T_g ~ 450-500 °C)
    - Facilitates process integration $T_{operation}$ up to ~400 °C
  - Mechanically Stable
  - Chemically resistant
    - Sulfur tolerant at operation temperatures
  - Processable



m-PBI

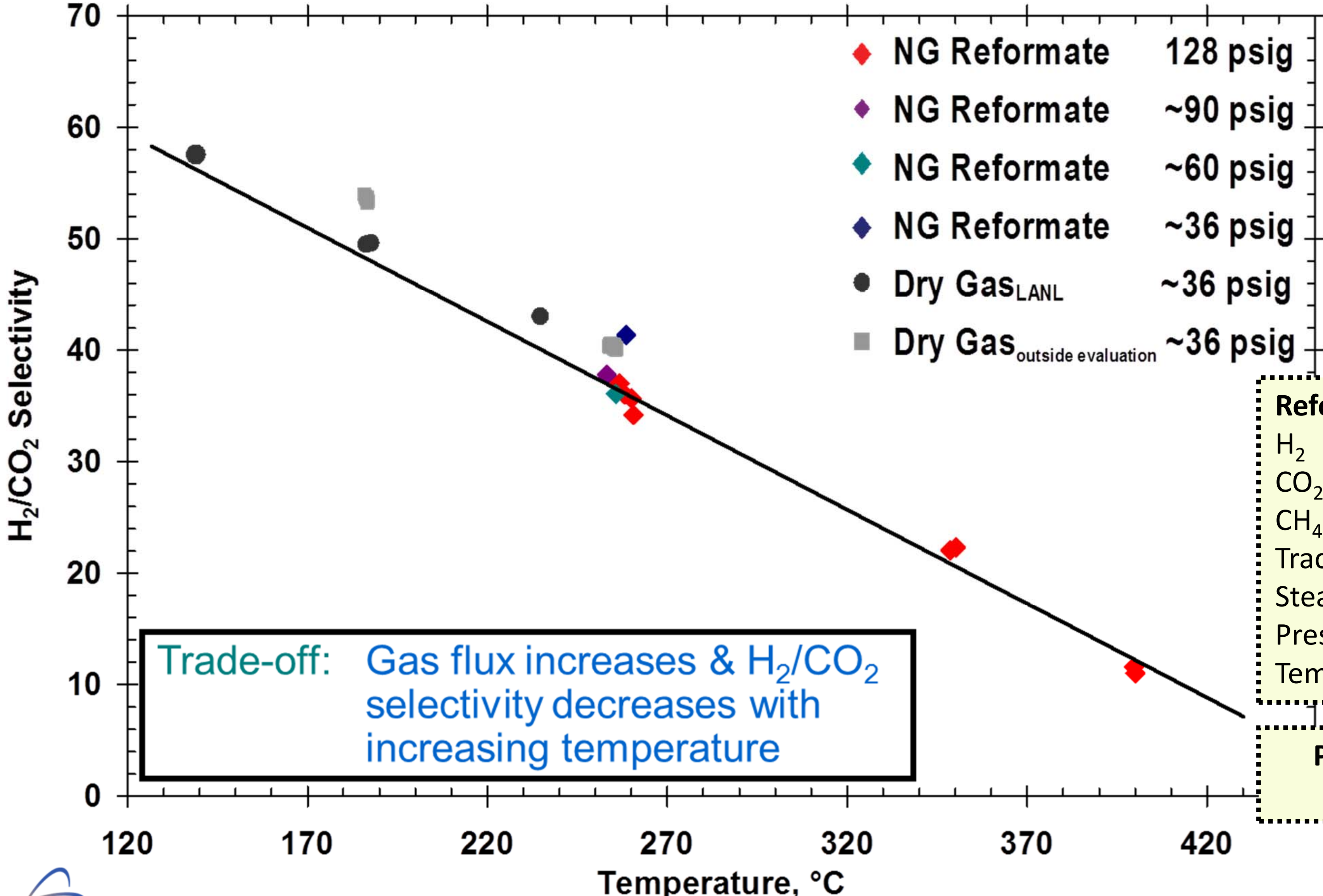


- Critical Evaluation of Developed Materials at Industrially Relevant Process Conditions

- Systems Integration Efforts to:
  - Maximize Energy Efficiency & Minimize Cost
  - Optimize H_2 Recovery/Purity & % CO_2 Capture

PBI Membrane Steam Tolerance

- Evaluated in steam saturated syngas slip stream existing natural gas reformer
- Exceptional tolerance to steam



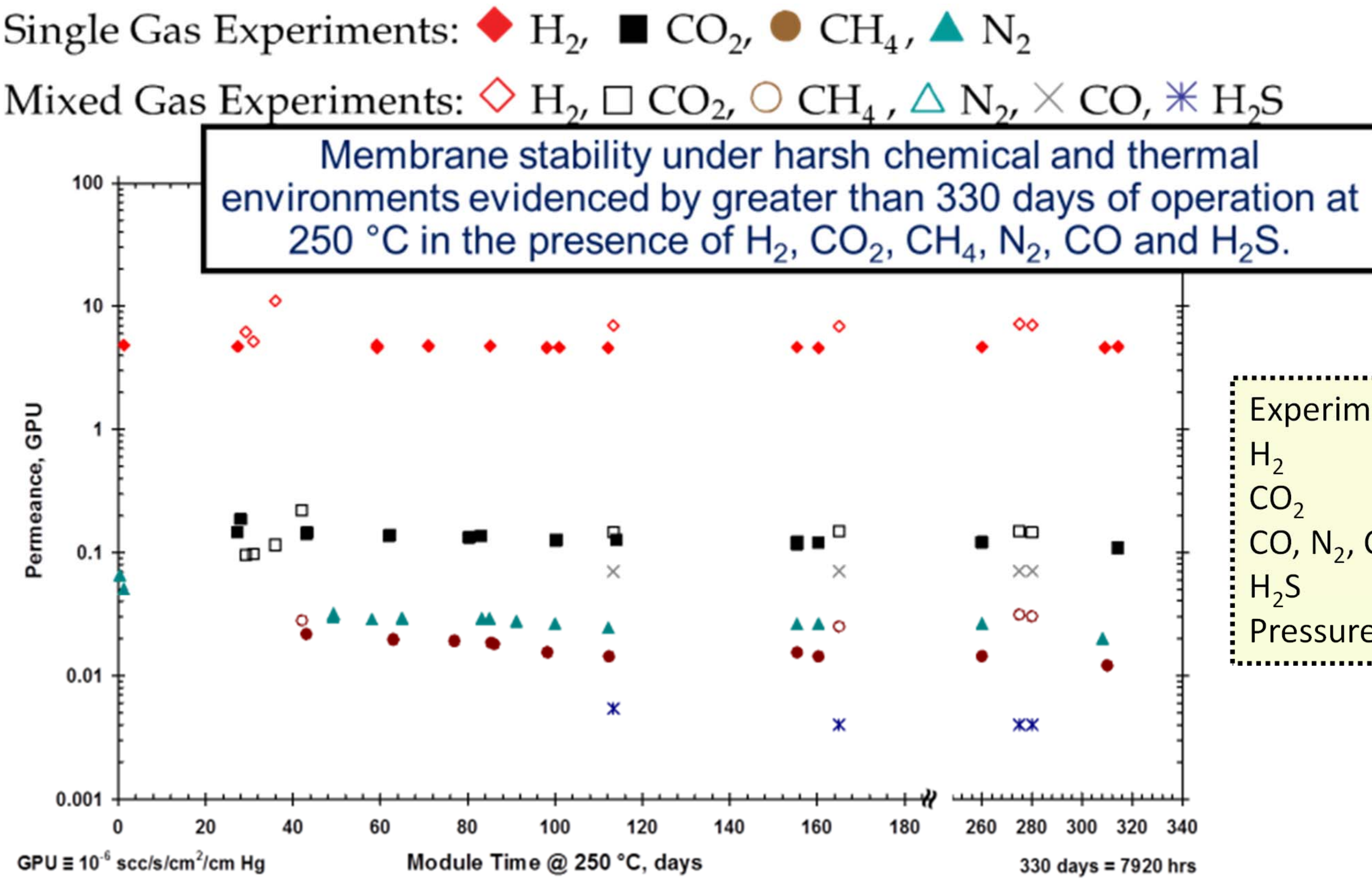
Reformer slip-stream

H_2	73%
CO_2	20%
CH_4	7%
Trace:	N_2 & CO
Steam	Saturated
Press:	36-128 psig
Temp:	150-400 °C

