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

LANL-FE-308-13

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Collaborators Past & Present on our High T_g Polymer for Carbon Capture Projects

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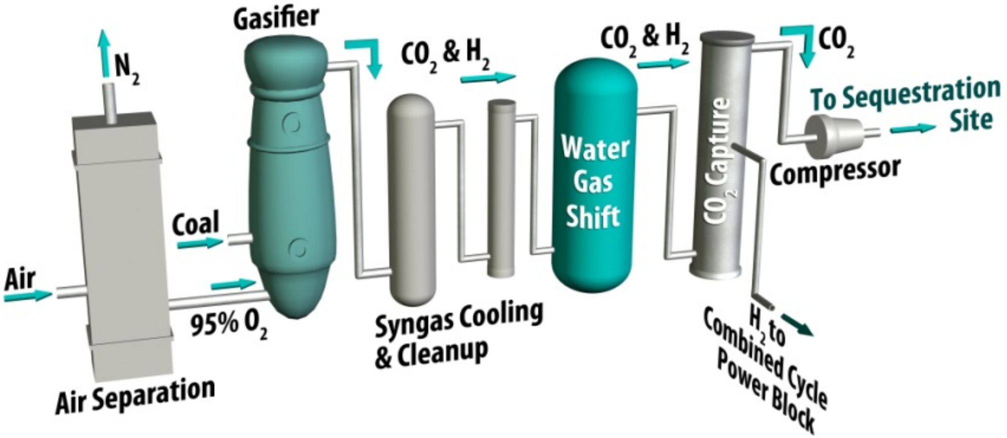
Project Summary

- Award Name:
  - Polymer-Based Carbon Dioxide Capture Membrane Systems
- Award Number:
  - FE-308-13
- Performance Period:
  - 03/2013-03/2016
- Current Budget Period:
  - BP3 of 3 (04/15-03/16)
- Project Cost (DOE):
  - $1,972K
- DOE NETL Project Manager:
  - C. Elaine Everitt



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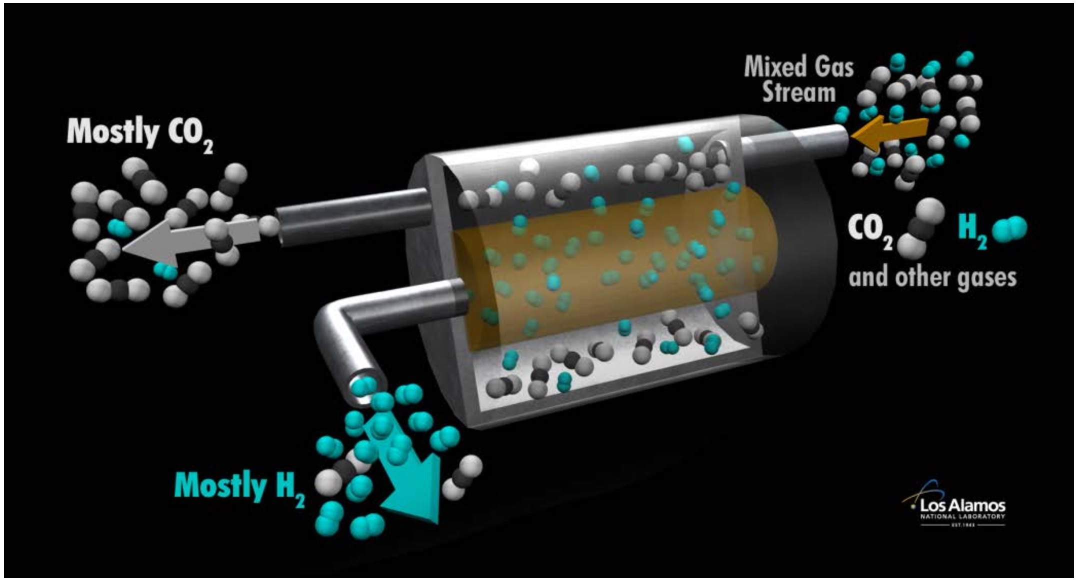
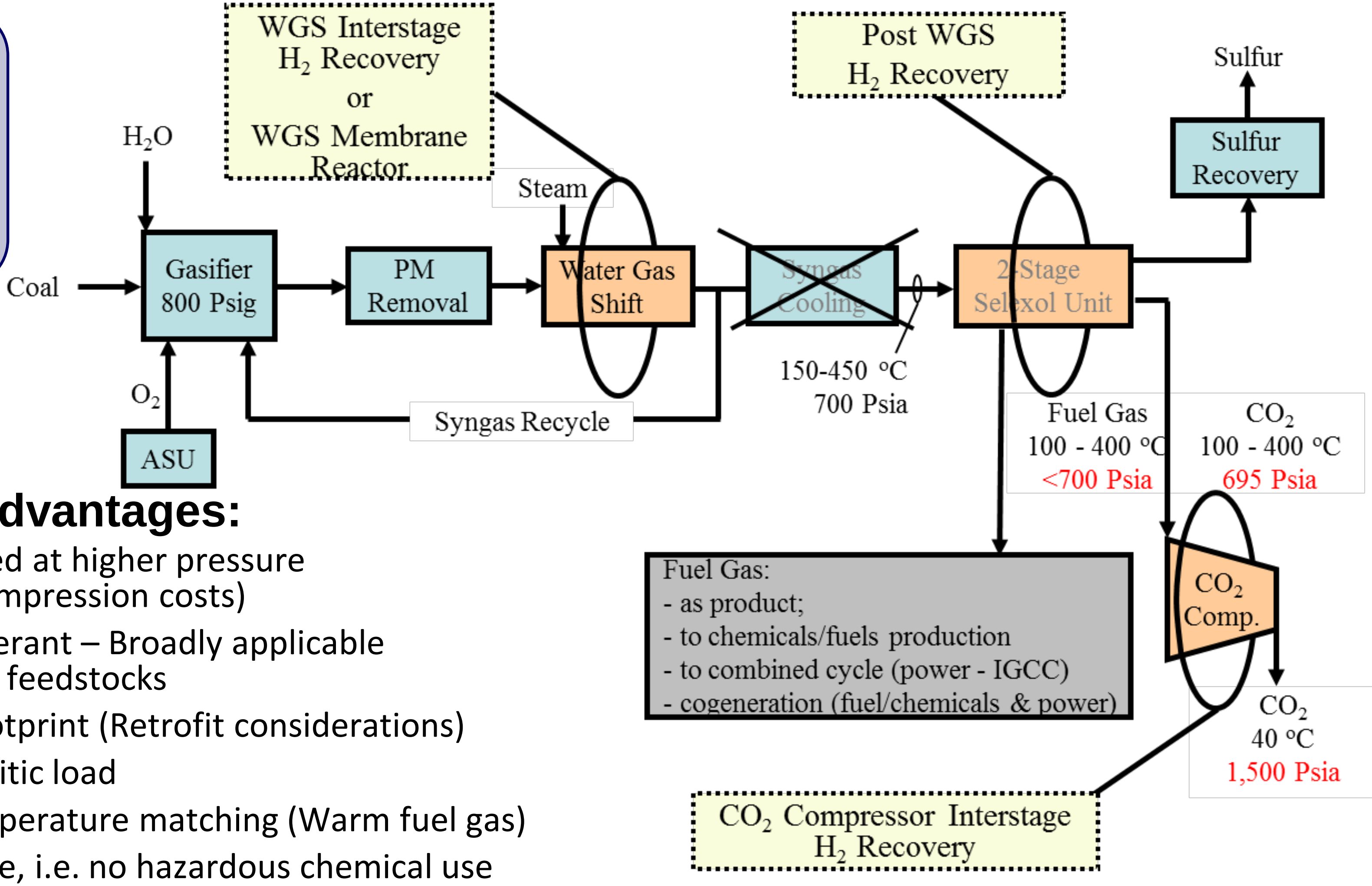
Overarching Objective



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.

