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

LANL-FE-308-13

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NETL CO_2 Capture Technology Meeting
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Collaborators Past & Present on our
High T_g Polymer for Carbon Capture Projects

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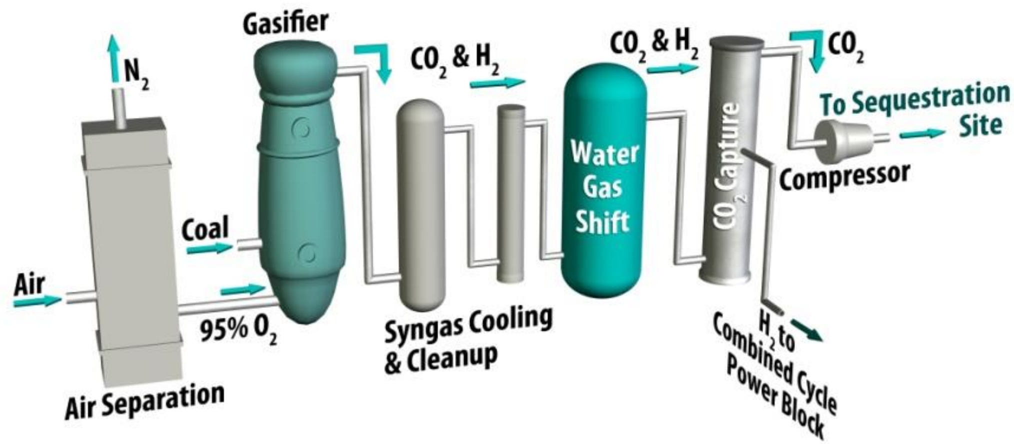
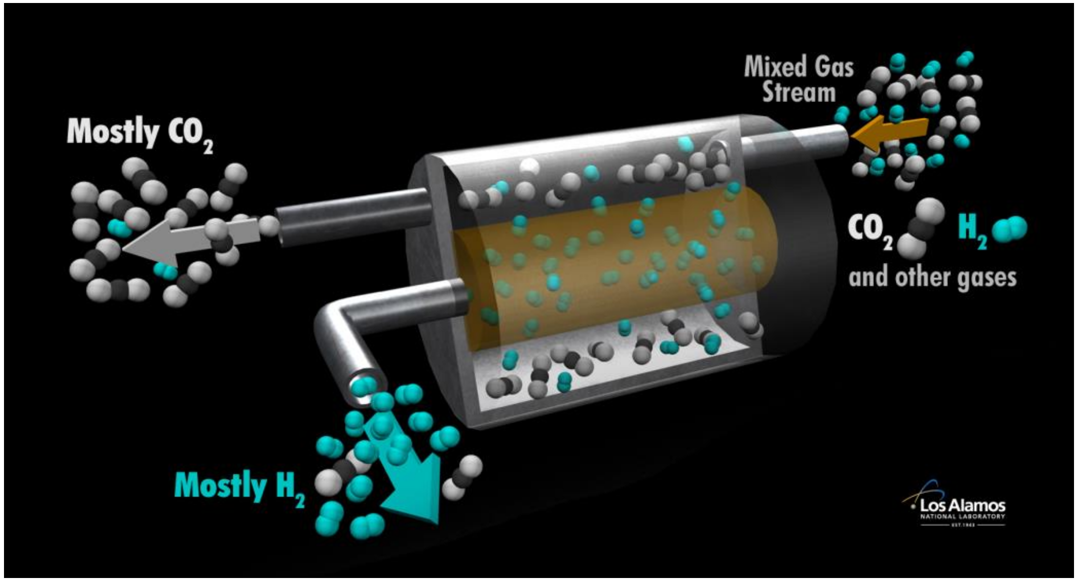
Project Summary

- Award Name:
  - Polymer-Based Carbon Dioxide Capture Membrane Systems
- Award Number:
  - FE-308-13
- Performance Period:
  - 03/2013-03/2016
- Current Budget Period:
  - BP2 of 3 (04/14-03/15)
- Project Cost (DOE):
  - $1,972K
- DOE NETL Project Manager:
  - C. Elaine Everitt



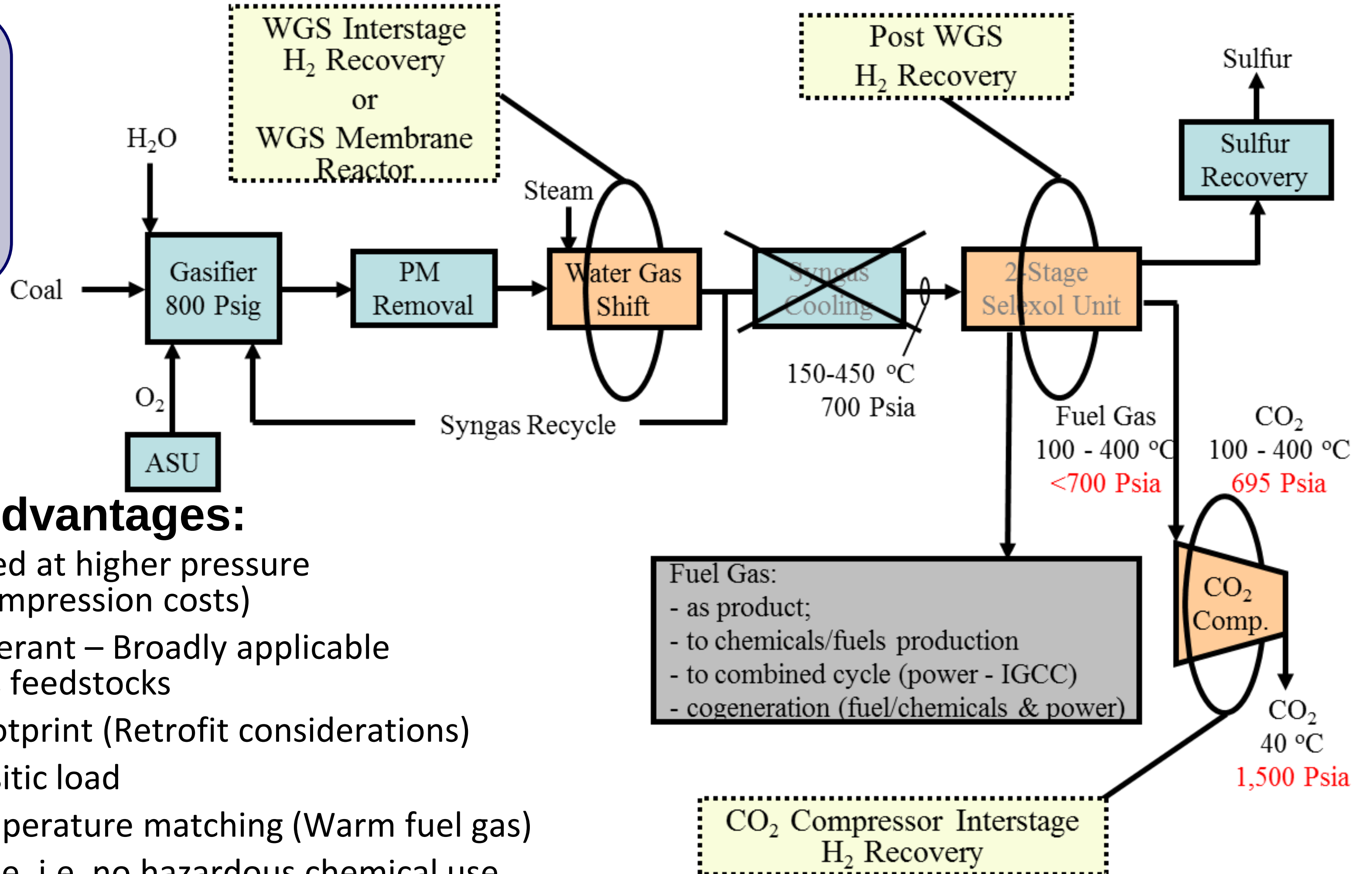
Overarching Objective



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.