Permeate H_2 purity 97-99.5 %

Ref: Berchtold and Singh *et.al.* Int. J. Hydrogen Energ., under submission

PBI Membrane Durability

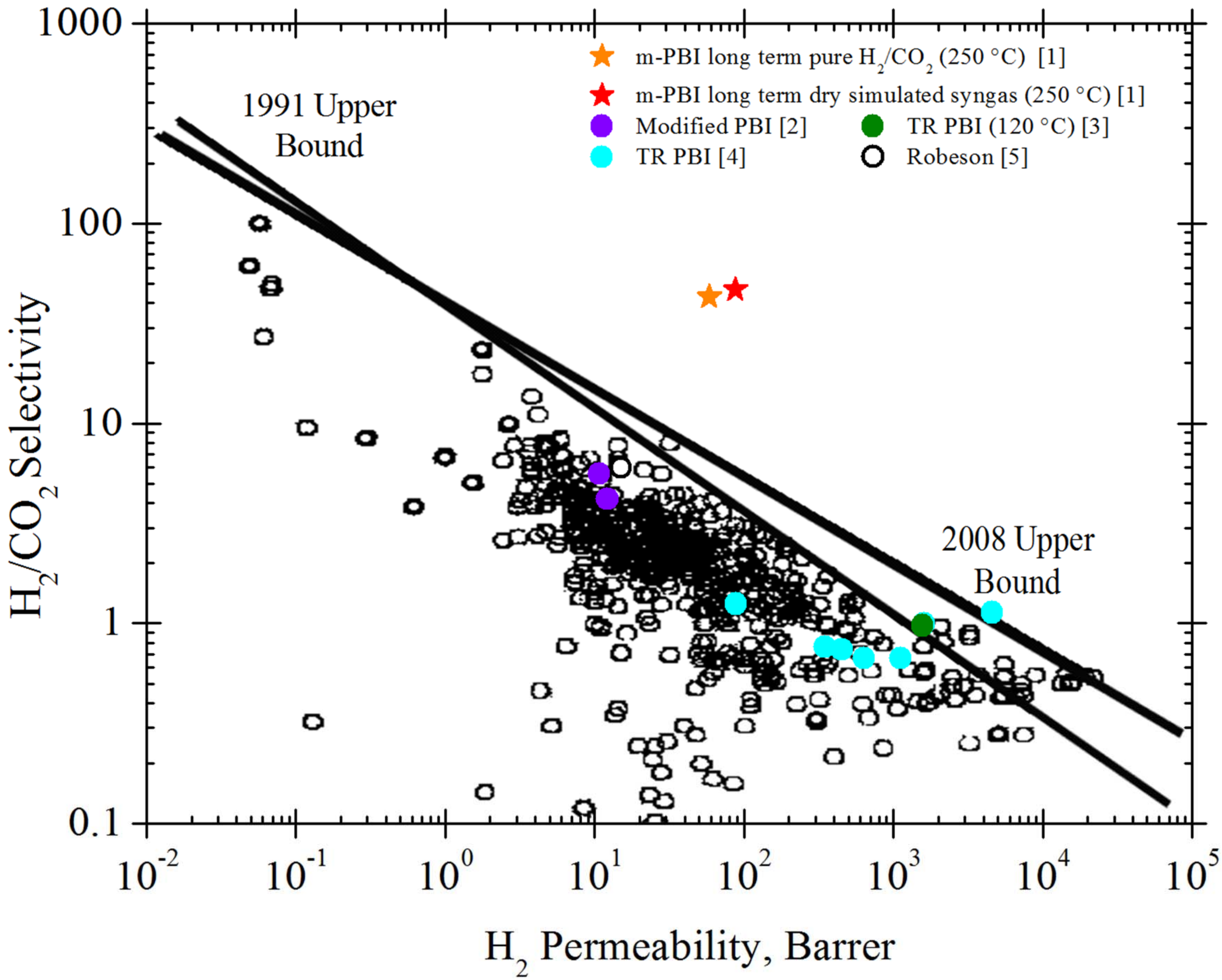


Experimental details	
H_2	55%
CO_2	41%
CO, N_2, CH_4	1%
H_2S	1%
Pressure	50 psid

- **No performance degradation over long term evaluation in simulated dry syngas at industrially relevant conditions**
- **Exceptional tolerance to sulfur compounds**

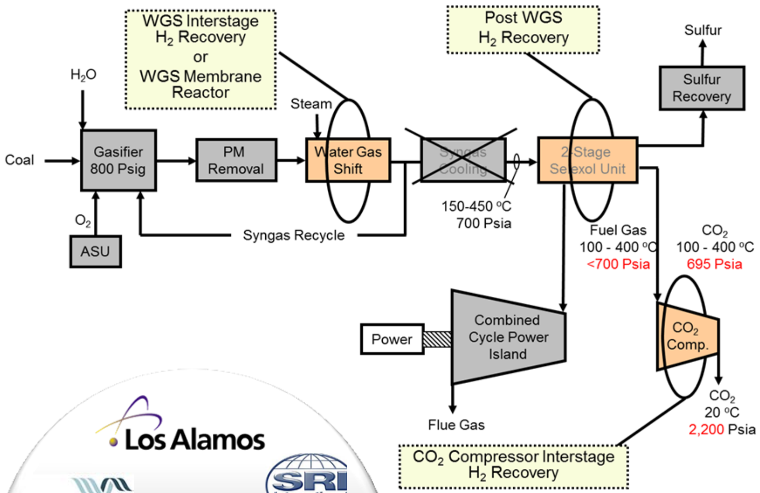
Ref: Berchtold and Singh *et.al.* JMS, in press.

PBI Membranes – Permselectivity Character



[1] Berchtold and Singh *et.al.* JMS, in press **[2]** Kumbharkar et.al., 286 (2006)
[3] Park et.al., 259 (2010) **[4]** Han et.al., 357 (2010) **[5]** Robeson, 320 (2008)

Systems/Economic Analysis: PBI Approaches the DOE Goals



The PBI-based hollow fiber platform offers a means to produce an economically viable, high area density membrane systems amenable to and tailorable for incorporation into syn-gas based chemicals, fuels, and power production processes for pre-combustion CO_2 capture.

CO_2 capture: 3.3 Million tonnes/yr

		Project Cases			
	Units	No Capture	Capture w/Selexol	Capture w/PBI	Capture w/PBI no H_2S removal
Power Production @100% Capacity	GWh/yr	5,455	4,461	4,943	5,035
Power Plant Capital	cents / kWh	4.50	6.19	5.49	5.02
Power Plant Fuel	cents / kWh	1.90	2.47	2.31	2.26
Variable Plant O&M	cents / kWh	0.78	1.00	0.92	0.91
Fixed Plant O&M	cents / kWh	0.60	0.79	0.71	0.70
Power Plant Total	cents / kWh	7.78	10.45	9.43	8.89
Cost of Electricity* (COE)	cents / kWh	7.78	10.45	9.43	8.89
Increase in COE (over no capture)	%	*n/a*	*34%*	*21%*	*14%*

* Separation and Capture Only

Plant operating life: 30 years; Capacity Factor: 80%; Capital charge factor: 17.5%

Scale-Up and Optimization: Transition to Hollow Fiber Platform

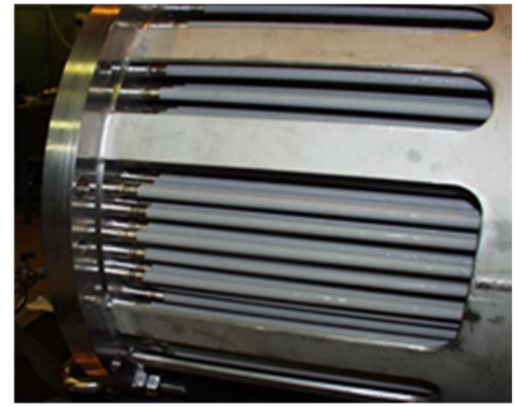
- Thin selective layer mandated for high throughput
- Defect mitigation required for selectivity retention

~30-80 cm^2

- High area density hollow fiber configuration desirable for large volume carbon capture applications

Hundreds of cm^2

Hundreds of m^2



- Design similar to heat exchanger
- ½″ OD x 96″ long tubes

~250 m^2/m^3

@ 75% packing density

High Area Density Hollow Fiber Platform

hundreds of cm^2

2000 – 30,000+ m^2/m^3

@ 75% or even lower packing densities

Additional Hollow Fiber Advantages

- Large mass transfer interface - efficiency advantages
- Opportunity for improved permeance
  - Increased capacity with a reduced footprint
- Easily scaled-up with versatile process design
- Widely used in commercial gas separation and water purification applications

Objectives

Execute the enabling science that will help lead to large scale deployment of a technically viable, energy efficient, and environmentally benign membrane-based CO_2 capture technology.