Project Overview: Technology Benefits

Process Areas Targeted: Membrane Separations



Membrane Advantages:

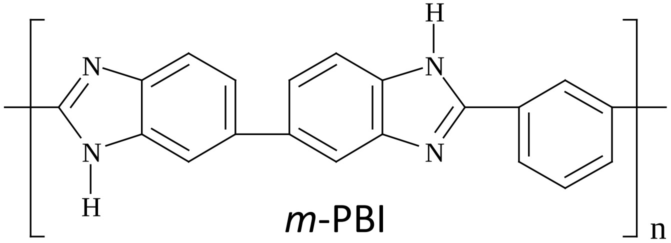
- CO_2 produced at higher pressure (reduced compression costs)
- Impurity tolerant – Broadly applicable to all syngas feedstocks
- Reduced footprint (Retrofit considerations)
- Lower parasitic load
- Process temperature matching (Warm fuel gas)
- Emission free, i.e. no hazardous chemical use
- Decreased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

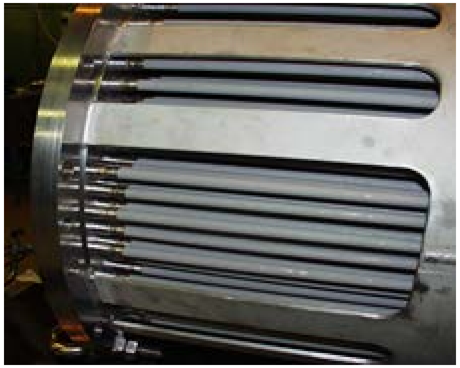
Technology Challenges & Opportunities

- **Commercial polymer membranes and module manufacture/sealing technologies are limited to $T_{operation}$ ~150 °C.**
  - Separation process economics are strongly tied to process/separation temperature.
- **Membrane materials and systems capable of withstanding IGCC syngas process conditions are required.**
  - Syngas temperatures (>200 °C) and compositions, including H_2S and steam, present a very challenging operating environment for any separation system.
- **Large process gas volumes mandate high membrane permeance.**
  - High permeance membranes are achieved via appropriate materials design/selection combined with minimization of the membrane selective layer thickness.
  - Thinner selective layers often result in increased defect formation during fabrication.
  - Defect mitigation strategies/sealing materials utilized for current commercial gas separation membranes are not compatible with the thermal and/or chemical environments present in this application.
  - Thermally and chemically robust defect mitigation strategies must be developed to retain the required membrane selectivity characteristics.

Background: PBI Membranes

- PBI-based membranes have commercially attractive H_2/CO_2 selectivity, exceptional thermal stability (T_g > 400 °C), and exhibit tolerance to steam and H_2S.
- Broad PBI $T_{operation}$ (150 to 300+ °C) indicates potential for PBI-based membrane module integration at IGCC relevant process conditions.
- The H_2 permeability of the state-of-the-art PBI-based membrane materials mandates ultra-thin selective layers.
- Economic considerations mandate use of a high surface area membrane deployment platform such as hollow fibers (HFs).



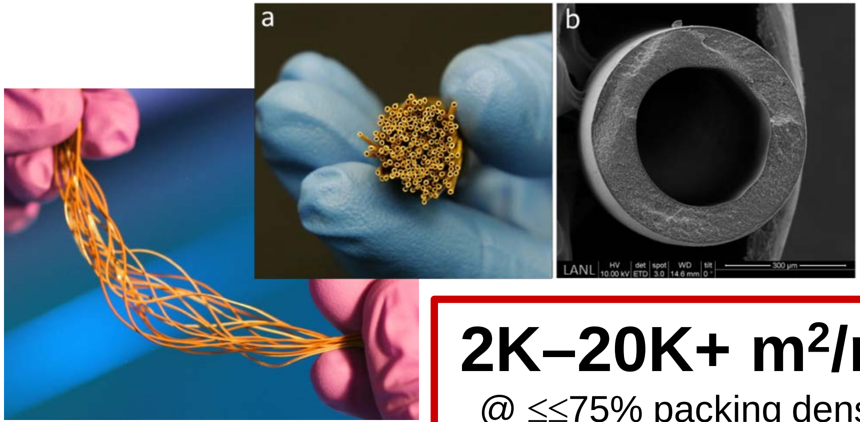


Hundreds of m^2

~250 m^2/m^3

@ 75% packing density

High Area Density Hollow Fiber Platform



hundreds of cm^2

2K–20K+ m^2/m^3

@ ≤≤75% packing density

Li, *J Membrane Sci* 461(2014)
Berchtold, *J Membrane Sci* 415 (2012)
Pesiri, *J Membrane Sci* 415 (2003)

Project Overview

Objectives

- Realize high performance PBI-based HF membranes for pre-combustion hydrogen separation/carbon capture
  - Minimize membrane support costs, maximize membrane flux, retain thermo-mechanical & thermo-chemical stability characteristics, and increase the area density achievable in a commercial module design
  - Produce an asymmetric PBI HF comprised of a thin, dense defect-minimized PBI selective layer and an open, porous underlying support structure with morphology characteristics tailored to optimize transport and mechanical property requirements (use and lifetime).
  - Develop materials and methods to further mitigate defects in ultra-thin selective layers for use under process relevant conditions.
  - Reduce perceived technical risks of utilizing a polymeric membrane based technology in challenging (thermal, chemical, mechanical) syngas environments

Project Focus Areas: Tasks

- **Hollow Fiber Fabrication**
  - PBI-based high area density, high permeance membrane development
- **Sealing Layer Development & Integration**
  - Membrane defect mitigation materials and methods development
- **Module Fabrication**
  - Single and multi-fiber membrane module fabrication
  - CFD utilization to aid in membrane and module performance validation and guide module design (with NETL)
- **Demonstration and Validation of Developed Materials and Methods**

Project Status

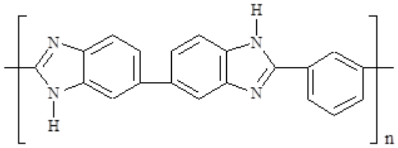
Milestones/ Decision Points M/D	BP1 & BP2 Milestones/Deliverables	Planned/Actual Completion Date
M-1	Demonstrate feasibility of coating sealing layer on hollow fibers	COMPLETE BP1Q1
M-2	Initiate mixed gas hollow fiber testing under realistic syngas conditions	COMPLETE BP1Q1
D-1	Demonstrate hollow fiber membrane with pure gas H2 permeance of at least 150 GPU and H2/CO2 selectivity of at least 20 under realistic process conditions	COMPLETE BP1Q3
M-3	Demonstrate ability to control the selective layer thickness	COMPLETE BP2Q1
M-4	Demonstrate sealing layer efficacy and composite structure tolerance to syngas operating environments	COMPLETE BP2Q3
D-2	Demonstrate single hollow fiber membrane with mixed gas H_2 permeance ≥ 250 GPU and H_2/CO_2 selectivity ≥25 in simulated syngas environments	COMPLETE BP2Q4

Goal: Minimize gas resistance of support:
Achieve porous support structure with interconnected pores
Goal: Achieve thermo-mechanical properties sufficient for handling and use