Project Overview: Technology Benefits

Process Areas Targeted: Membrane Separations



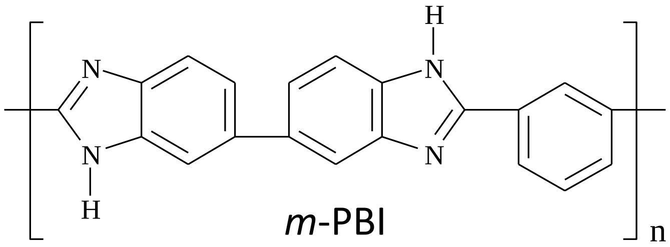
Membrane Advantages:

- 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

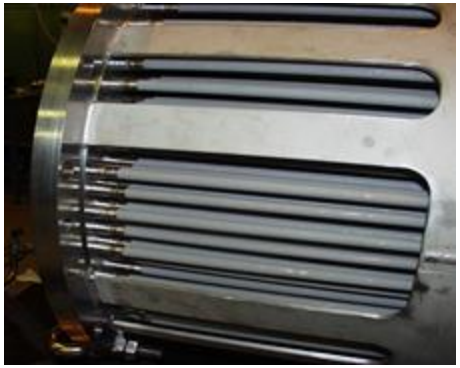
Technology Challenges & Opportunities

- **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



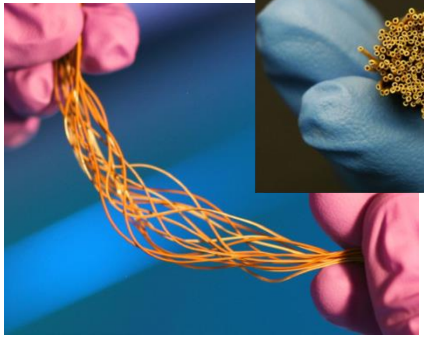
- PBI-based membranes have commercially attractive H_2/CO_2 selectivity, exceptional thermal stability (T_g > 400 °C), and exhibit tolerance to steam and H_2S.
- Broad PBI $T_{operation}$ (150 to 300+ °C) indicates potential for PBI-based membrane module integration at IGCC relevant process conditions.
- 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).

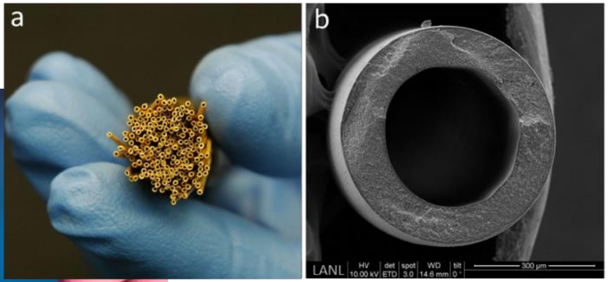


Hundreds of m^2

~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 guide module design and aid in membrane and module performance validation (with NETL)
- **Demonstration and Validation of Developed Materials and Methods**

Goal: Minimize gas resistance of support:

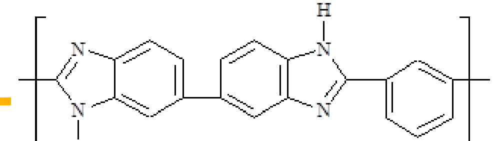
Achieve porous support structure with interconnected pores

Goal: Achieve thermo-mechanical properties sufficient for handling and use

Hollow Fiber Fabrication

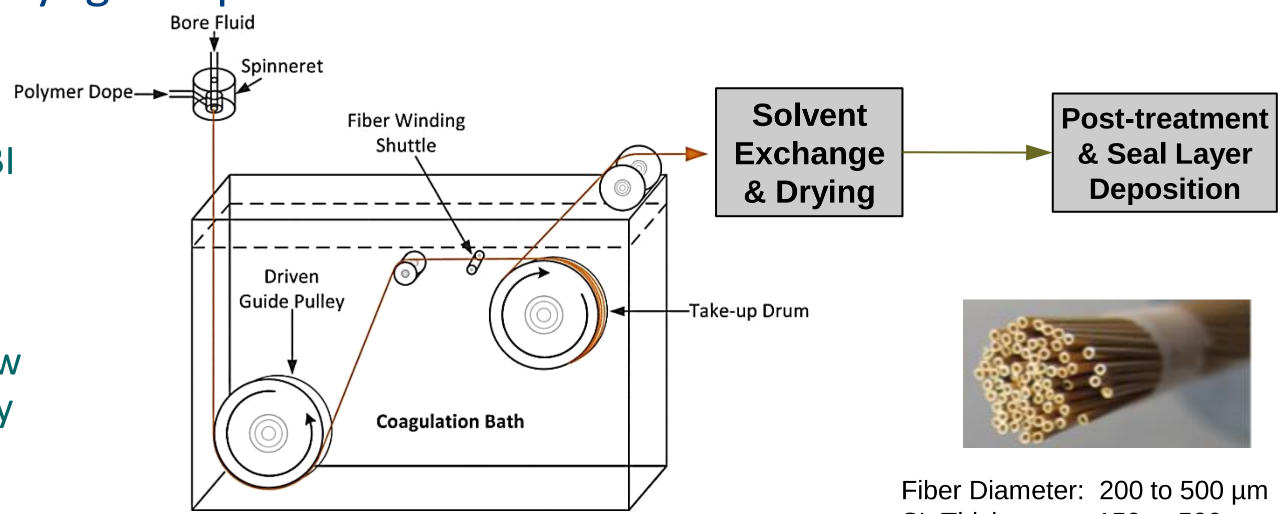
PBI-based material, morphology & High area density membrane development

Polybenzimidazole Hollow Fiber Fabrication

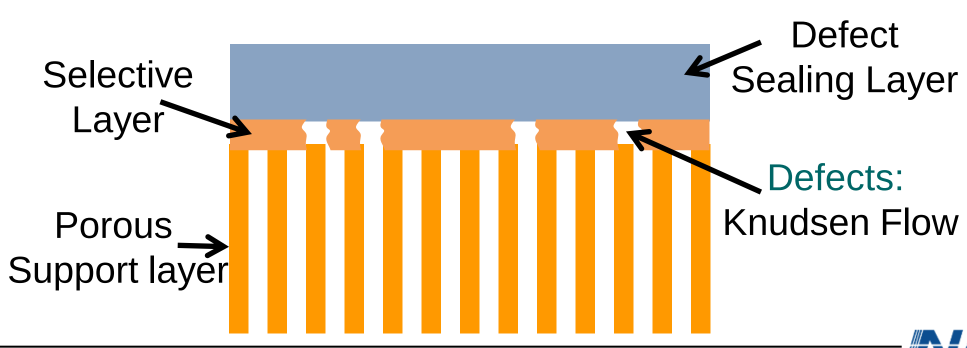


m-PBI
Commercially available

- High membrane surface area platform
  - The H_2 permeability of the state-of-the-art PBI-based membrane materials mandates ultra-thin selective layers and high surface area membrane deployment platforms
- 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
  - *In-situ* formation of an integrally skinned hollow fiber using commercially available PBI material
  - Defect mitigation by thermally and chemically tolerant seal layer material and deposition technique development *(All presented membrane performance data is for HFs comprising an integrated seal layer)*