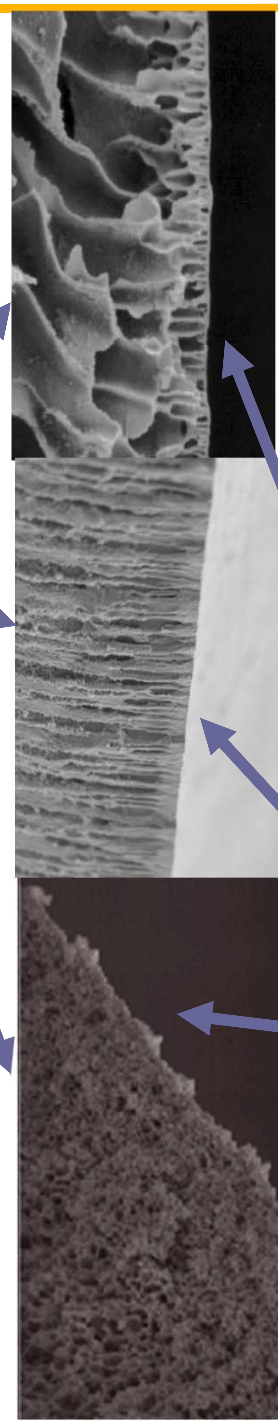
- Development of technically, economically, and commercially viable materials, materials synthesis and membrane fabrication methodologies, deployment platforms, sealing technologies, and separation schemes to support the separations technology integration into an advanced IGCC plant
  - Development and demonstration of LANL developed polymer-based materials and molecular morphologies as separation media for carbon capture and hydrogen purification from syngas
  - Develop the fabrication materials and methods required to realize those materials and morphologies as defect-free high area density hollow fiber membranes and modules
    - Further developing the capability to fabricate defect-free hollow fibers comprised of PBI-based selective layers via commercially viable methods
    - Developing a barrier/potting material and deployment technique compatible with the target process' thermal, chemical, and mechanical environments
    - Developing methods to mitigate and seal defects in the thin hollow fiber membrane selective layer
  - Demonstration of technology potential via materials and membrane performance evaluation under industrially relevant process conditions

PBI-BASED MATERIAL, MORPHOLOGY, & HIGH AREA DENSITY MEMBRANE DEVELOPMENT

Components of an Asymmetric HF

Support Structure

The support structure/ morphology MUST be tailored to optimize mechanical stability AND transport properties



Objective: **Production of an asymmetric PBI hollow fiber.**

Either the inner or outer surface will consist of a thin but dense PBI selective layer.

The underlying support structure should comprise an open porous structure that meets mechanical property requirements (use and lifetime)

Selective (Thin Dense) Layer

Multi-Parameter Challenge

Fiber spinning involves a complex interplay between phase equilibria, phase inversion kinetics, and interfacial mass transfer processes. These processes are influenced by numerous variables including:

- PBI polymer molecular weight (MW) and MW distribution
- Dope (polymer, additives, etc) composition and concentration
- Lumen fluid composition and concentration
- Spinnerette design
- Air gap residence time and atmosphere
- Coagulation fluid composition and concentration
- Dope, coagulation, and lumen fluid temperatures and pressures
- Spinning speed & take-up velocity - bath resonance times
- Drying conditions

All material properties, chemistries, and design parameters influence the ultimate characteristics of your hollow fiber membrane product

Understanding this complex interplay of process parameters has largely been the focus of our ongoing efforts

Fundamental Studies: Polymer Solutions and Membrane Formation

Solution Properties

- ✓ Reliable PBI quality (MW, purity, and particle size)
- ✓ High concentration (>20wt%)
- ✓ Good viscoelastic properties (>20,000cP)
- ✓ Deaggregation of polymer in dope (mechanical property influences)
- ✓ Phase diagrams, inversion kinetics
- ✓ Long term spinnability/stability
- ✓ No chemical degradation

Solution Characterization

- ✓ GPC, UV spectroscopy – dilute solutions
- ✓ Rheological and spectroscopic characterization

Membrane Formation Parameters

- ✓ Dope (polymer, additives, etc) composition and concentration
- ✓ Lumen fluid composition and concentration
- ✓ Spinnerette design
- ✓ Air gap residence time and atmosphere
- ✓ Coagulation fluid composition and concentration
- ✓ Dope, coagulation, and lumen fluid temperatures and pressures
- ✓ Spinning speed & take-up velocity - bath resonance times
- ✓ Drying conditions

Membrane Characterization

- ✓ SEM, 3D x-ray tomography, optical microscopy – morphology
- ✓ Dynamic thermomechanical testing - mechanical properties
- ✓ TGA and DSC – thermal stability and crystallinity
- ✓ Gas permselectivity

Hollow Fibers from PBI/DMAc/Additive Solutions:

Solution properties, Fiber Spinning, and Morphology Control

Additive incorporation is utilized to:

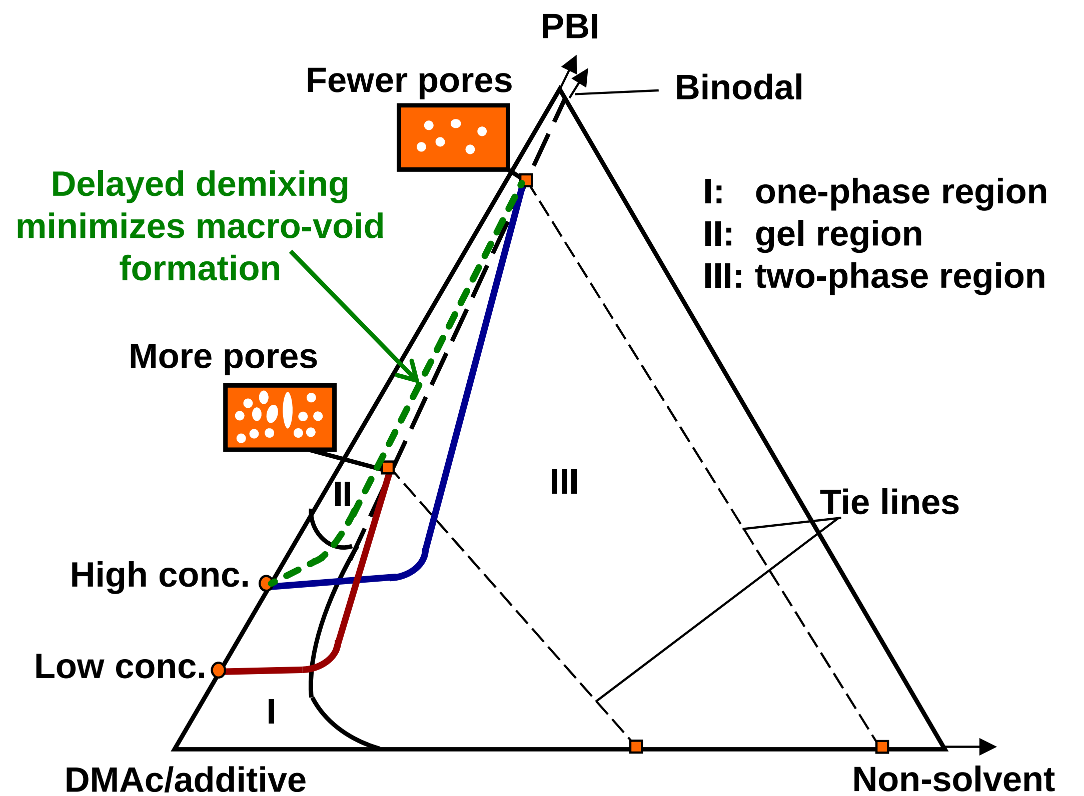
- Tailor phase behavior
- Prevent aggregation/gelation
- Optimize HF material properties
- Improve dope stability

Objectives

✓ Improved mechanical properties
  – Concentrated dope solution with good viscoelastic properties
  – Macrovoid minimization

✓ High Selectivity/Permeability
  - Asymmetric membrane
  - Defect mitigation

✓ Optimized economics
  – Minimization of solvent/additive cost
  – Utilization of environmentally benign materials and materials recovery/reuse schemes