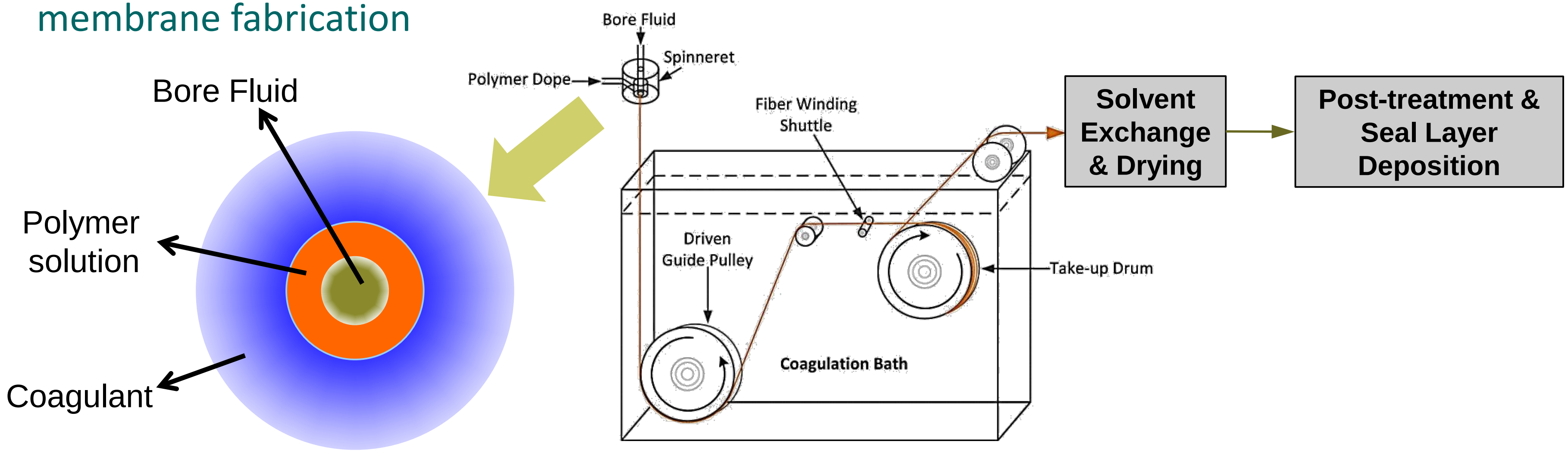
Hollow Fiber Fabrication

PBI-based material, morphology & High area density membrane development

Polybenzimidazole Hollow Fiber Fabrication



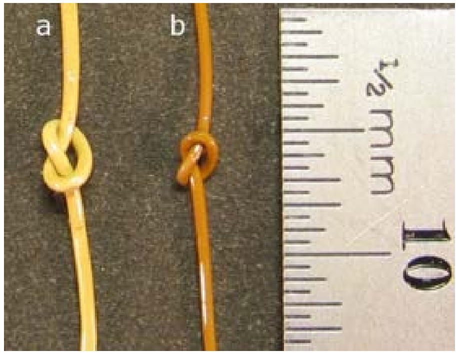
- Developed methods for PBI hollow fiber membrane with high H_2 permeance and H_2/CO_2 selectivity for syngas separations
  - Controlling liquid-liquid demixing based phase inversion process for PBI hollow fiber membrane fabrication



Solvent Exchange & Drying

Post-treatment & Seal Layer Deposition

- *In-situ* formation of an integrally skinned hollow fiber using commercially available PBI material

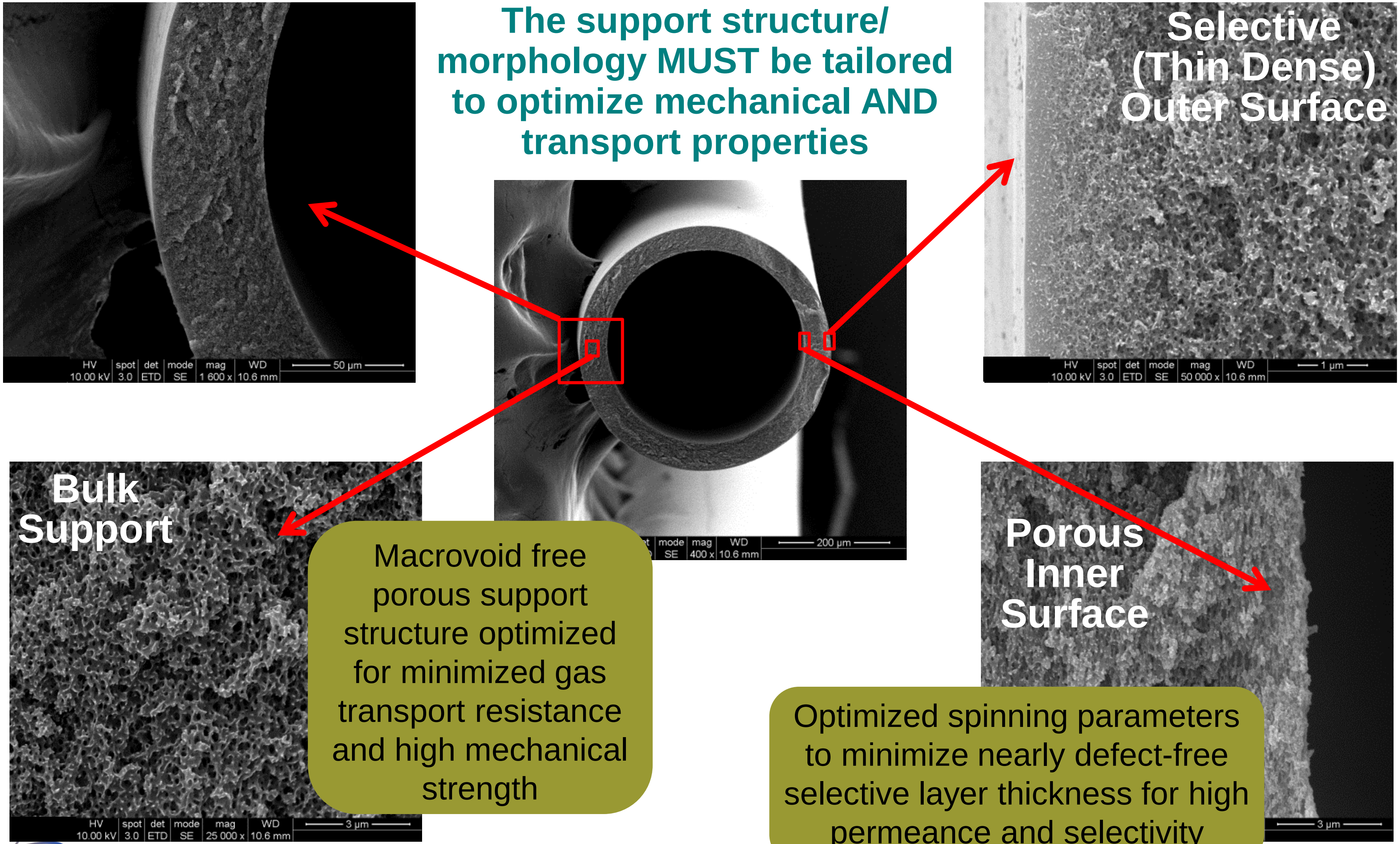


Fiber Diameter: 200 to 500 µm
SL Thickness: 150 to 500 nm

Components of an Asymmetric HF

Spinning process optimized to obtain high performance PBI HF membranes

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

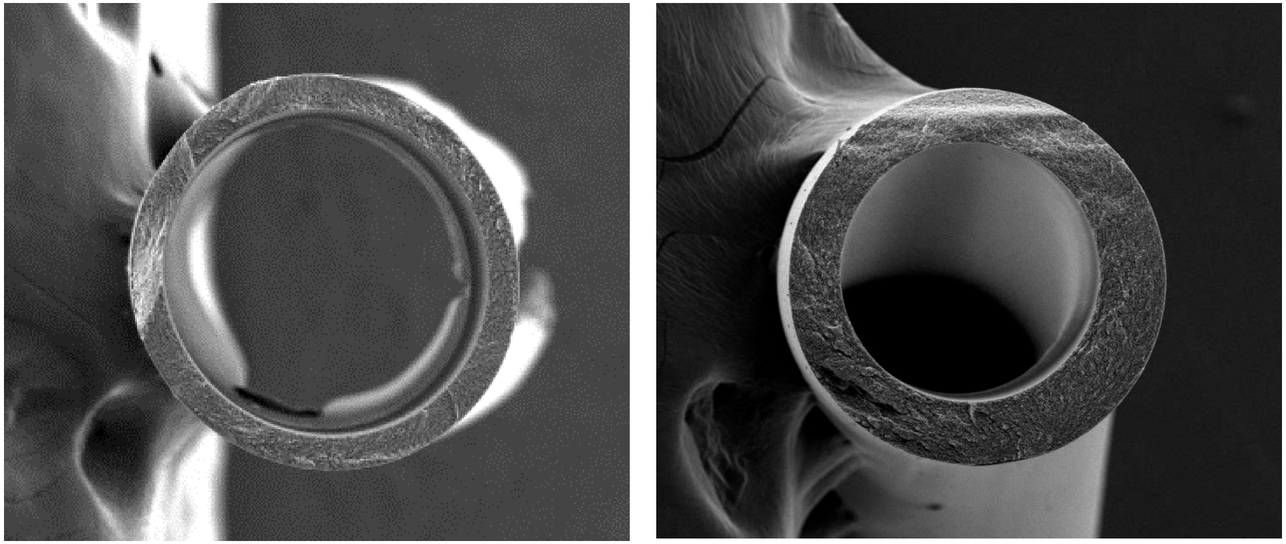


Macrovoid free porous support structure optimized for minimized gas transport resistance and high mechanical strength