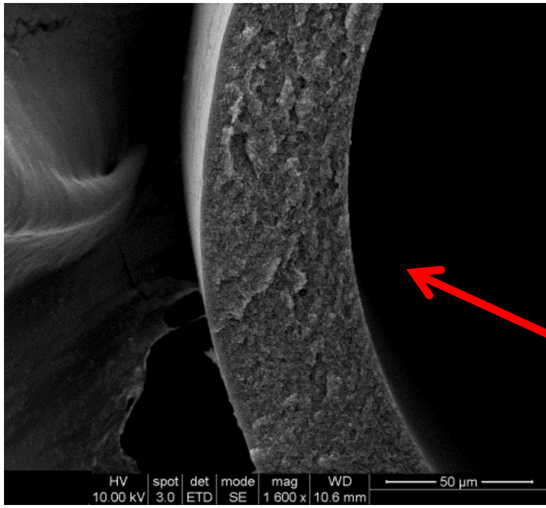


Fiber Diameter: 200 to 500 μm
SL Thickness: 150 to 500 nm

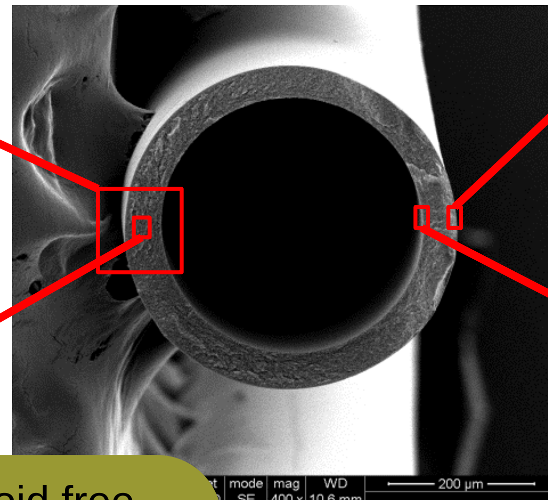


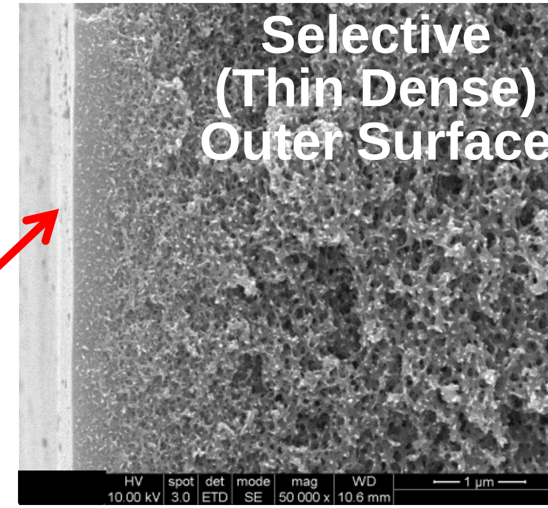
Components of an Asymmetric HF

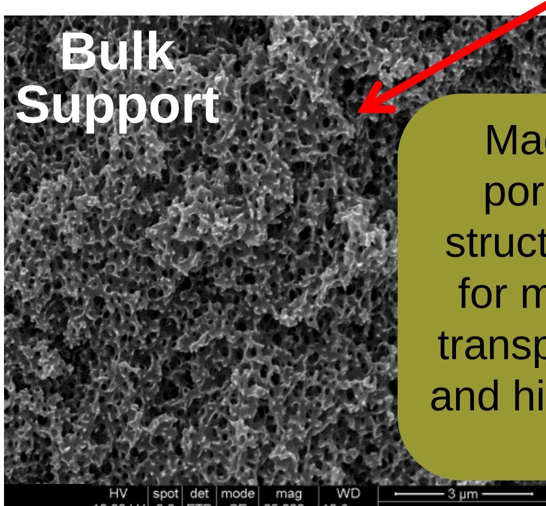
Spinning process optimized to obtain high performance PBI HF membranes



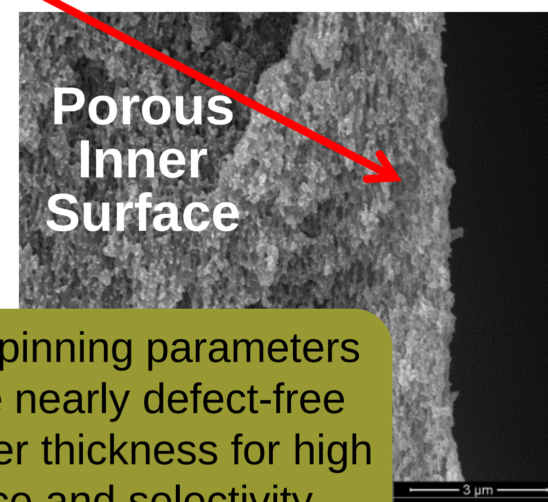
The support structure/ morphology MUST be tailored to optimize mechanical AND transport properties





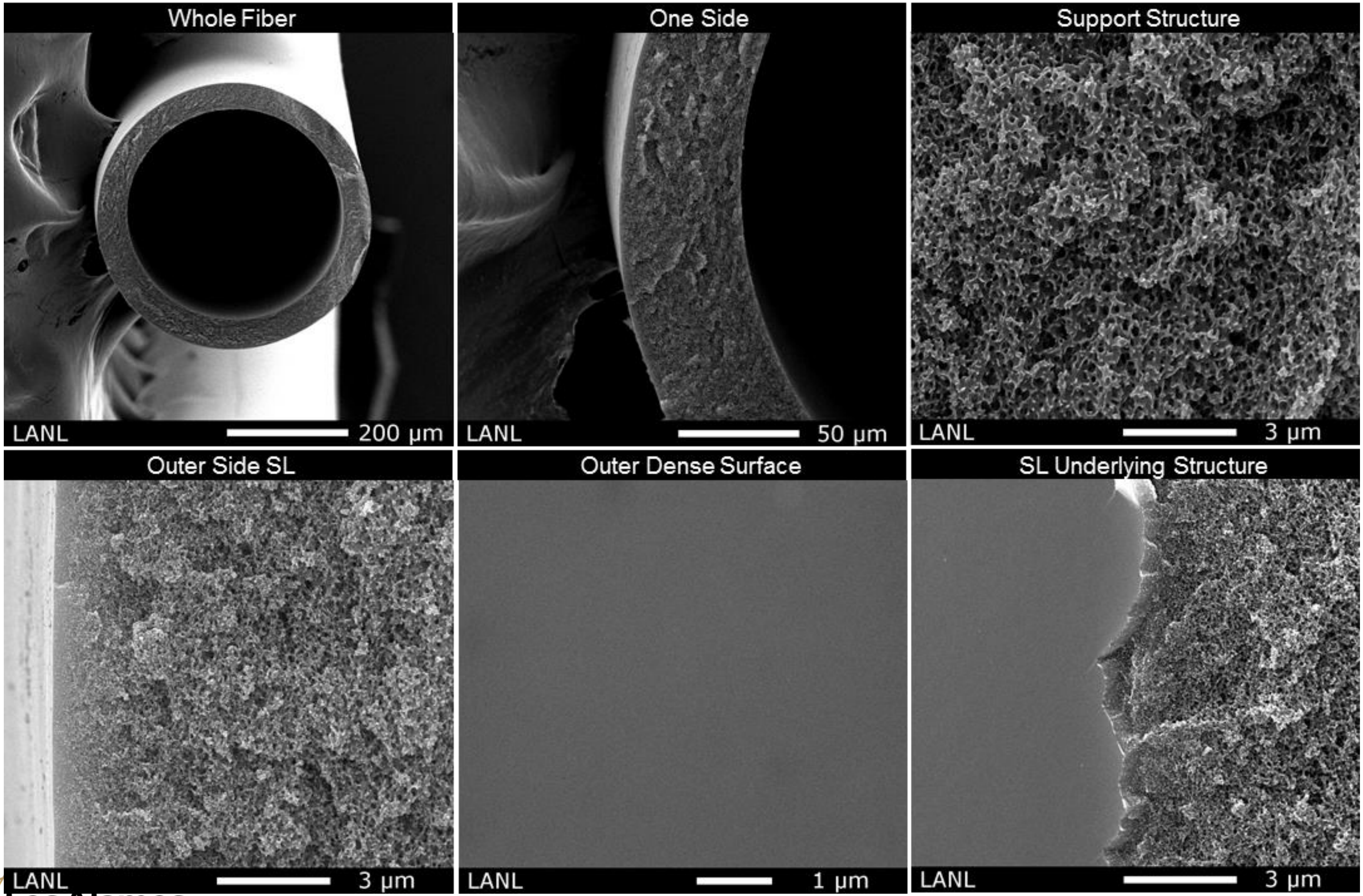


Macrovoid free porous support structure optimized for minimized gas transport resistance and high mechanical strength