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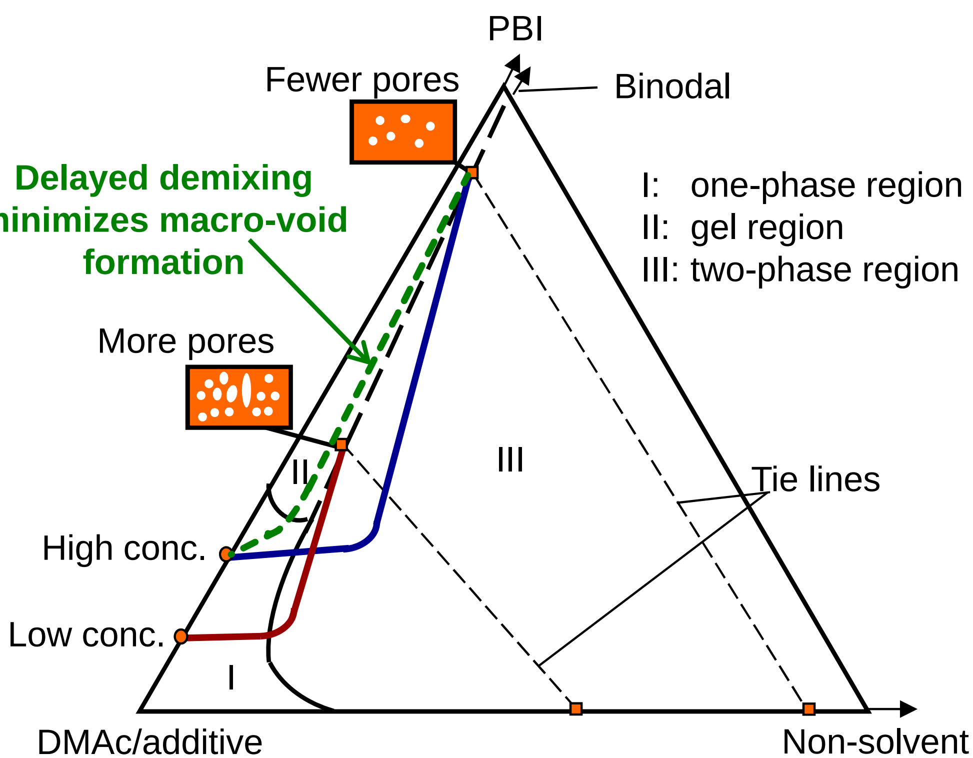
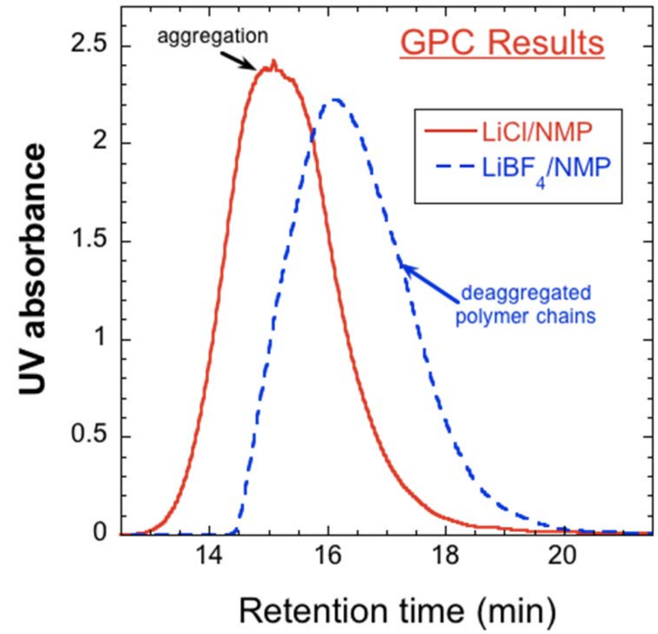
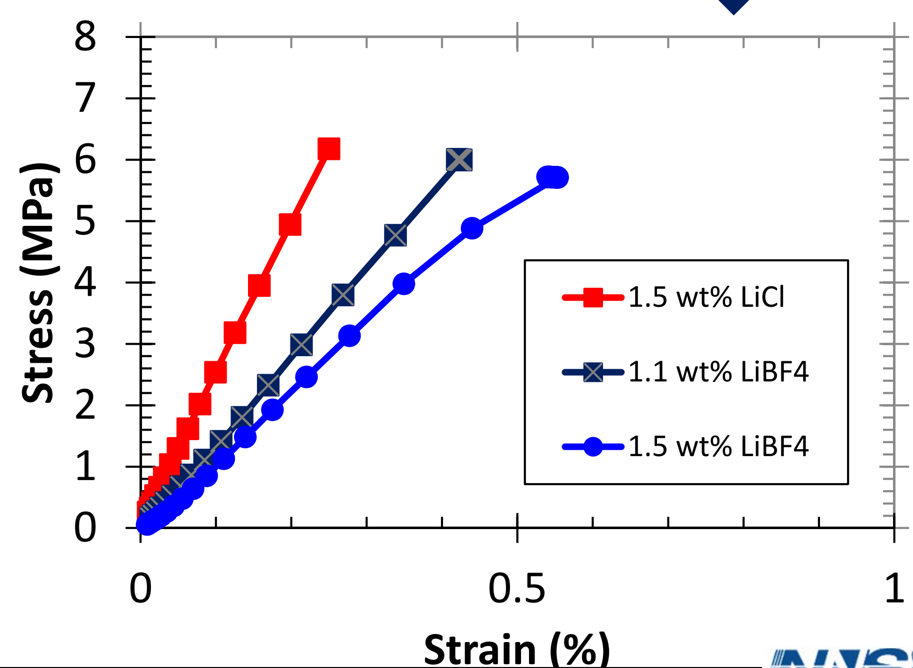






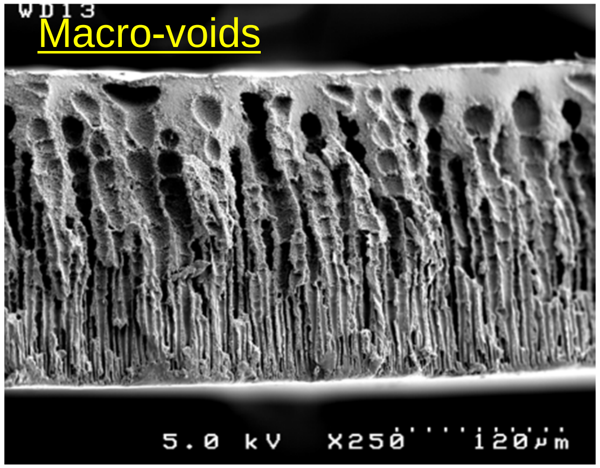
PBI Hollow Fibers by Phase Inversion

- **Fabrication by a wet or dry-wet phase inversion spinning process**
- **Liquid - liquid demixing is key to support structure formation**

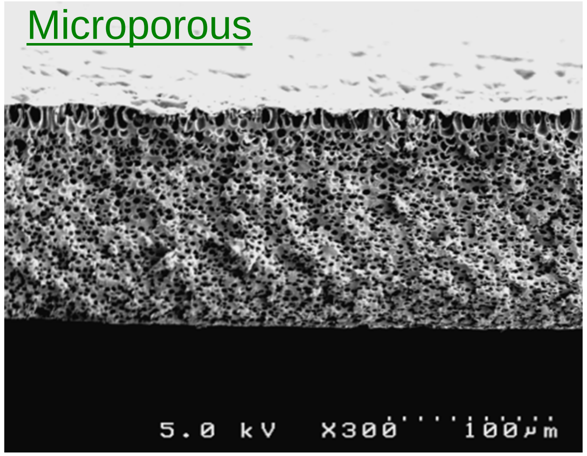
Two primary mechanisms lead to different structures

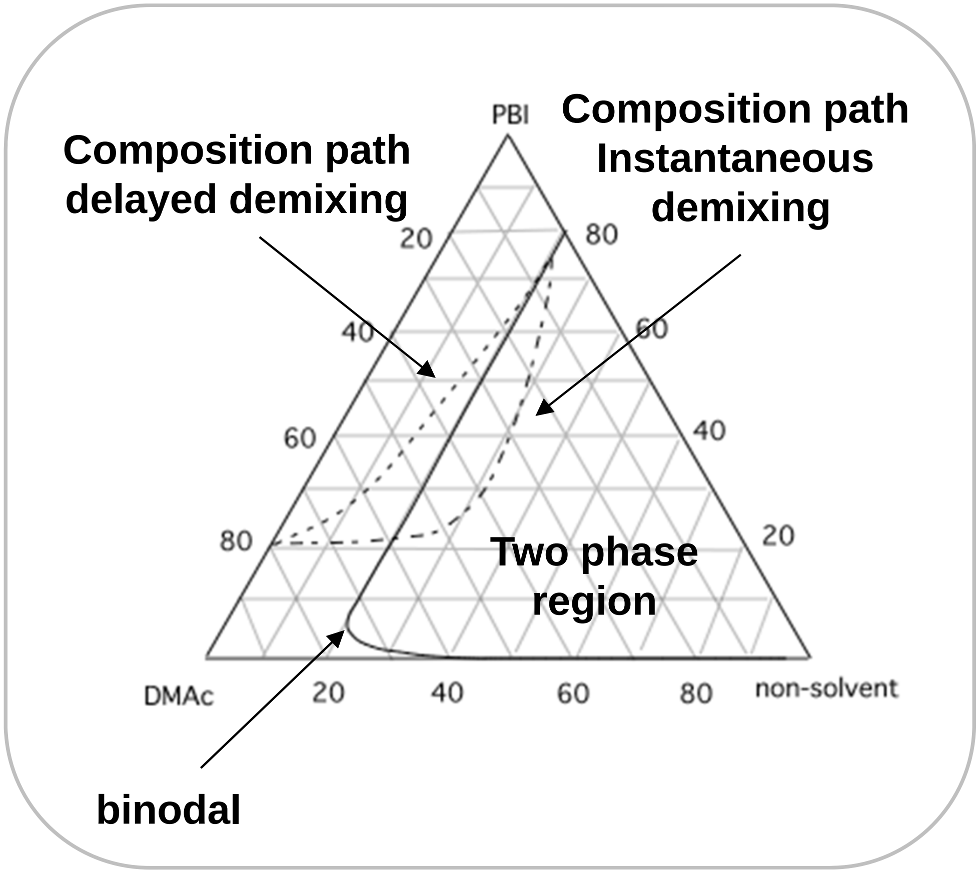
- Instantaneous demixing – open porous structure