Optimized spinning parameters to minimize nearly defect-free selective layer thickness for high permeance and selectivity

Thermo-Mechanical Stability In-Process

- Thermally robust PBI HFM developed
  - Macro-void free fiber essential for high temperature operation under high pressure gradient for efficient syngas separations
  - Fiber geometry optimization will lead to further improvements in thermo-mechanical robustness (process target >400 psi)



	Fiber Geometry 1	Fiber Geometry 2
Outer Diameter	468 μm	425 μm
Wall Thickness	44 μm	68 μm
Pressure Stability	≈ 200 psi	> 200 psi

- Commercial gas separation hollow fibers are 50 to 200 μm for high P applications
- Current fiber dimensions controlled by LANL designed/built custom spinneret specifications
- Further reduction in fiber dimensions to improve thermo-mechanical strength achievable by using reduced dimension spinneret

Goal: Maximize membrane permeance
by minimizing defect–free selective layer thickness

Goal: Demonstrate fabrication protocols sufficient for multi-fiber module fabrication

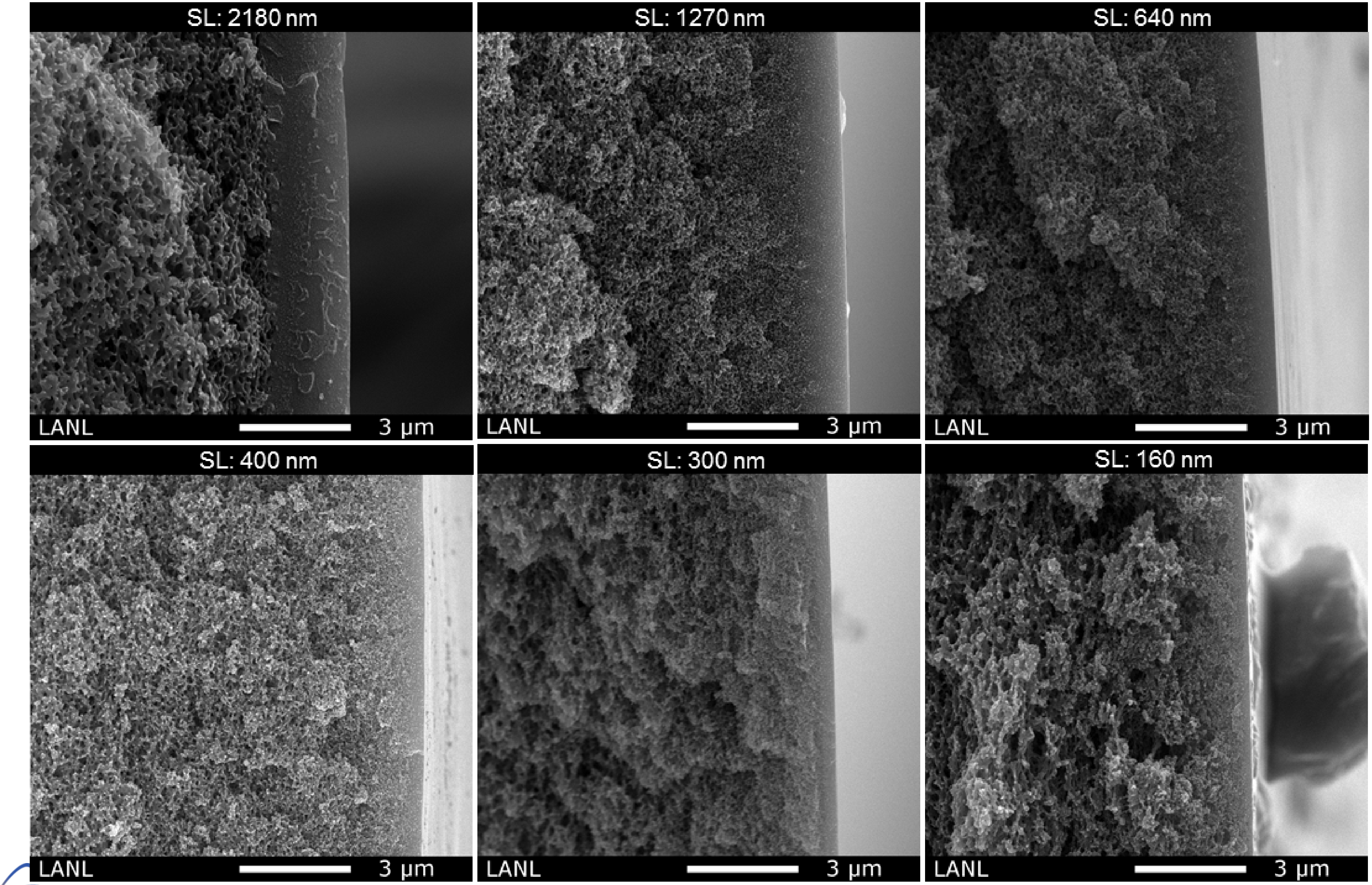
Hollow Fiber Fabrication

Selective Layer Thickness Control

&

Robust Manufacturing Processes

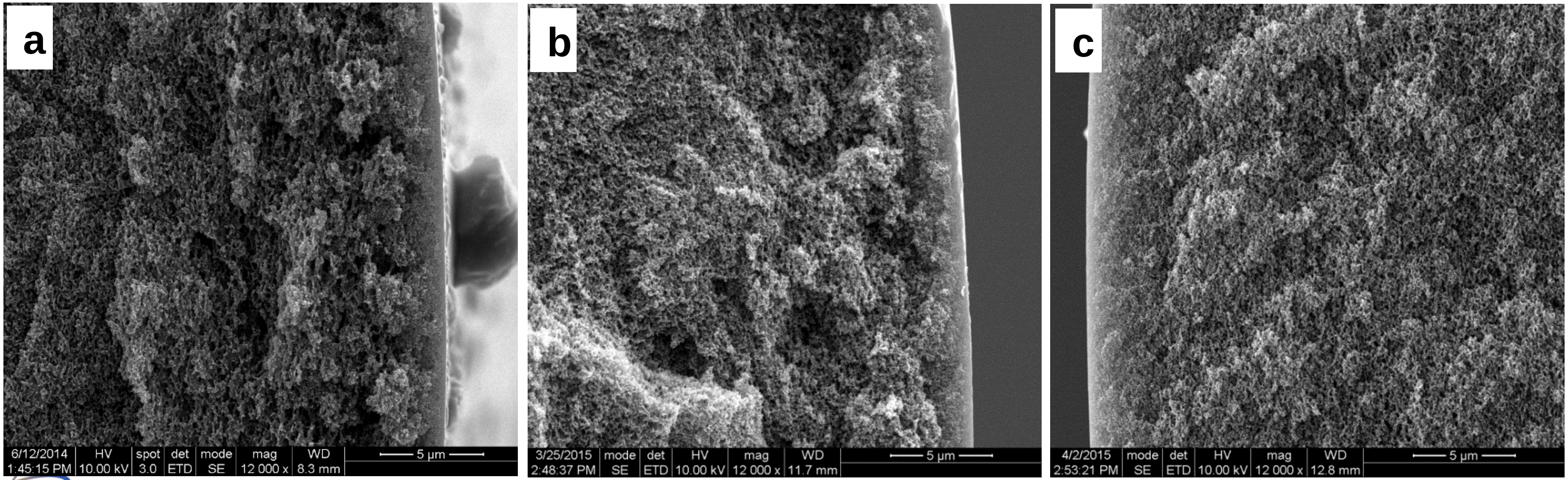
PBI Hollow Fiber (Shell Side @25kX): SL Thickness Variation



SEM micrographs - HF shell side – all taken at the same magnification (25kX)

Robust Spinning Process Demonstration

- Demonstrated successful manufacture of multiple batches of our high performance fiber
  - Evaluated fiber manufacturing process reproducibility using the optimized fiber spinning process parameters anticipated for multi-fiber module production
  - Demonstrated consistency of dope preparation and dope stability over extended periods of time (2 different batches of polymer dope produced and used over a 12 month period)
  - Demonstrated manufacturing process robustness
    - Batches produced by multiple operators yielding the same resultant fibers
    - Multiple batches produced in FY14/FY15 yielding nearly identical wall thickness, overarching geometry, and morphology