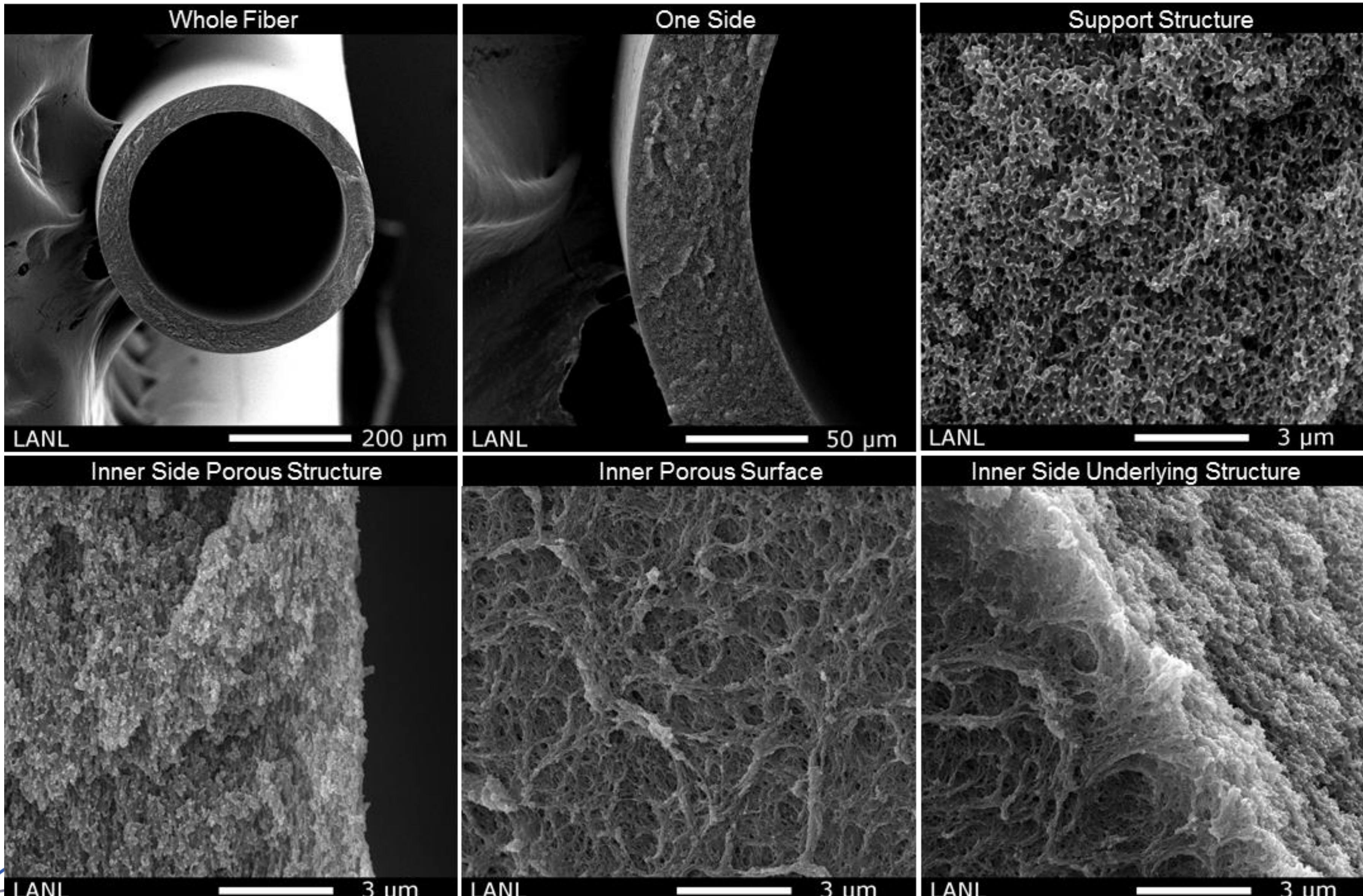


Optimized spinning parameters to minimize nearly defect-free selective layer thickness for high permeance and selectivity

HFM Morphology: Current State-of-Development (shell)



HFM Morphology: Current State-of-Development (bore)



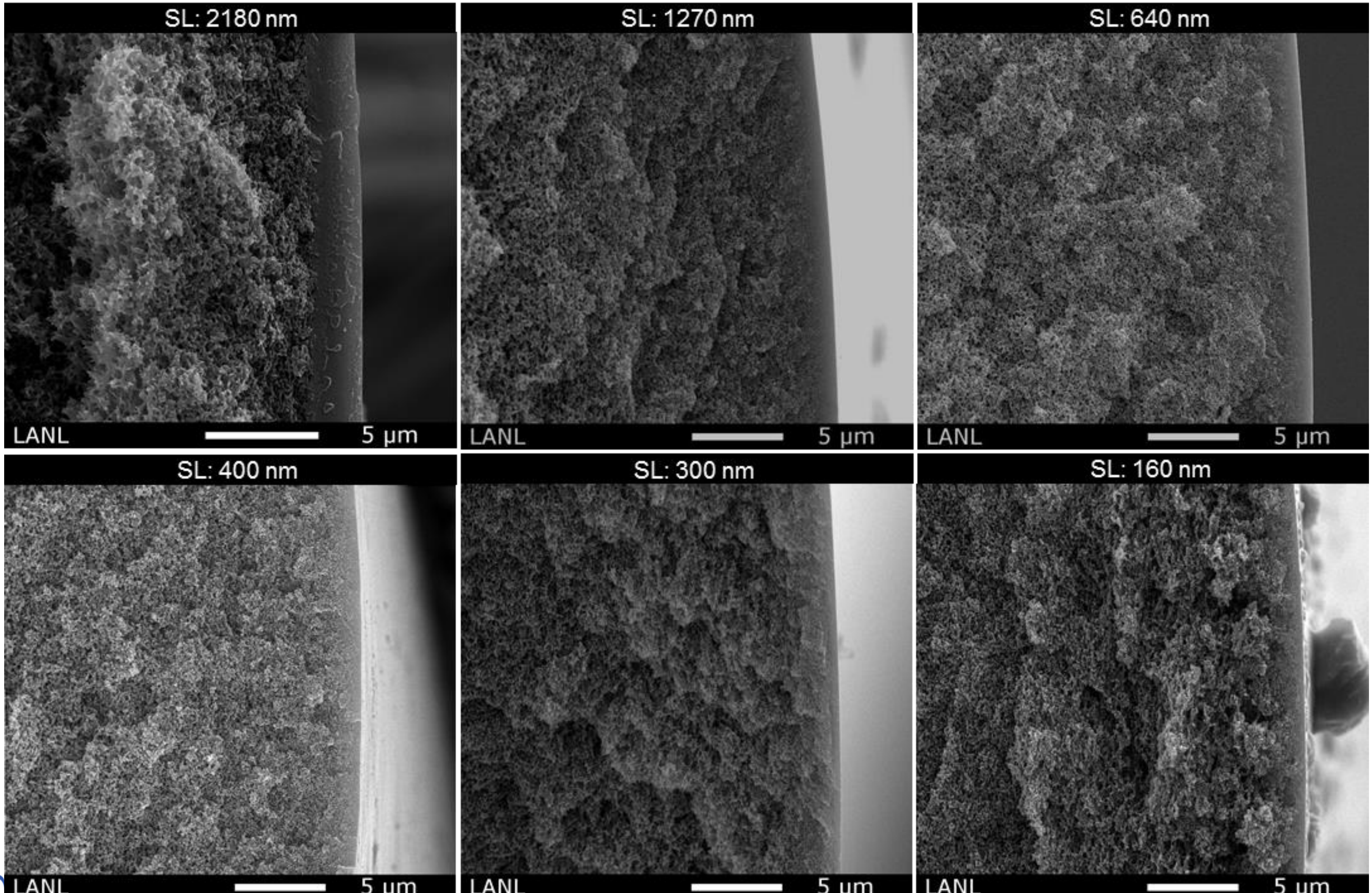
Goal: Maximize membrane permeance by minimizing defect-free selective layer thickness

Hollow Fiber Fabrication

Selective Layer Thickness Control

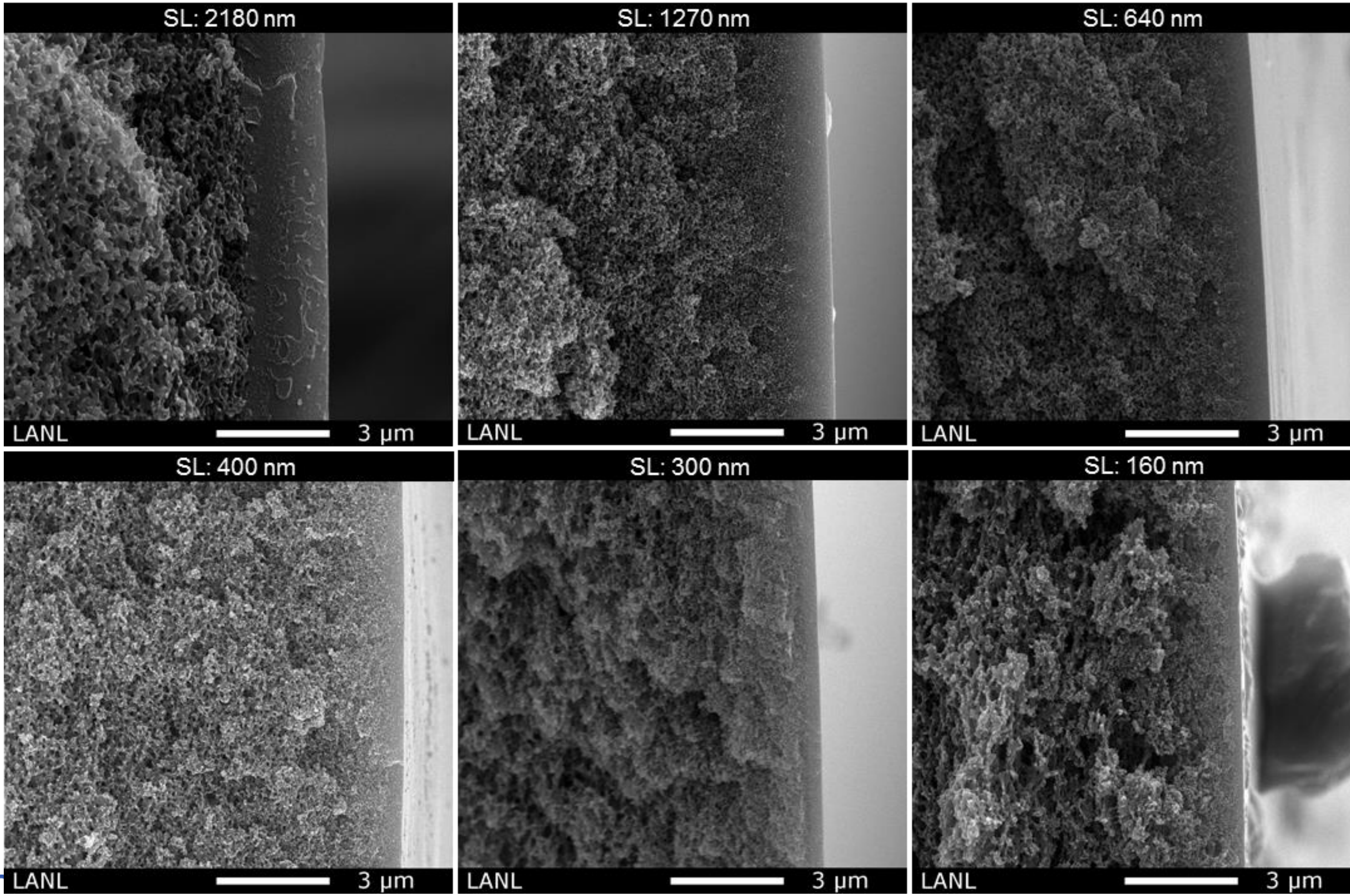
BP2Q1 (Jun '14) Milestone:
Demonstrate ability to control the selective layer thickness