Importance of components and composition



- Delayed demixing – dense sponge structure



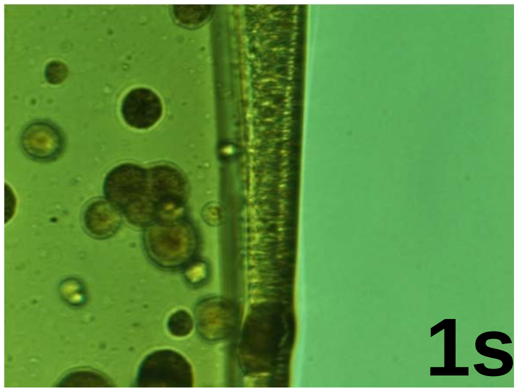


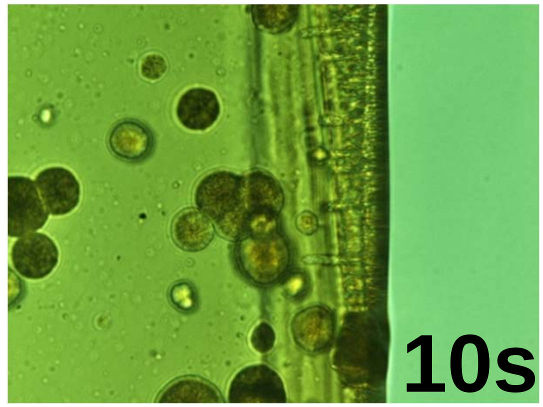
Membrane Development: Dope/Coagulant System

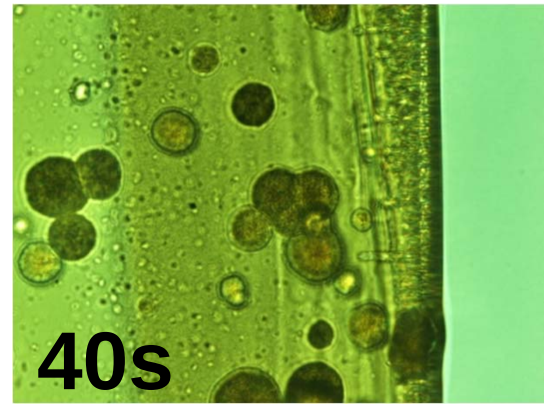
Micro-structural evolution with different precipitants

Precipitant A

Slower moving precipitation front and more uniform structure

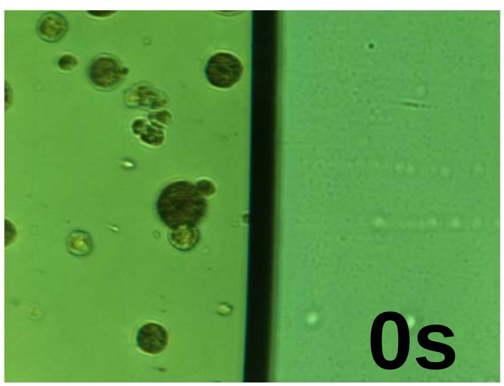


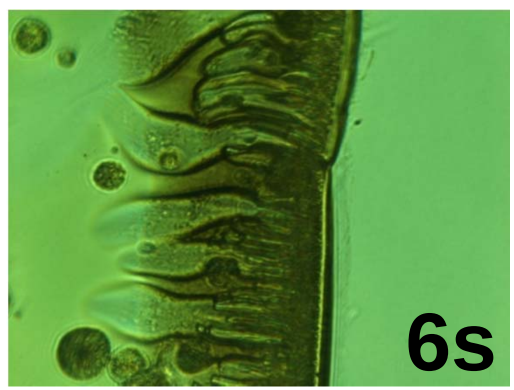


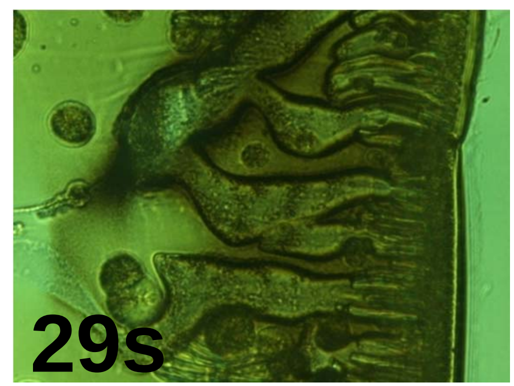


Precipitant B

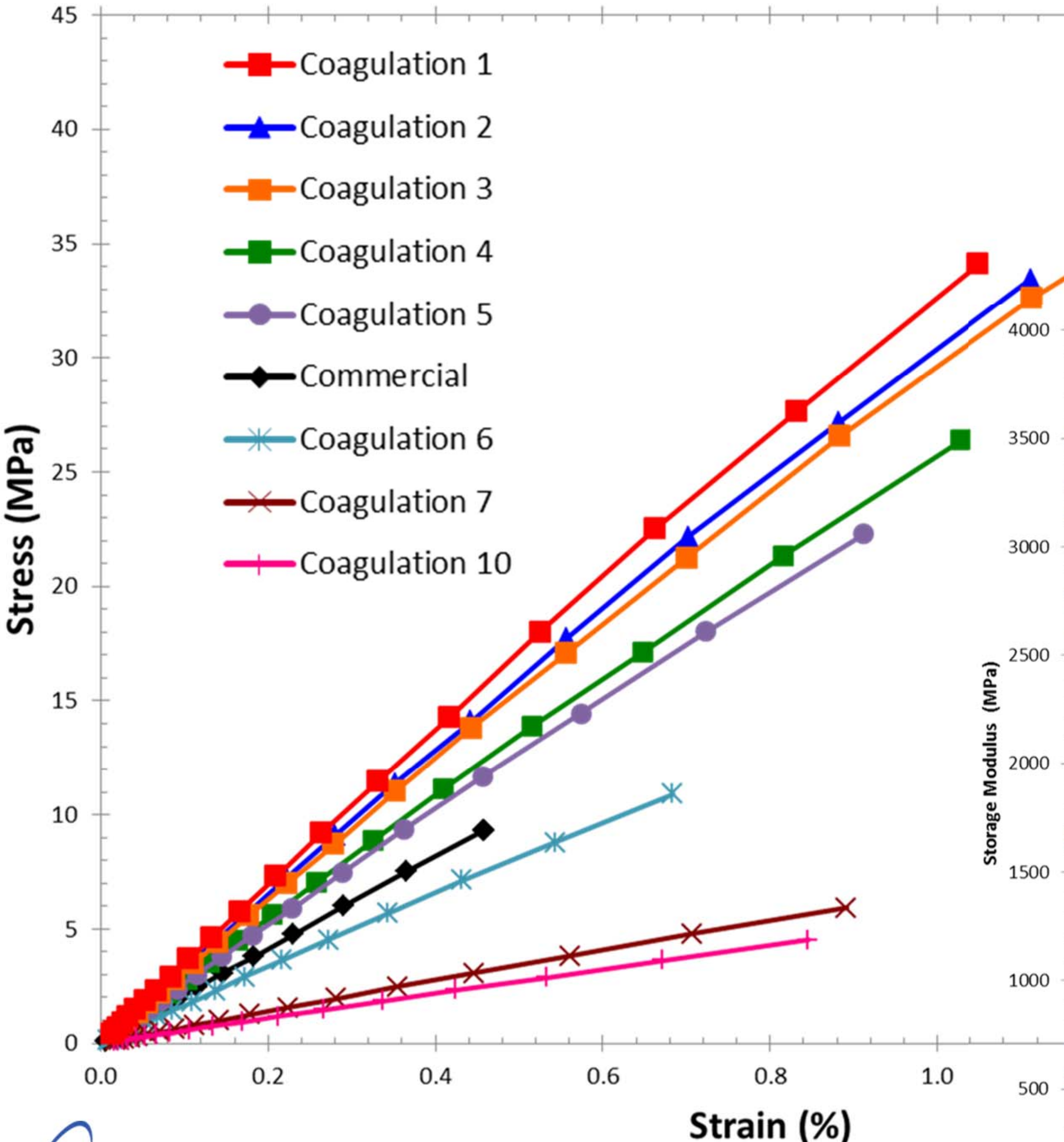
Instantaneous demixing with clear evidence of convective intrusion