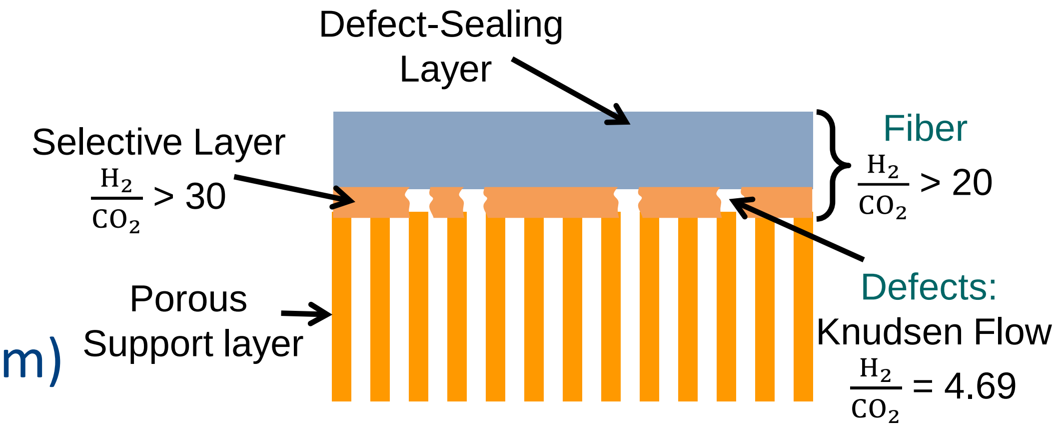


Goal: Develop and demonstrate defect-sealing materials and deployment strategies

Sealing Layer Development & Integration

Sealing Layer – Material and Deposition

- Developed novel defect-sealing layer materials
- Demonstrated readily scalable methods for deposition of a thin (ca. 200 nm) seal layer on PBI hollow fibers



Defect-Sealing Layer

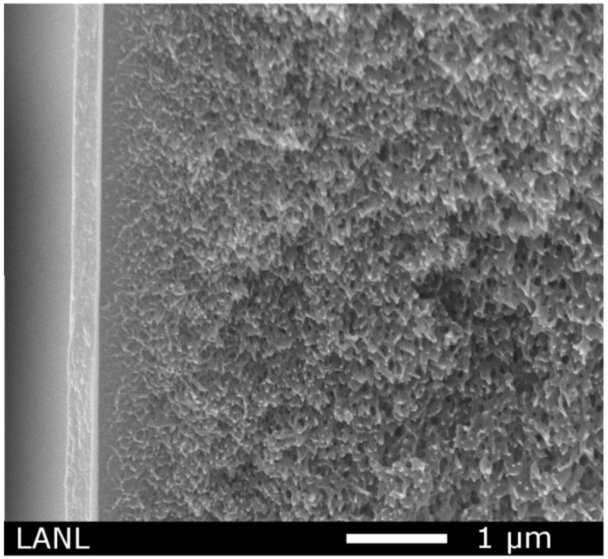
Selective Layer $\frac{H_2}{CO_2} > 30$

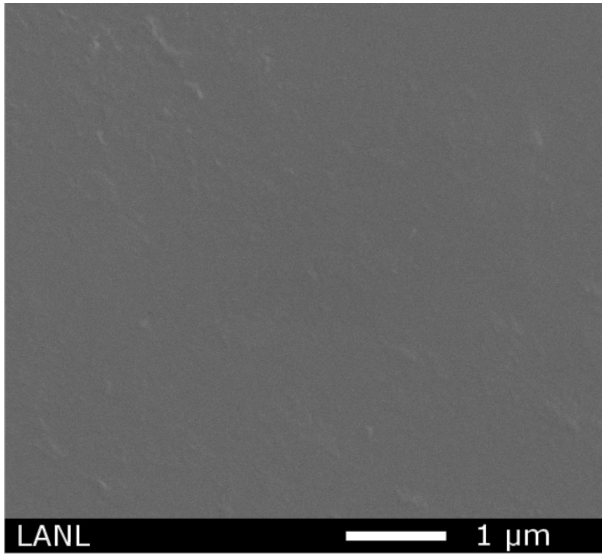
Porous Support layer

Fiber $\frac{H_2}{CO_2} > 20$

Defects: Knudsen Flow $\frac{H_2}{CO_2} = 4.69$

- Demonstrated thermal and chemical stability to withstand syngas operating environments (Next section: all presented data are for membranes comprising a seal layer)





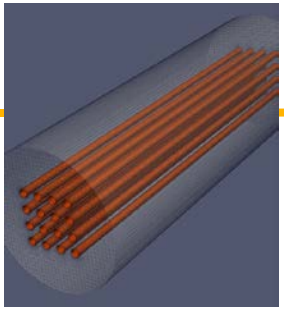
Goal: Utilize CFD Simulations to Advance Membrane and Module Development and Demonstration Efforts

Module Fabrication/Assessment

CFD Simulations

(LANL / NETL ORD Collaboration)

LANL/ORD Collaboration



Goals

- Use simulations to investigate and understand observed differences between ideal **membrane** performance and **module** performance
- Estimate (via. simulation tools) the effective performance of a hollow fiber system at **scales** and/or **operating conditions** which are not readily accessible experimentally

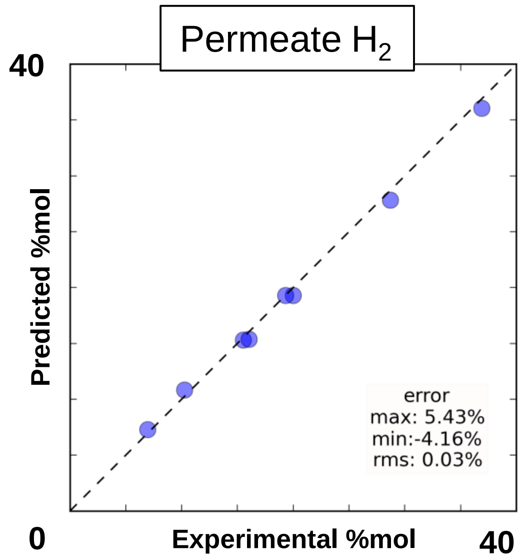
Approach

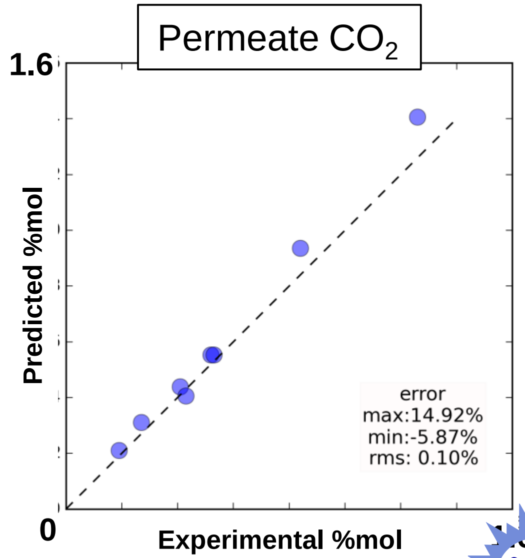
- Model construction, calibration, and initial model validation using single fiber experiments
- Additional model validation using multi-fiber experiments
- Model utilization

Model Construction and Validation: Initial Results

Membrane Performance (Permeance) Calibration and Model Verification

- Single fiber counter-flow system
- Curve fit membrane performance from initial experimental data-set (8 Conditions: single fiber, wet syngas feed, varied: temperature, trans-membrane pressure, stage-cut)
- Perform simulations to predict the same experiments (example plots on right) →
- Model validation efforts utilizing experimental data outside of the initial calibration data-set





Other On-going Activities

- Mesh Sensitivity Analysis
- Operational Sensitivity Analysis –e.g., influences of flow rates and support layer resistance
- Model development for multi-fiber analysis

Goal: Demonstrate sealing layer efficacy and composite structure tolerance to syngas