PBI Hollow Fiber Shell Side (12kX): SL Thickness Variation



SEM micrographs - HF shell side – all taken at the same magnification (12kX)

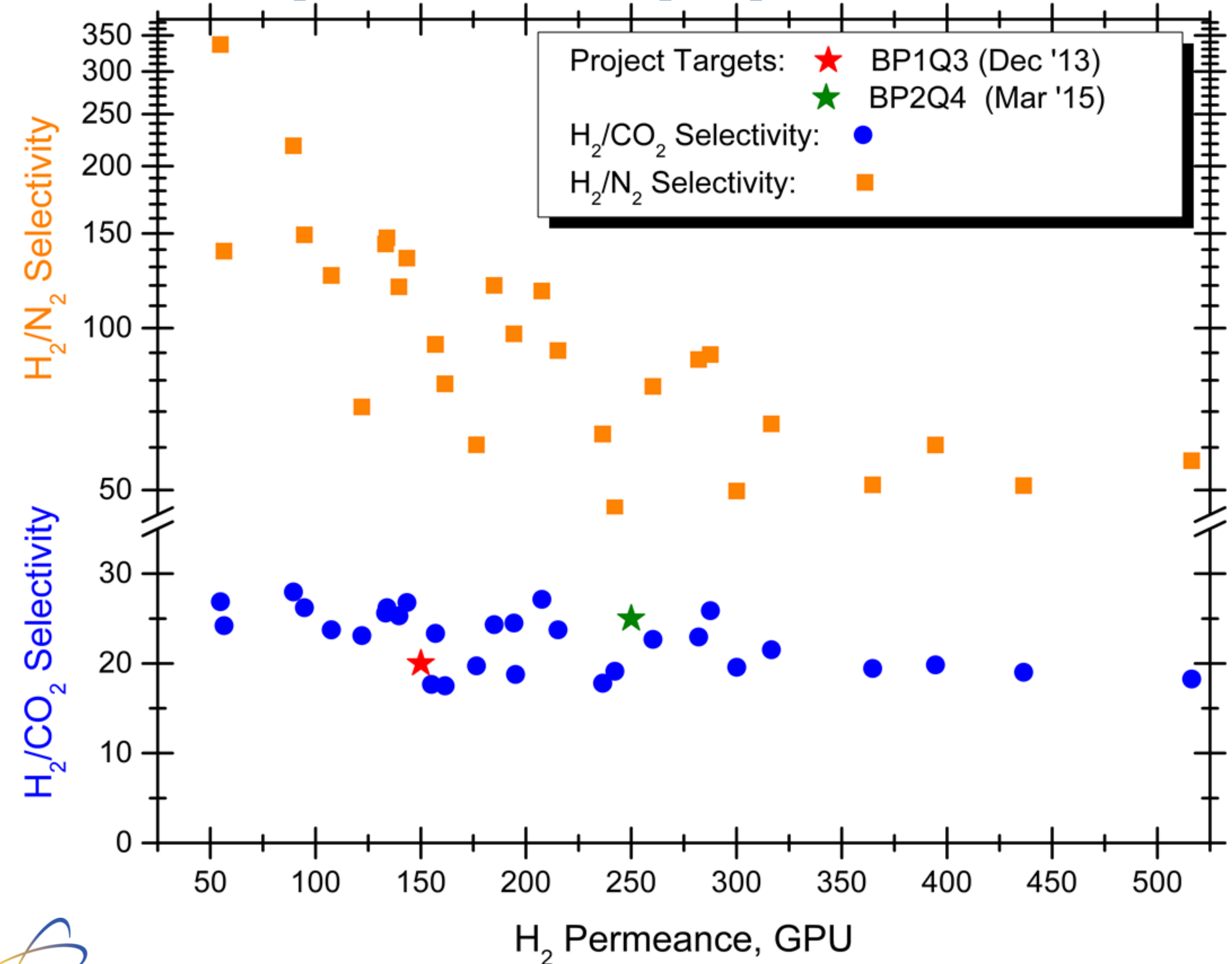
PBI Hollow Fiber Shell Side (25kX): SL Thickness Variation



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

Exceptional H_2 Perm-Selectivity Performance

- Developed high performance PBI hollow fiber membranes with industrially attractive H_2 permeance and H_2/CO_2 selectivity



- Pure gas evaluation
- T = ≥ 250 °C
- TMP 20-100 psid
- Constant-volume variable-pressure membrane evaluation protocol utilized

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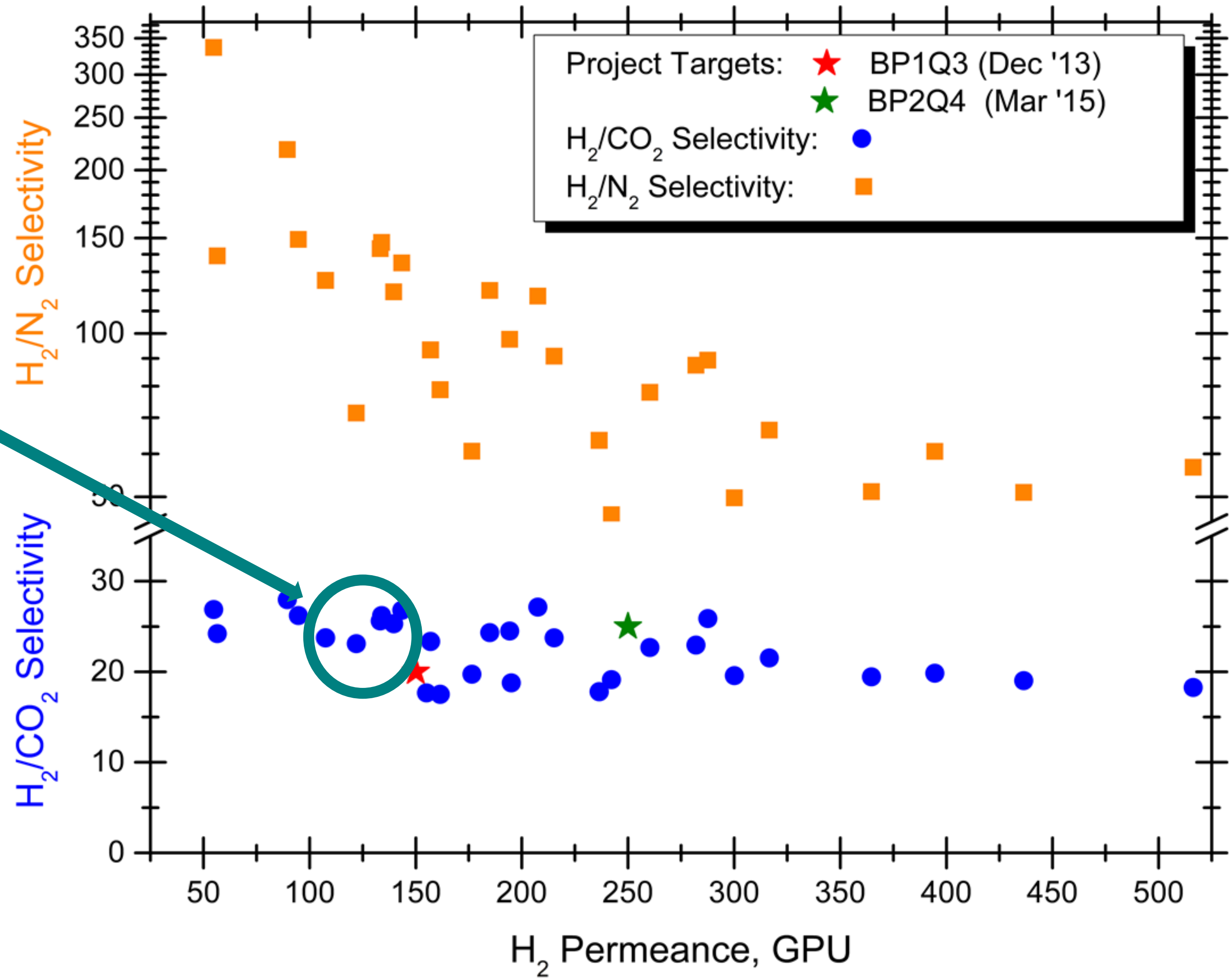
Demonstration and Validation of Developed Materials and Methods:

Dry Pure and Mixed Gas Performance

Exceptional H_2 Perm-Selectivity Performance

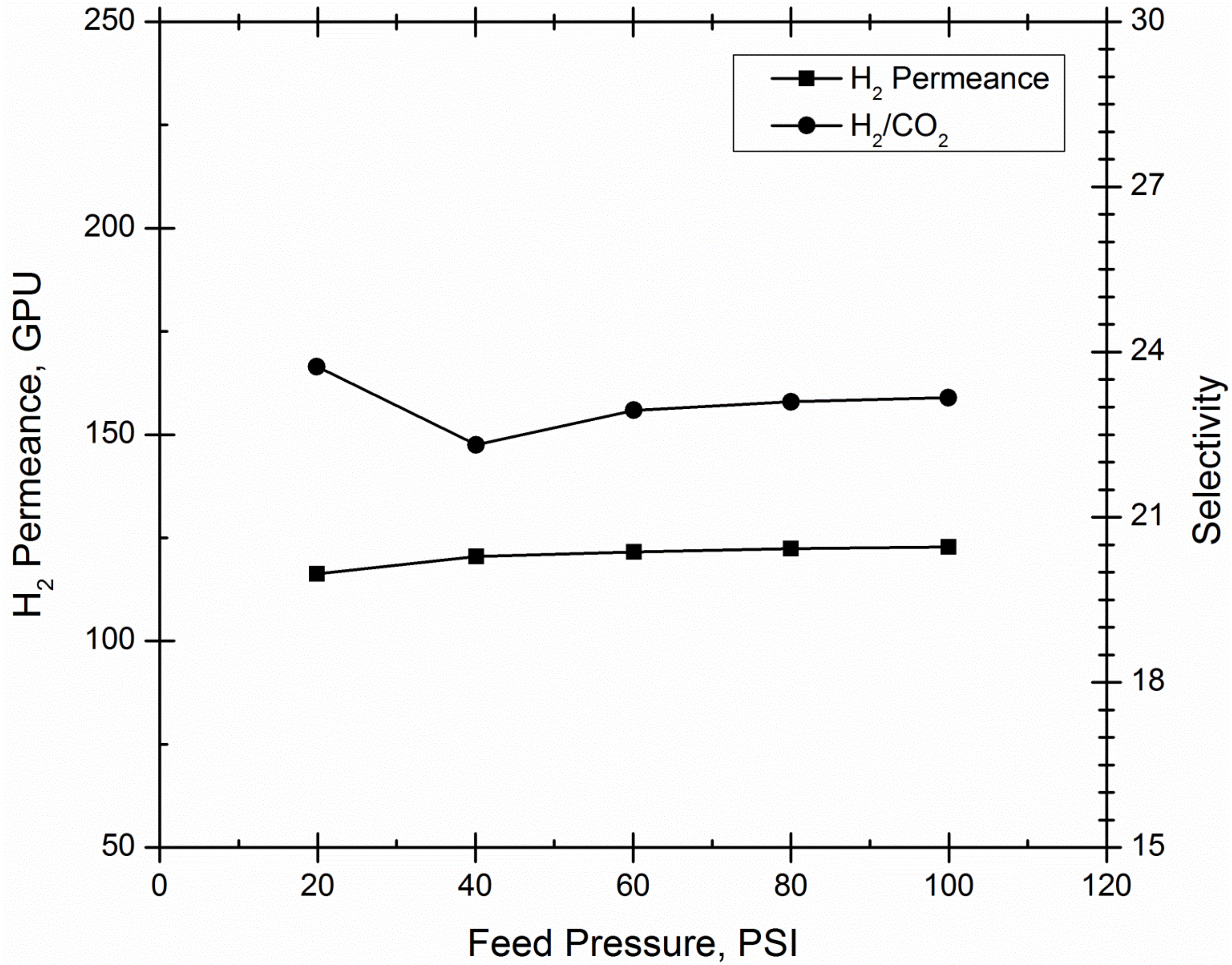
- Earlier stage PBI hollow fiber membranes were selected for further performance validation activities while HF membrane development continued in parallel

Membranes selected for BP1/BP2Q1 demonstration and validation activities



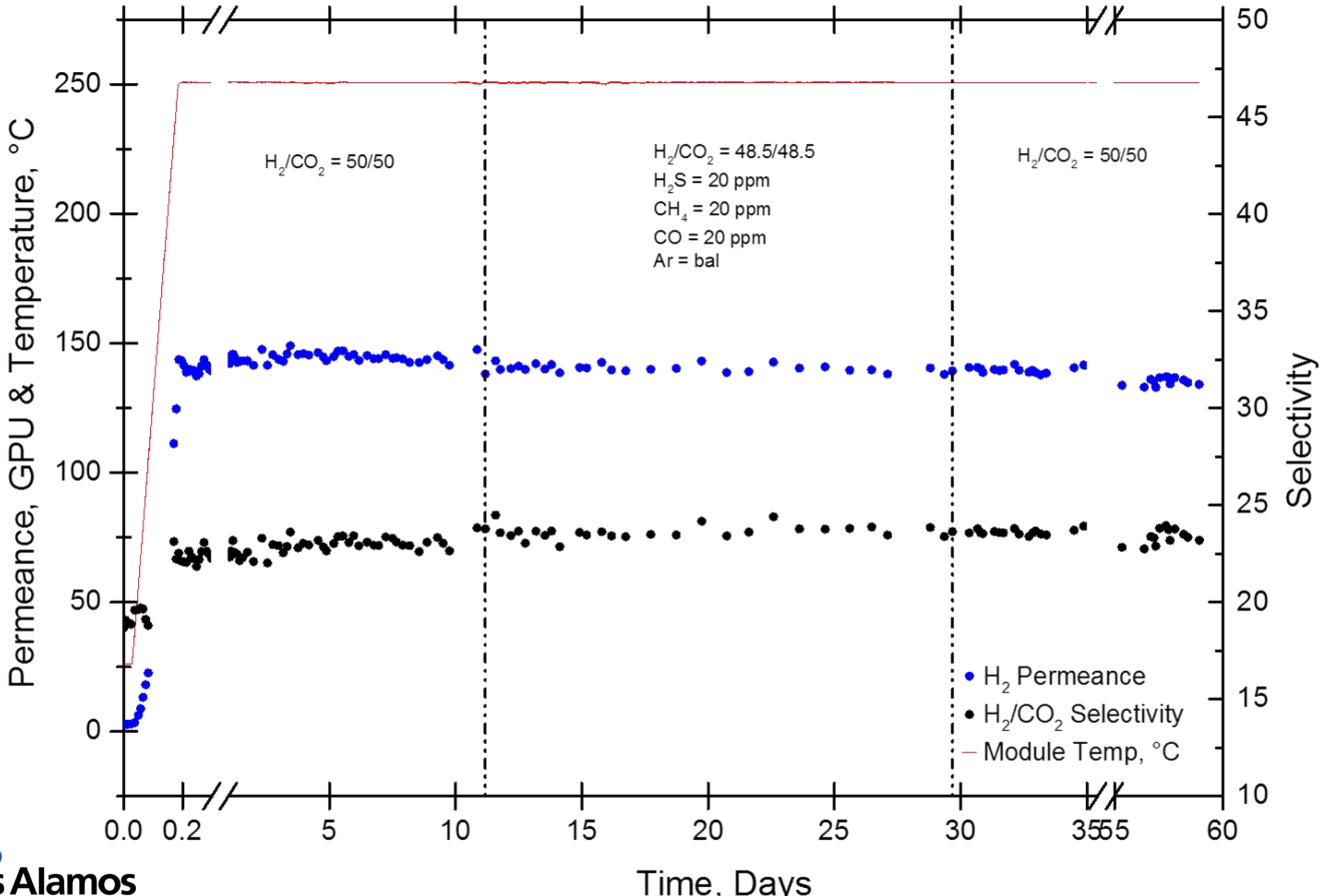
Driving Force Independent Permselectivity

- H_2 permeance and H_2/CO_2 selectivity independent of feed pressure
  - Absence of pressure-dependent viscous flow transport mechanism indicates nearly defect free fiber and seals