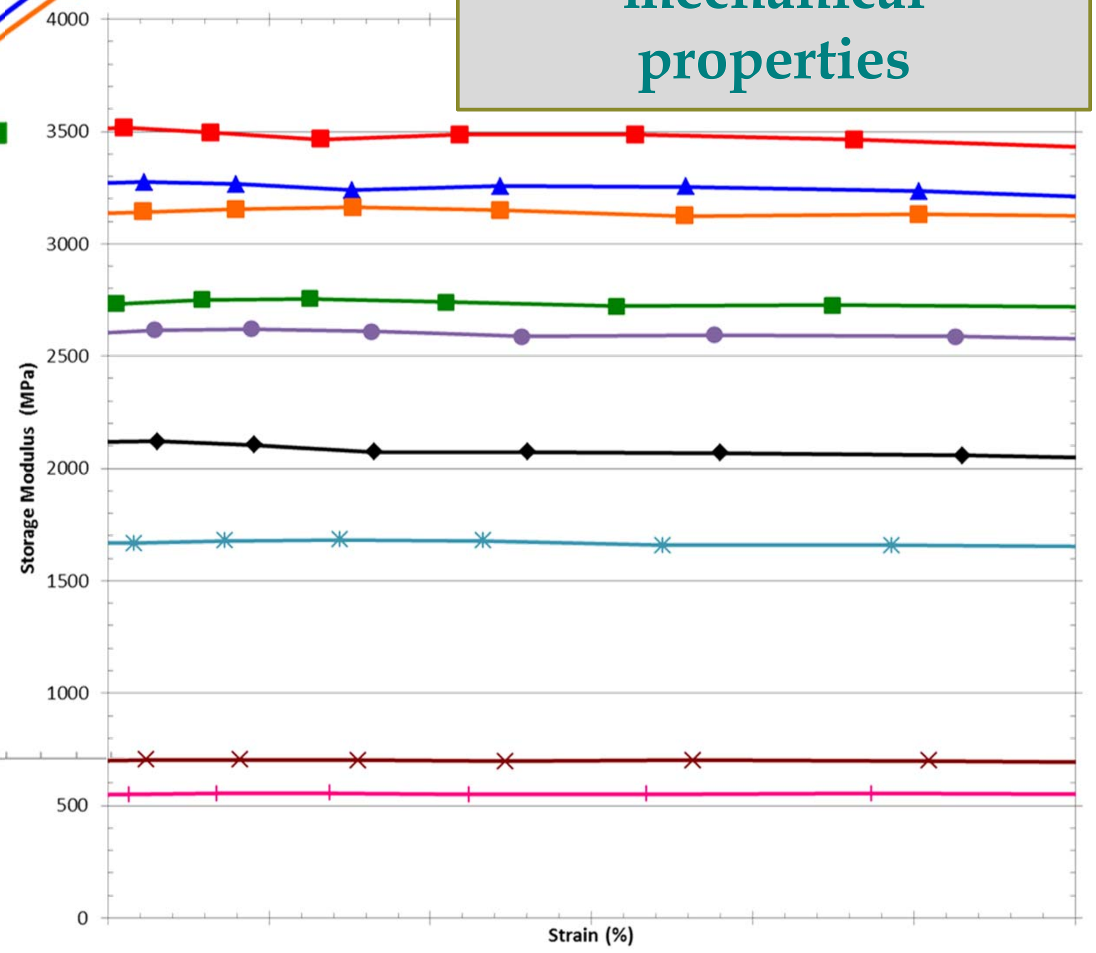






Tailoring of Phase Inversion Dynamics for Material Property Optimization

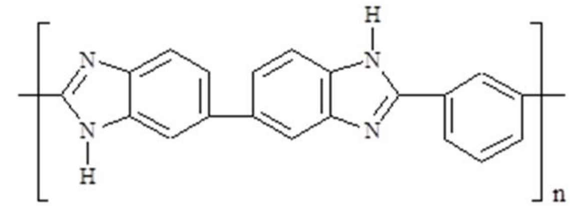


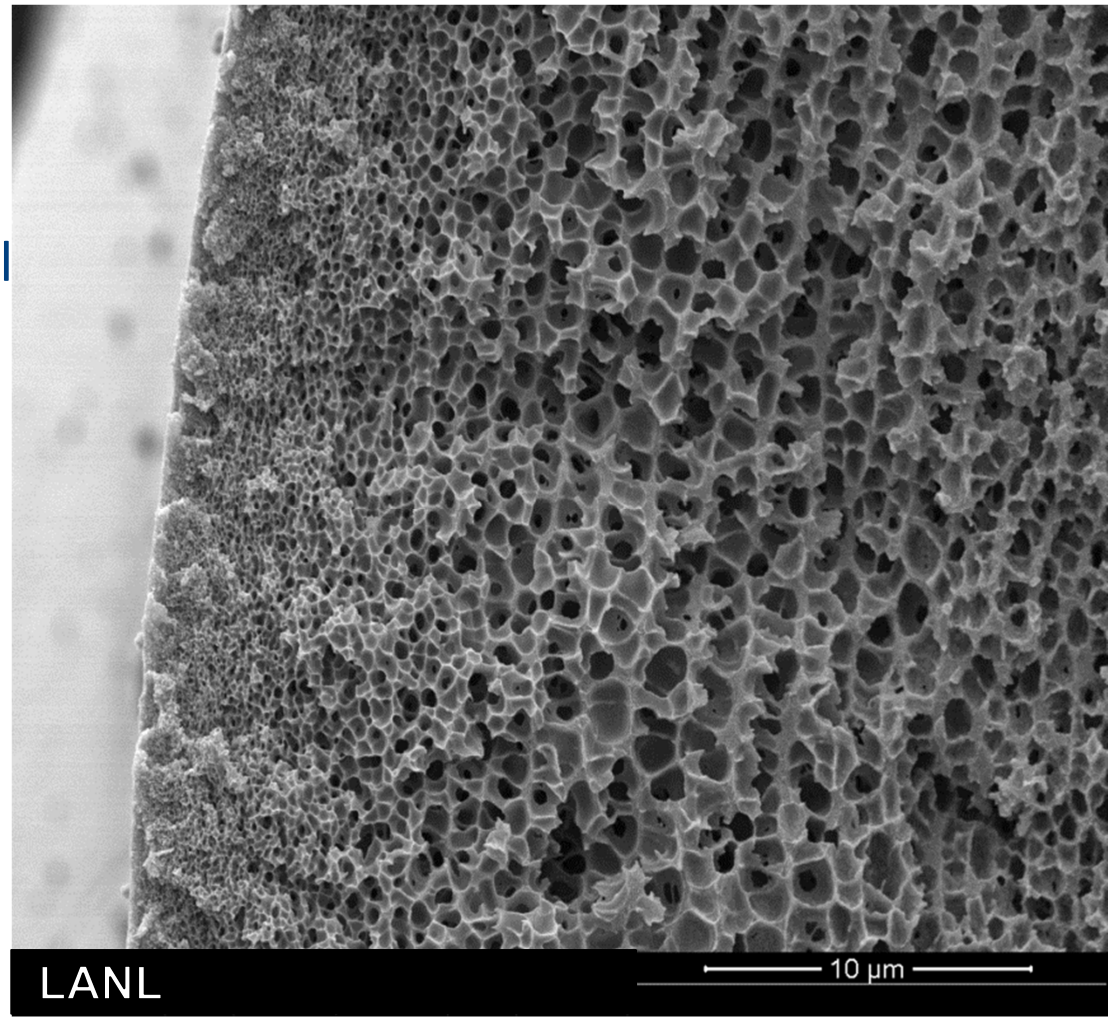


Coagulation bath composition strongly influences pore structure and correspondingly mechanical properties

Working Towards Optimized HF Morphology

- High perm-selectivity for H_2 over other syngas components
  - Minimized dense layer thickness at hollow fiber surface
  - Selective layer defect mitigation strategies employed
  - Minimize gas resistance of support: porous support structure with interconnected pores achieved





- Fiber morphology thermo-mechanical stabilty and ductility optimization
  - Maximize strength and toughness with minimized permselectivity impact
  - Minimize macrovoid formation in support structure

HIGH-TEMPERATURE POTTING MATERIAL DEVELOPMENT

Potting material development

- **Evauations of commercially available and specialty materials**
  - Chemical, thermal, mechanical stability evaluations
  - Permselectivity evaluations: barrier material context
  - Chemical compatibility and membrane/potting interface evaluations
- **Potting material/method that allows for testing of hollow fibers in a simulated syngas environment and preconditioning of those fibers at temperatures of at least 250 °C achieved**
  - High potential options identified
  - Ultimate down-selection will be driven by final membrane characteristics and preconditioning and operating requirements