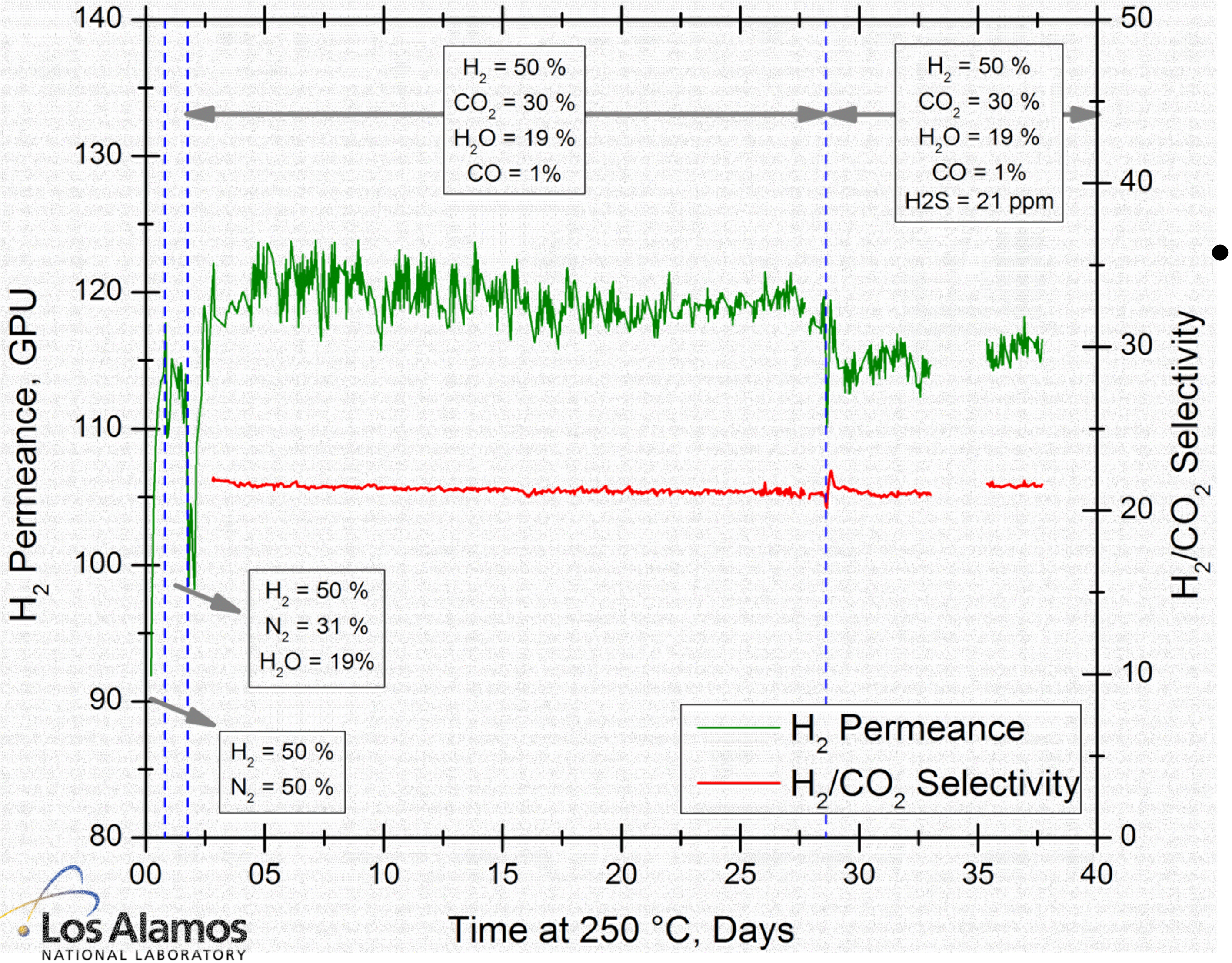
Goal: Demonstrate single hollow fiber membrane H_2 permeance ≥ 250 GPU and H_2/CO_2 selectivity ≥25 in simulated syngas

Demonstration and Validation of Developed Materials and Methods

Simulated Syngas Performance

Durability Wet Synthesis Gas– Membrane with Seal-Layer (>950 h)

- **PBI HFM demonstrated stable gas transport characteristics and durability**



- **Exceptional tolerance to carbon, steam and sulfur at process realistic temperatures**
- **H_2 permeance and H_2/CO_2 selectivity unaffected by the presence of CO and H_2S**

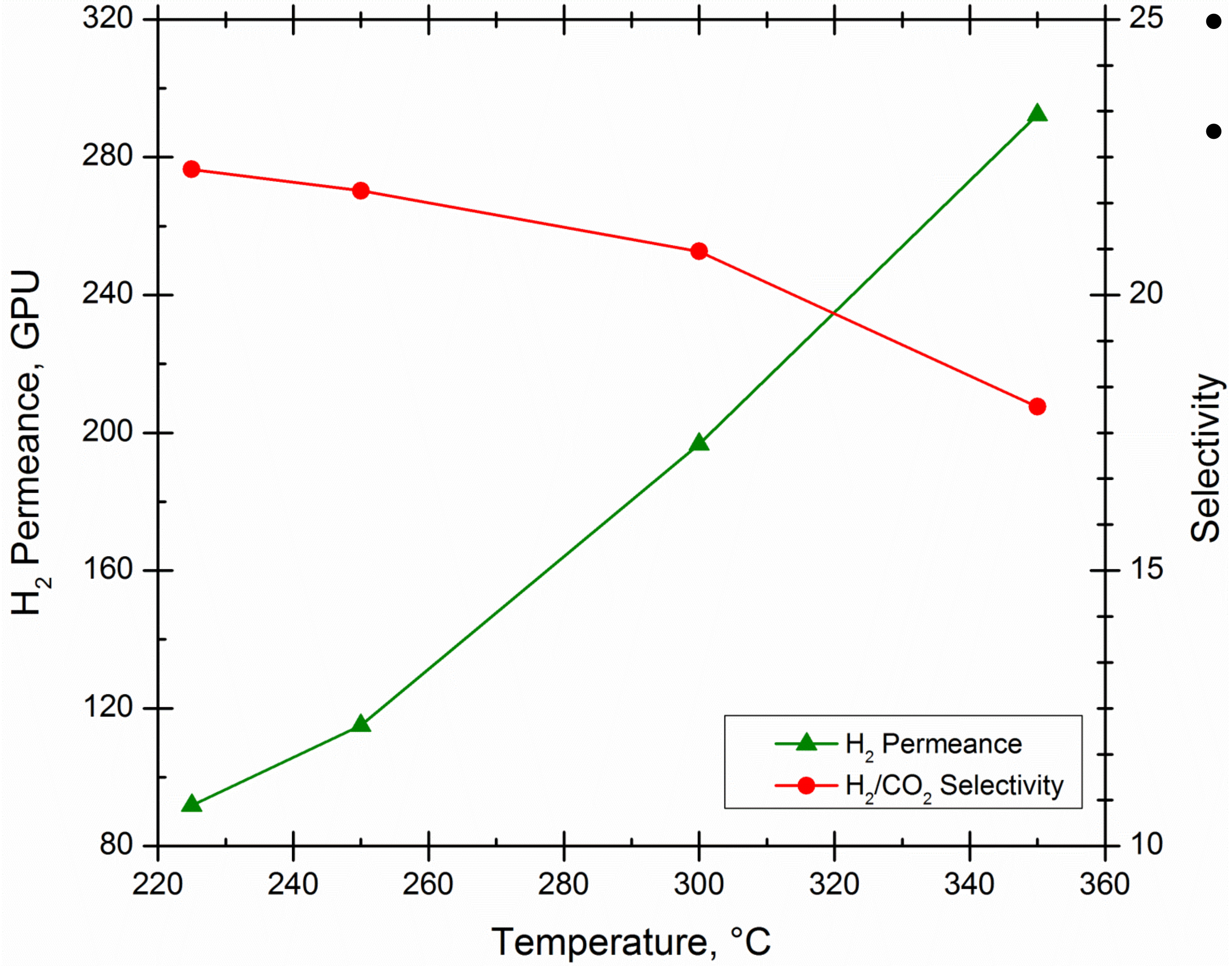
- Pure gas performance:
  P(H_2) → ~110 GPU
  α (H_2/CO_2) → 22
- T = 250 °C