Dry Mixed Gas Performance - 60 days (>1400 h) @ 250 °C

- ✓ **First long term evaluation of HFM incorporating seal layer**
- ✓ **First evaluation of seal layer integrated HFM in the presence of H_2S**

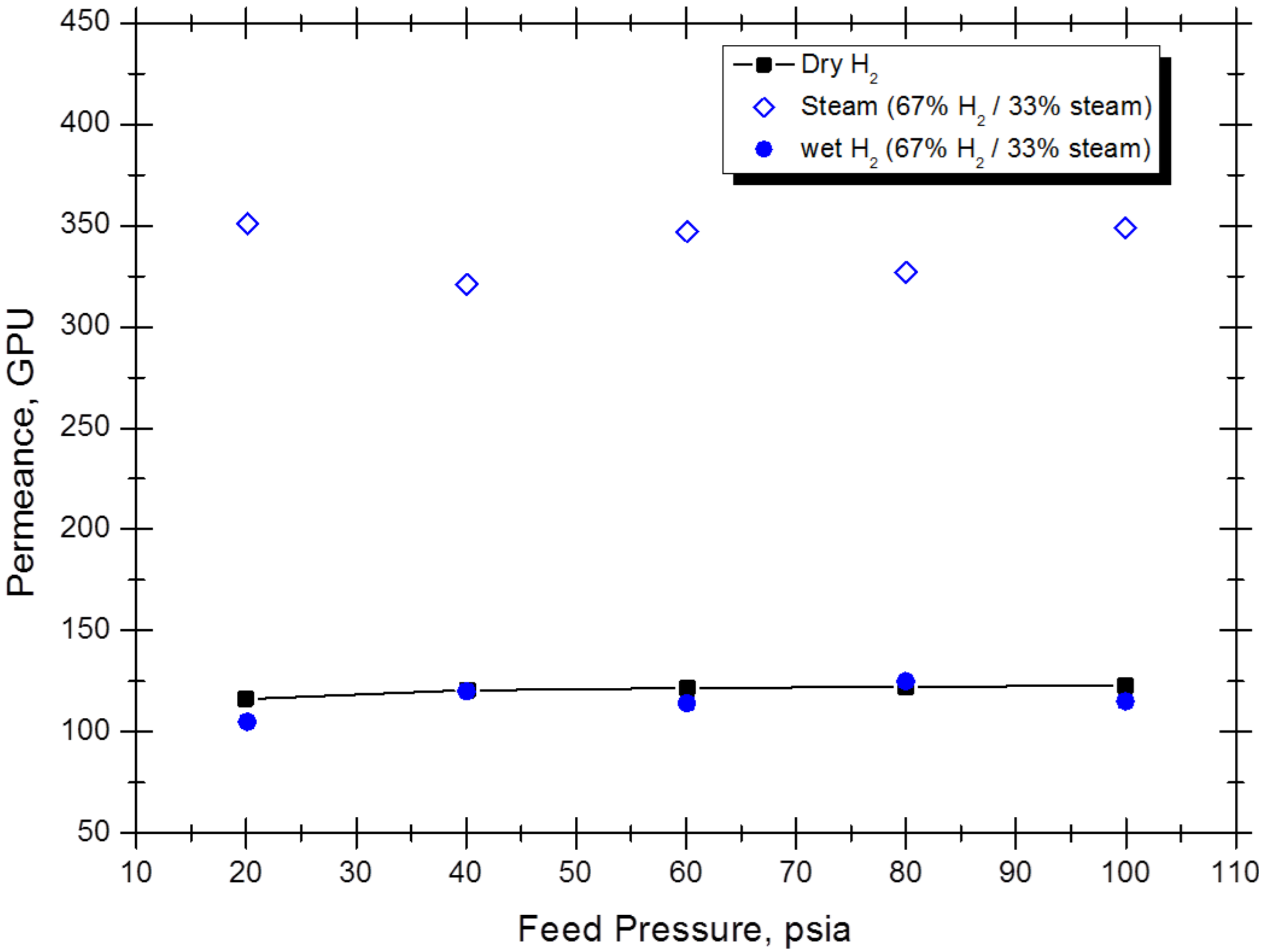


Demonstration and Validation of Developed Materials and Methods:

Wet Pure Gas and Simulated Syngas Performance

Mixed Gas (H_2 with Steam): Feed Pressure Effect

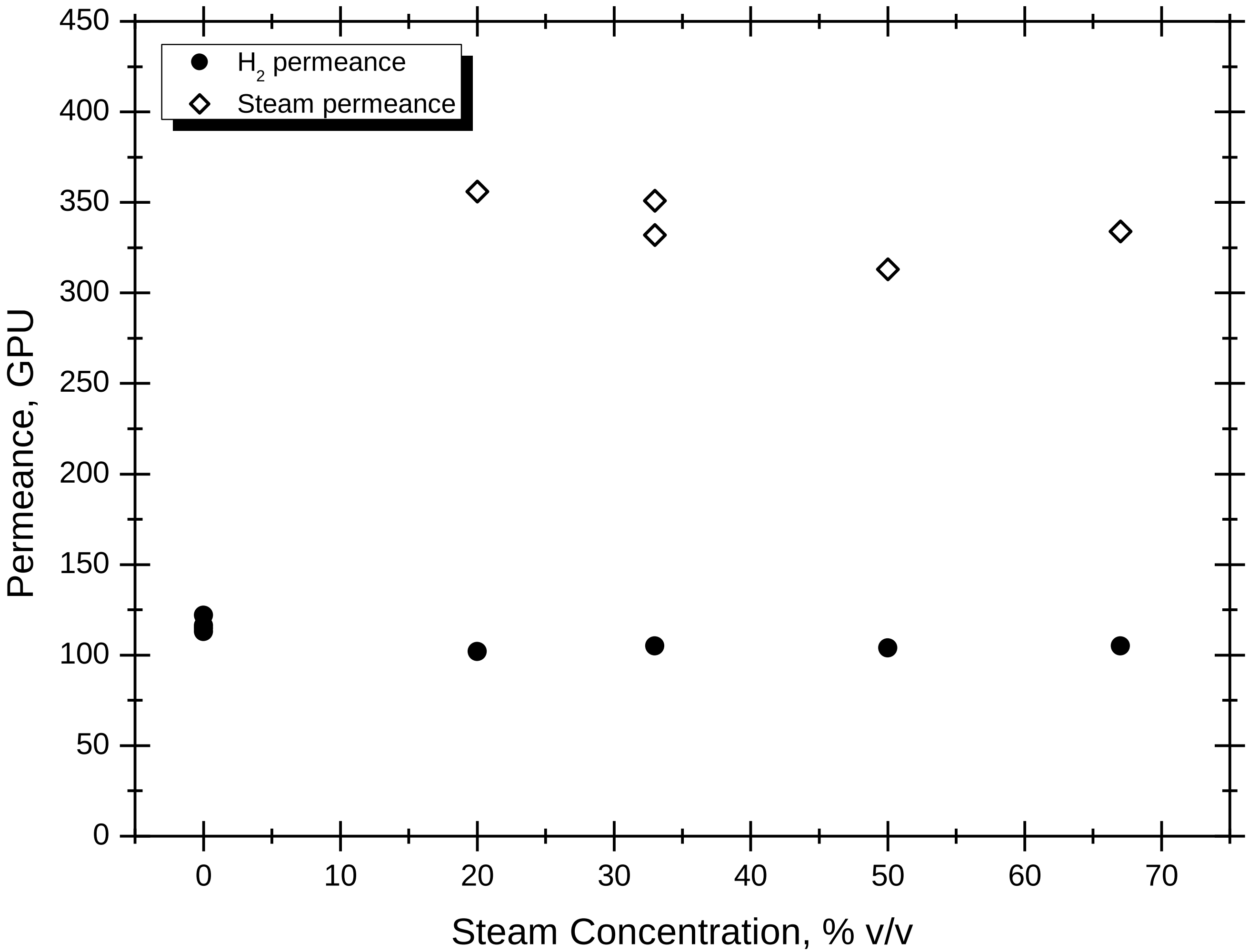
- **First time measurement of PBI hollow fiber membrane steam permeation**



- PBI HF FAB4-117 series:
  P(H_2) → ~110 GPU
  P(H_2O) → 325-350 GPU
  α (H_2/CO_2) → 22-26
  α (H_2O/H_2) → ~3.0
- T = 250 °C
- TMP 20-100 psid
- Wet gas feedstocks
- Wet H_2, N_2, CH_4, CO_2 evaluated
- Dual chamber pressure-rise protocol utilized
  - Method developed by LANL to look at R&D scale membrane performance in steam containing environments