MEMBRANE DEFECT MITIGATION MATERIALS AND METHODS DEVELOPMENT

Two Primary Manufacturing Pathways Pursued

Develop materials for improved membrane manufacturability and defect sealing post-selective layer formation

- ***In situ* formation of an integrally skinned PBI-based hollow fiber**
  - Fiber spinning parameter space optimized to minimize defect levels during fiber fabrication (Discussed in Previous Section)

- **Sealing layer utilized with fiber formation occurring via dual layer spinning or multistep formation methods**
  - Chemistries selected to optimize manuafacturability, maximize permeance, and minimize defect levels

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Gen1 Seal: Transport Resistance & Thermal Stability Characteristics

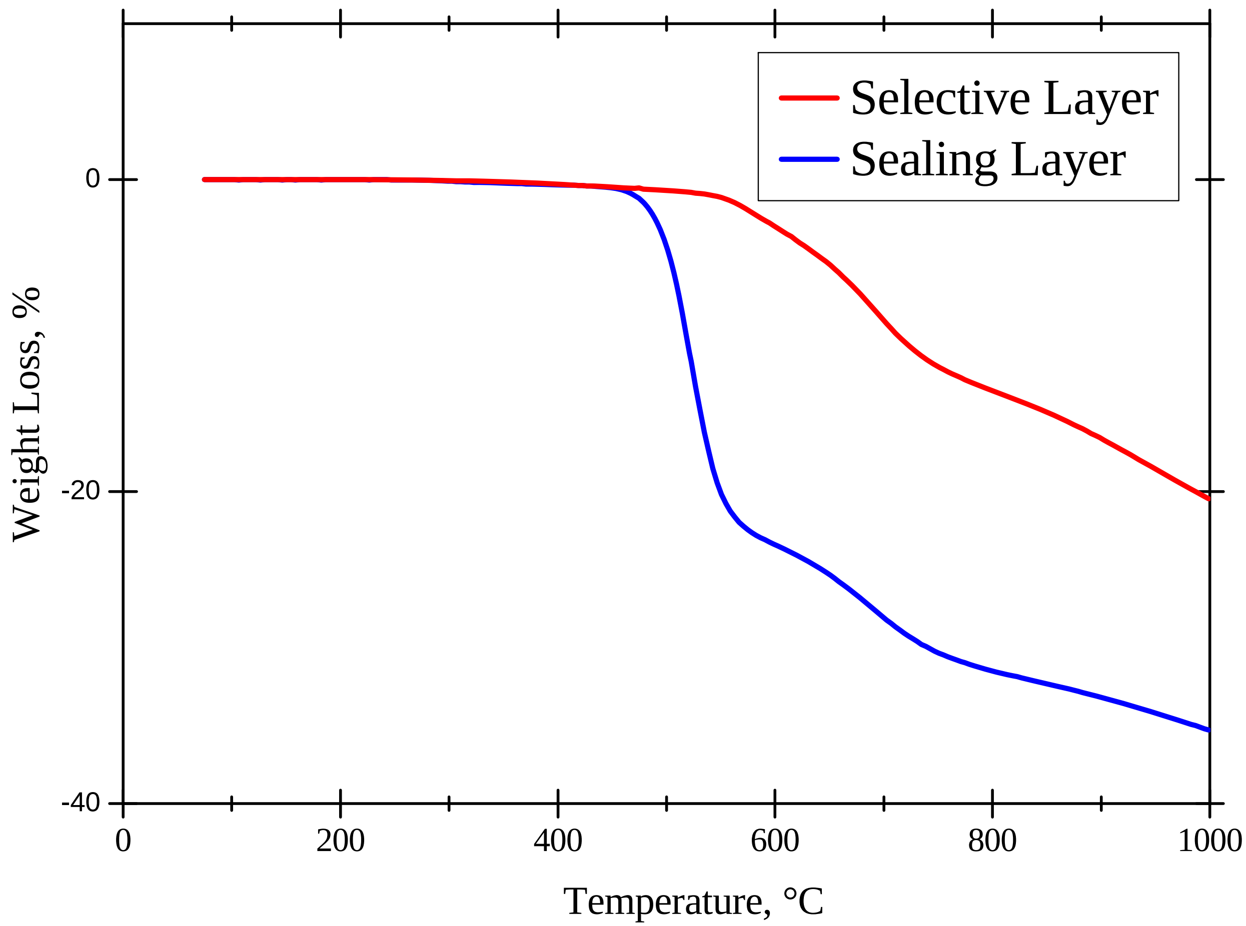
Material	Temperature [°C]	H_2 Permeability [barrer]	H_2/CO_2 Selectivity
HT Seal - 1	250	1008	5.2
PBI SL	250	78	23-43*

Data: Pure gas, P_{feed} = 50 psia

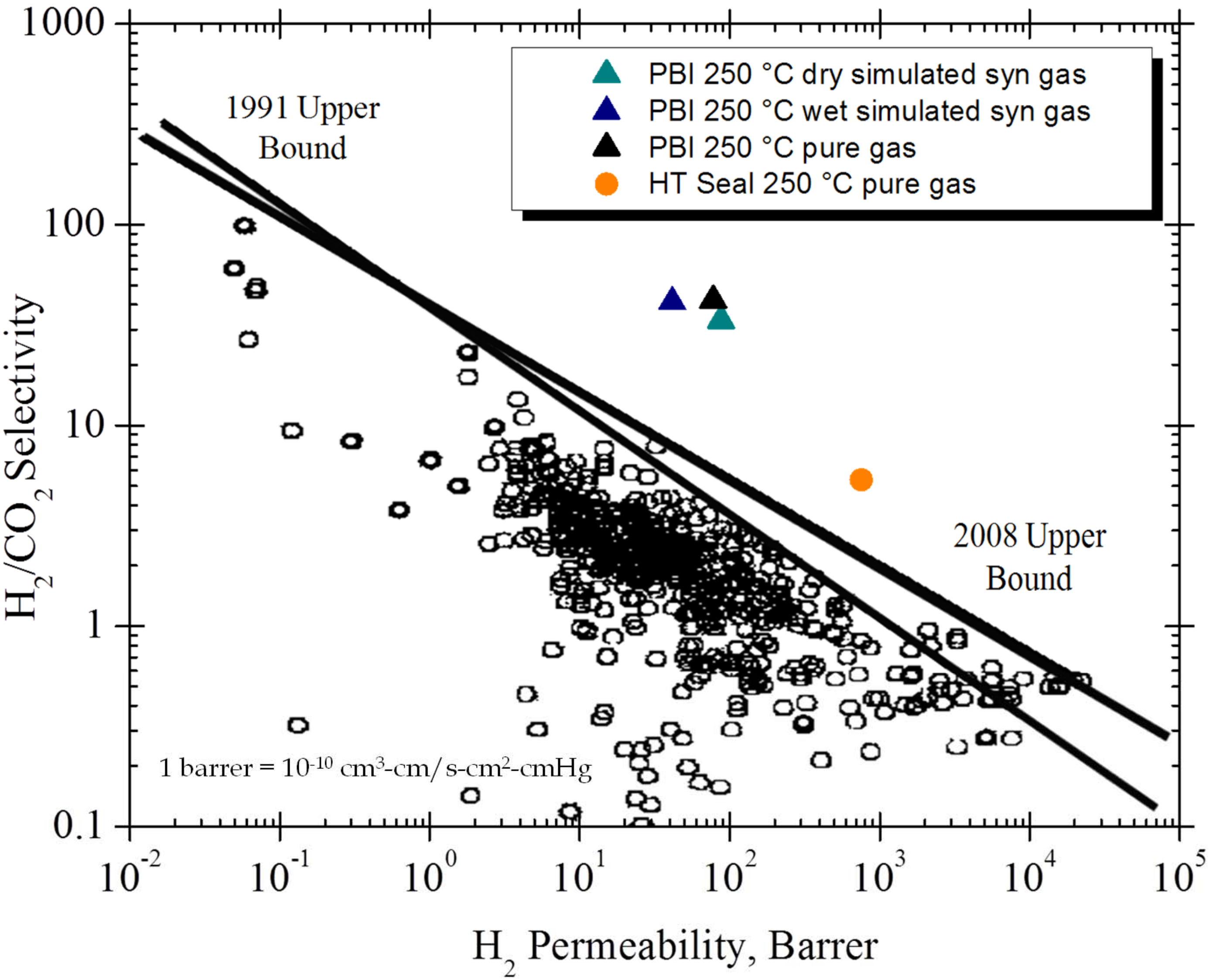
* Thermal conditioning dependent effect on CO_2 permeance

HT Seal-1 / PBI Comparison

- Large H_2 permeability low selectivity compared to the PBI selective layer material
  - Minimized – but not zero! – transport resistance
- Gen 1 seal thermally stable to ≥ 300 °C
- Initial chemical stability experiments indicate tolerance to anticipated syn gas environment



Gen1 HT Sealing Material Permselectivity



Excellent sealing layer candidates identified:

- **Preliminary evaluations of Gen1 material demonstrate potential**
- **Seal chemistry compatible with PBI-selective layer chemistries**
- **High permeability minimizes transport resistance**

Material	Temperature [°C]	H_2 Permeability [barrer]	H_2/CO_2 Selectivity
HT Seal - 1	250	1008	5.2
PBI SL	250	78	23-43*

○ Literature data from: Robeson, L.M., Polymer, 35(23) 1994 & J. Membr. Sci., 320 2008.