Additional Performance Improvements Desired

- Techno-economic evaluations indicate the advantages of a PBI-based membrane system over industry standard CO_2 separation techniques facilitated by favorable process integration into power generation schemes for carbon capture
  - High hydrogen permeance (>150 GPU) leads to reduced footprint and cost
  - These PBI specific evaluations AND literature studies for hydrogen selective membranes in IGCC process schemes indicate the need for ***improved selectivity*** to achieve the desired NETL conceptual design guidelines (QGESS), i.e., ***90% CO_2 capture producing a 95% pure CO_2 stream***

Optimizing Operating Conditions for Enhanced Performance

- H_2 permeance significantly increases while H_2/CO_2 selectivity decreases with increased operating temperature



- Transport mechanism: Activated diffusion
- Tolerant to steam (19%), CO (1%) and H_2S (20 ppm) at high differential pressure (200 PSI) and 200 to 350 °C

Feed Gas	
H_2	50%
CO_2	30%
H_2O	19%
CO	1%
H_2S	20 ppm

Feed Pressure

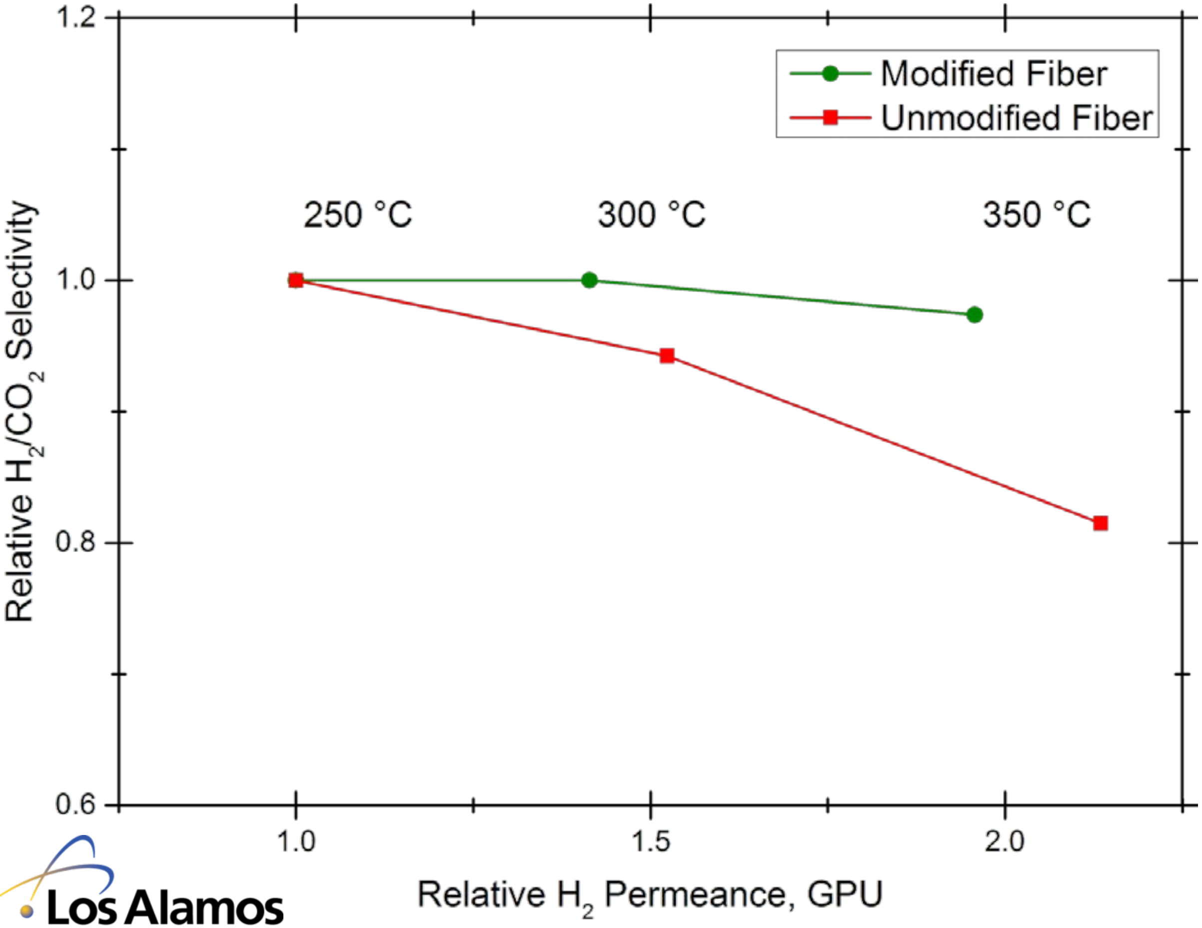
200 PSIA

Permeate Pressure

20 PSIA

Towards Realizing Additional Performance Improvements: Post Fabrication Membrane Modification

- Higher H_2/CO_2 selectivity required to achieve > 90% CO_2 purity & 90% carbon capture
  - Exploring strategies to control PBI structure for improved selectivity



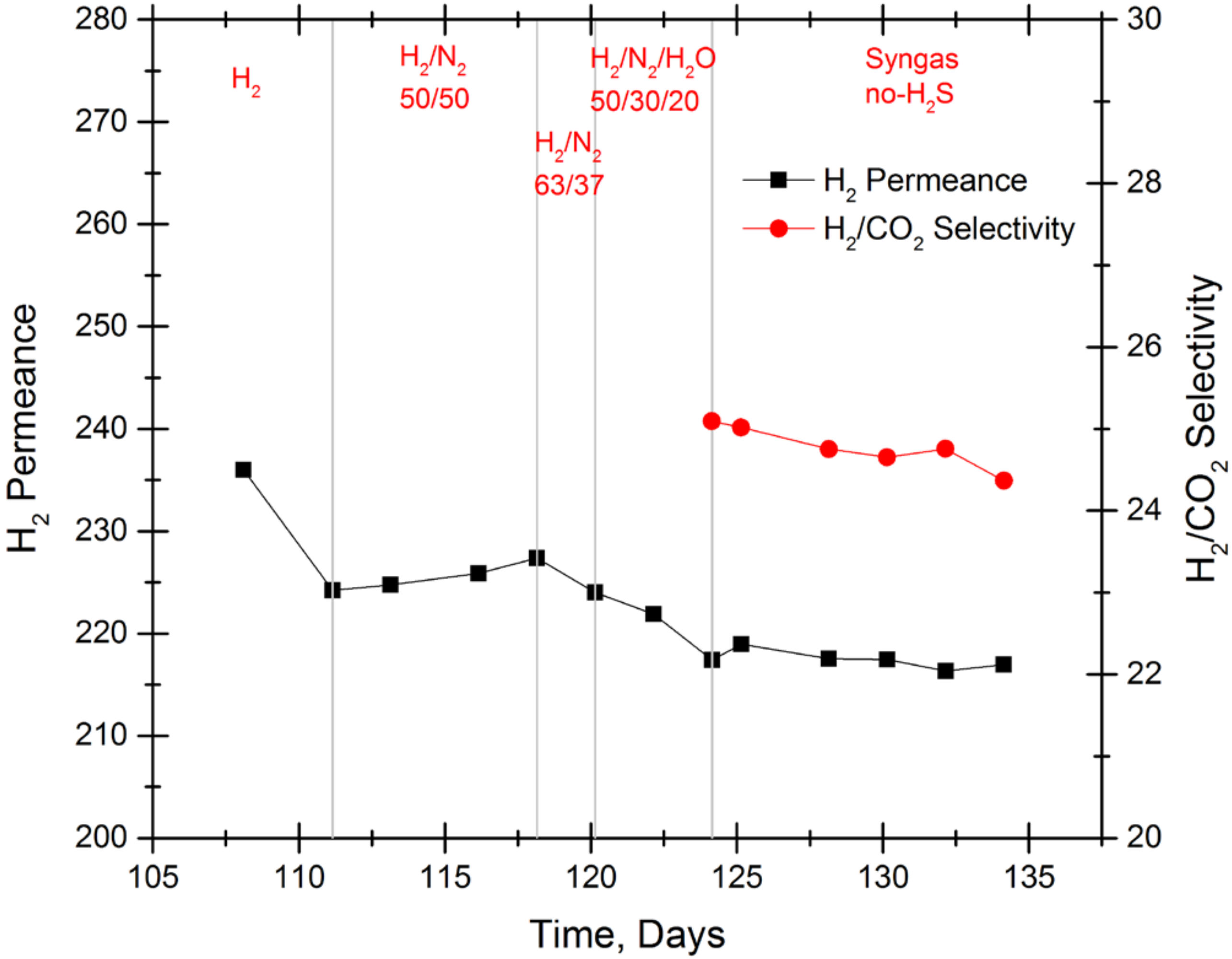
- Structure tightening via post-synthesis modification
  - Enhanced H_2/CO_2 selectivity retention at higher temperatures
  - Potentially influenced polymer chain mobility at elevated temperatures