Table Data: Pure gas 50 psid

* Thermal conditioning dependent effect on CO_2 permeance

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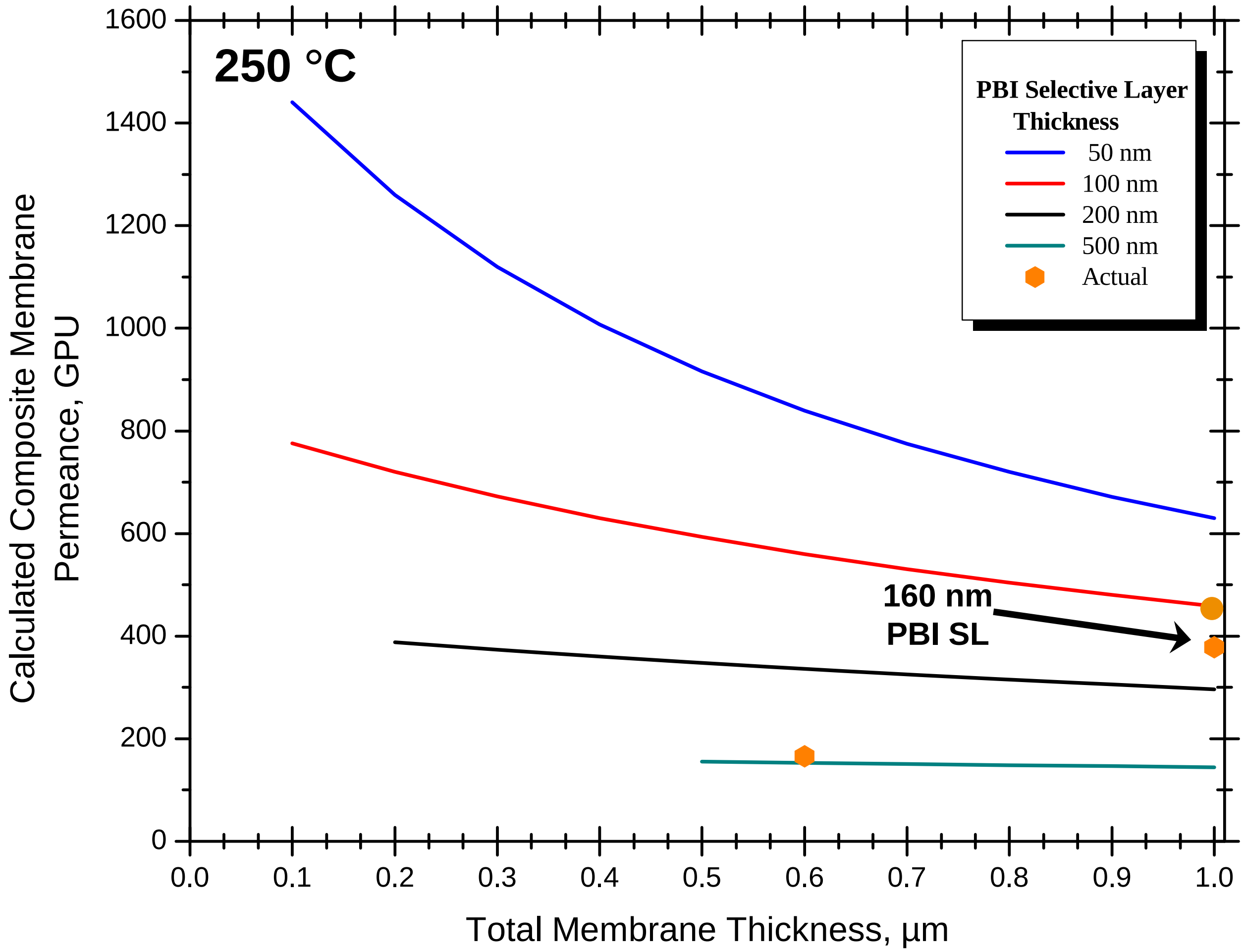
Composite Membrane Predicted/Actual Performance

Calculated PBI and HT Seal-1 composite membrane performance. Calculated H_2 permeance based on H_2 permeability data at 250 °C as a function of total membrane and PBI layer thicknesses



Material	Temperature [°C]	H_2 Permeability [barrer]	H_2/CO_2 Selectivity
HT Seal - 1	250	1008	5.24
PBI SL	250	77.58	23-43*

Gas transport is controlled by the PBI selective layer

Initial permselectivity validation achieved on 1 µm composite films (900 nm Seal/100 nm PBI) at 25 °C and (840 nm Seal/160 nm PBI) at 25 and 250 °C

- **Using this method with HT Seal, this 1st generation "sealing" material, results in the achievement of *unprecedented and commercially attractive* H_2 permeances at 250 °C**

Path Forward

2012

- Continue to optimize and refine the hollow fiber spinning parameter space
  - Define and down-select critical parameter sets for use as starting points for pilot scale fabrication
    - Overarching goals: maximize *in-situ* defect mitigation, optimize mechanical properties/support and selective layer morphology
    - Key parameters include: dope composition, bore composition, spinnerette/dope temperature, air gap length/ resonance time, air gap environment, coagulation bath 1 composition

2013 | 2014

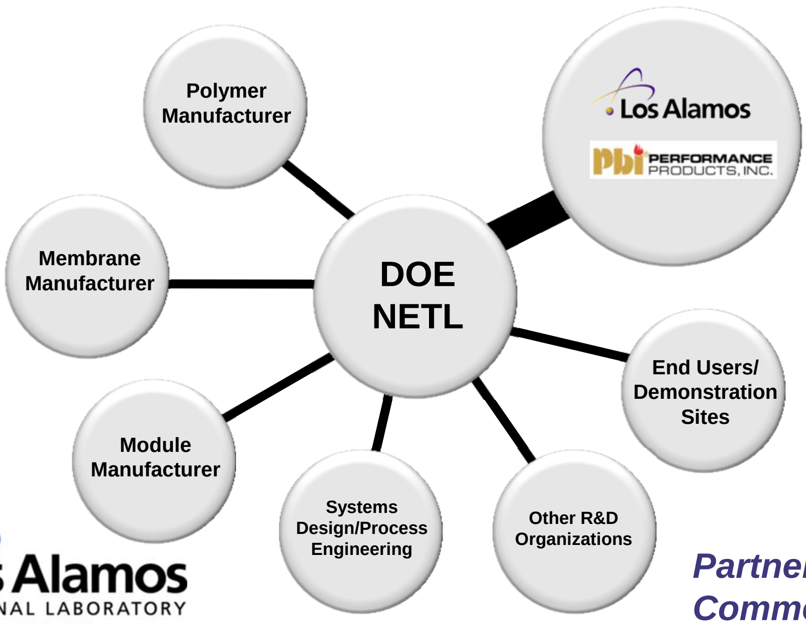
- Initiation of hollow fiber manufacture on a single fiber pilot-scale line with refined parameters derived from bench-scale experiments
  - Pilot scale design planned to facilitate near-direct translation of defined fabrication conditions to a multi-fiber commercial scale fabrication line
- Optimization of spinning parameters on pilot line
- Further develop sealing layer fabrication methodologies and materials
- Further develop fiber potting methods for application to module configurations for 2015 demonstration
- Continued demonstration and validation of developed materials and methods in simulated synthesis gas environments at realistic process conditions

2015

- Realization of a PBI-based hollow-fiber gas separation membrane manufacturing capability for tech-transfer to our industrial partners for further scale-up/commercialization
- Realization of a prototype PBI-based hollow fiber membrane modules for a ≥50 lb syngas/day demonstration on coal derived syngas in 2015

Project Team

- Materials Design, Synthesis, & Evaluation
- Membrane Design & Fabrication
- Technology Transfer
- Module Demonstration



- Commercial Scale Materials Synthesis
- Module Design & Fabrication
- Market Penetration Opportunity Analysis
- Commercialization Plan Development
- Strategic Selection/ Incorporation of Additional Project Partners/Capabilities

Partnerships Under Continued Optimization to Maximize Commercialization Potential & Market Impact

Summary

The PBI-based hollow fiber platform offers a means to produce an economically viable, high area density membrane system amenable to incorporation into an IGCC plant for pre-combustion CO_2 capture.

Our team is developing the tools required for translation of this unique class of "bench scale proven" materials into a commercially viable technology platform

Thank You

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