PBI based Material	H_2 Permeance (GPU)	H_2/CO_2
PBI	203	24.3
mod-PBI	141	26.6

Temperature = 250 °C

Modified PBI Fiber – Syngas Separation Performance

- Modified PBI HFM demonstrated stable gas transport characteristics and durability in simulated syngas at 250 °C



Feed Gas

H_2	49%
CO_2	28%
H_2O	22%
CO	1%

Temperature

250 °C

Feed Pressure

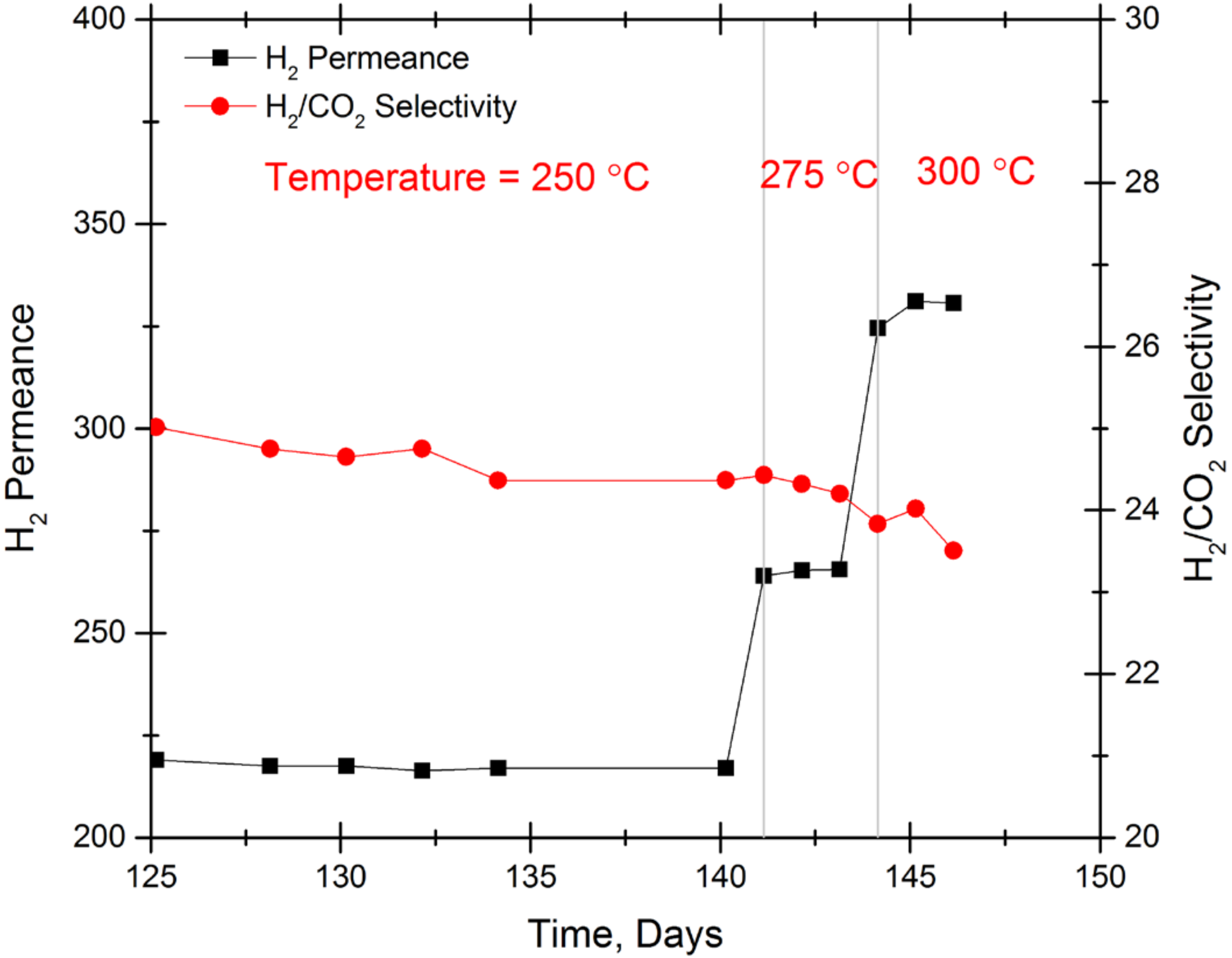
20 PSIA

- Pure gas:
  $P(H_2)$ → ~207 GPU
  α (H_2/CO_2) → 25.1
- T = 250 °C
- TMP 20 psid

Simulated syngas with and without H_2S at temperatures ≥ 250 °C

Effect of Temperature – Wet Synthesis Gas

- Modified-PBI HFM demonstrated stable gas transport characteristics up to 300 °C
  - **H_2 permeance 330 GPU and H_2/CO_2 = 24**



Improved Selectivity Retention with Increasing Temperature/ Permeance

Feed Gas

H_2	49%
CO_2	28%
H_2O	22%
CO	1%

Temperature

250 °C

Feed Pressure

20 PSIA

Simulated syngas at temperatures ≥ 250 °C

Wrap-Up & Path Forward

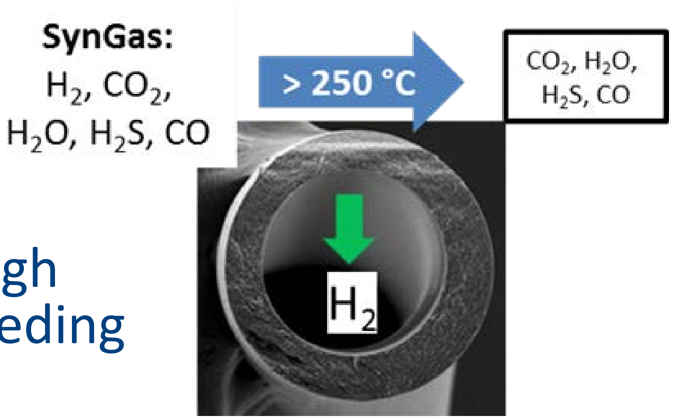
Path Forward – **BP3 Goals** and Beyond

- **Hollow Fiber Fabrication**
  - Fabrication optimization to achieve high permeance defect minimized membranes with in-process stability/durability - Further SL optimization thickness (≤100nm)
  - **Further demonstrate fabrication consistency via performance demonstration of fibers from multiple, replicate spinning campaigns**
- **Sealing Layer Development & Integration**
  - Further develop materials and methods to mitigate and seal defects in the thin HFM selective layer
  - Demonstrate materials and methods functionality, stability, and durability in process environments
- **Module Fabrication**
  - **Further develop and demonstrate materials and methods for multi-fiber module fab**
  - **CFD utilization to guide multifiber module design and aid in membrane and module performance validation (with NETL)**
  - Fabrication of multi-fiber modules for evaluation in syngas process environments
- **Demonstration and Validation of Developed Materials and Methods**
  - **Demonstrate multi-fiber HFM performance**
  - **Development and protection of PBI hollow fiber membrane manufacturing protocols for transfer/licensing to industry for scale-up/commercialization**

Conclusions

- PBI-based membrane materials have suitable thermal, chemical and mechanical stability & durability for pre-combustion carbon capture
- Low H_2 permeability of m-PBI mandates high permeance high area density platforms development

- Novel PBI fiber fabrication methods including seal layer material and deposition technique developed for high performance at industrially attractive operating conditions
- Developed manufacturing protocols to obtain high performance PBI HFMs with H_2 permeance exceeding 200 GPU and $H_2/CO_2 \approx 25$.
  - Additional improvement in H_2 permeance accessible with further reductions in selective layer thickness (ca. 100 nm)



- Post-fabrication modification of PBI HFM promising approach to retain H_2/CO_2 selectivity at elevated temperatures. Further evaluation and modification mechanism understanding required.

Thank You

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