Mixed Gas (H_2 with Steam): Steam Concentration Effect

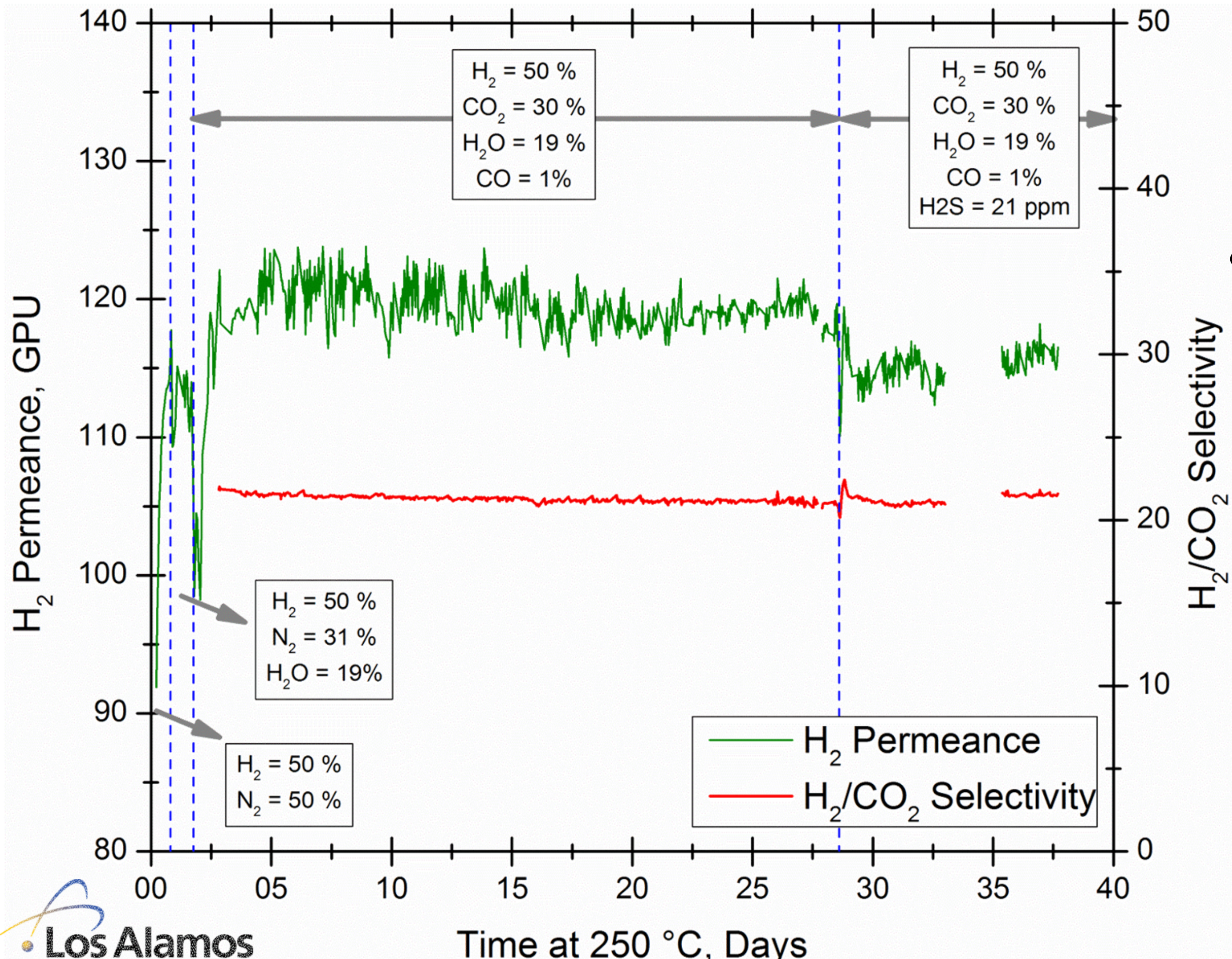
➢ **Stable performance in the presence of varied feed composition**



- PBI HF FAB4-117 series: $P(H_2) \rightarrow$ ~110 GPU $\alpha\ (H_2/CO_2) \rightarrow$ 22-26
- T = 250 °C
- Steam: 0 – 67% v/v
- TMP 20 psid
- Wet gas feedstocks
- Wet H_2, N_2, CH_4, CO_2 evaluated
- Dual chamber pressure-rise protocol utilized
  - Method developed by LANL to look at R&D scale membrane performance in steam containing environments

Long Term Durability – Wet Synthesis Gas (>950 h)

➢ **Long term evaluation of HFM in simulated syngas with and without H_2S**

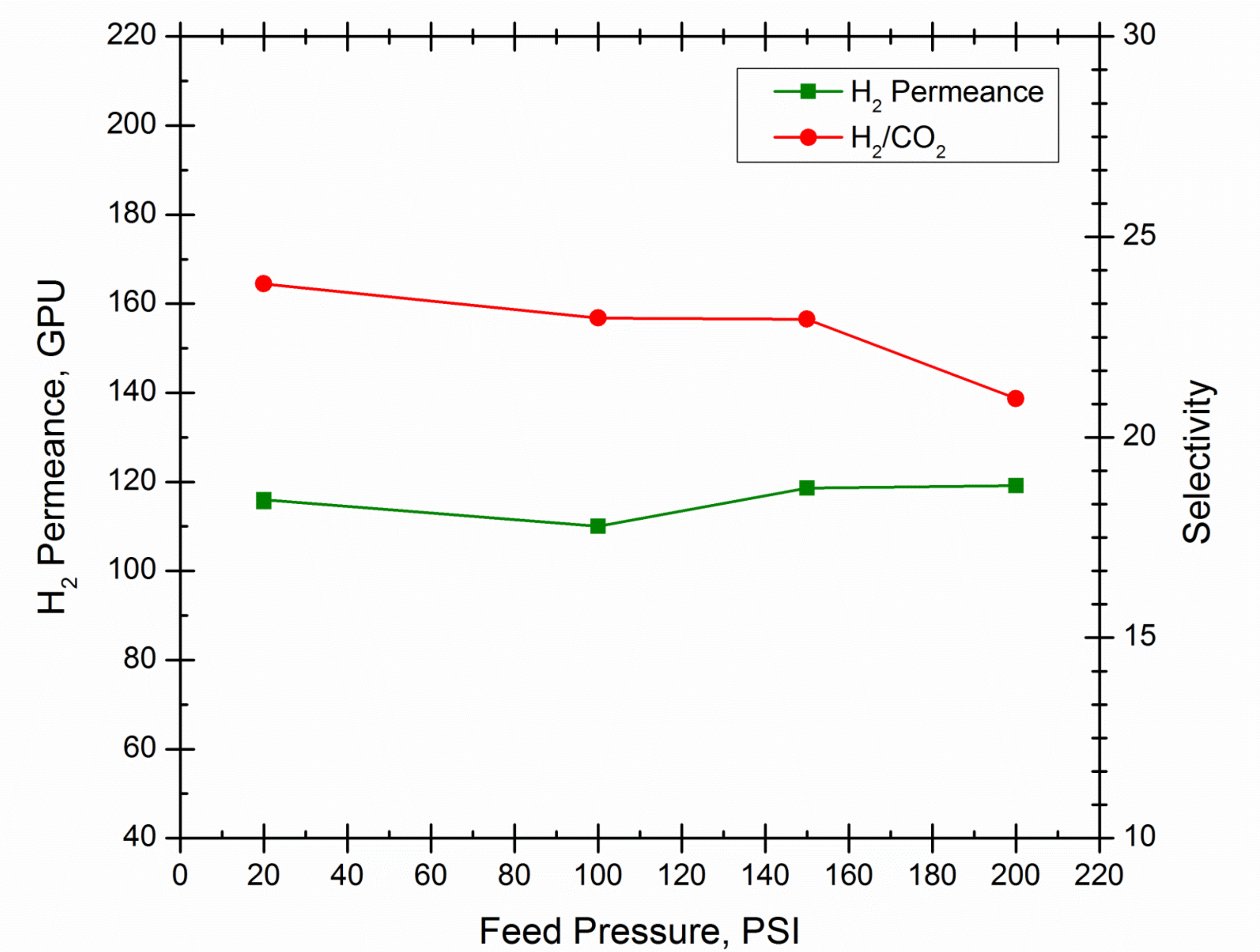


- **Exceptional tolerance to carbon, steam and sulfur at process realistic temperatures**
- **H_2 permeance and H_2/CO_2 selectivity unaffected by the presence of CO and H_2S**

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

Mixed Gas Testing: Effect of driving force

- Minimal variation in H_2 permeance and H_2/CO_2 selectivity at 250 °C as a function of driving force (feed pressure varied).



- PBI HFM tolerant to syngas environment at elevated temperature and pressures

Feed Gas

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

Temperature

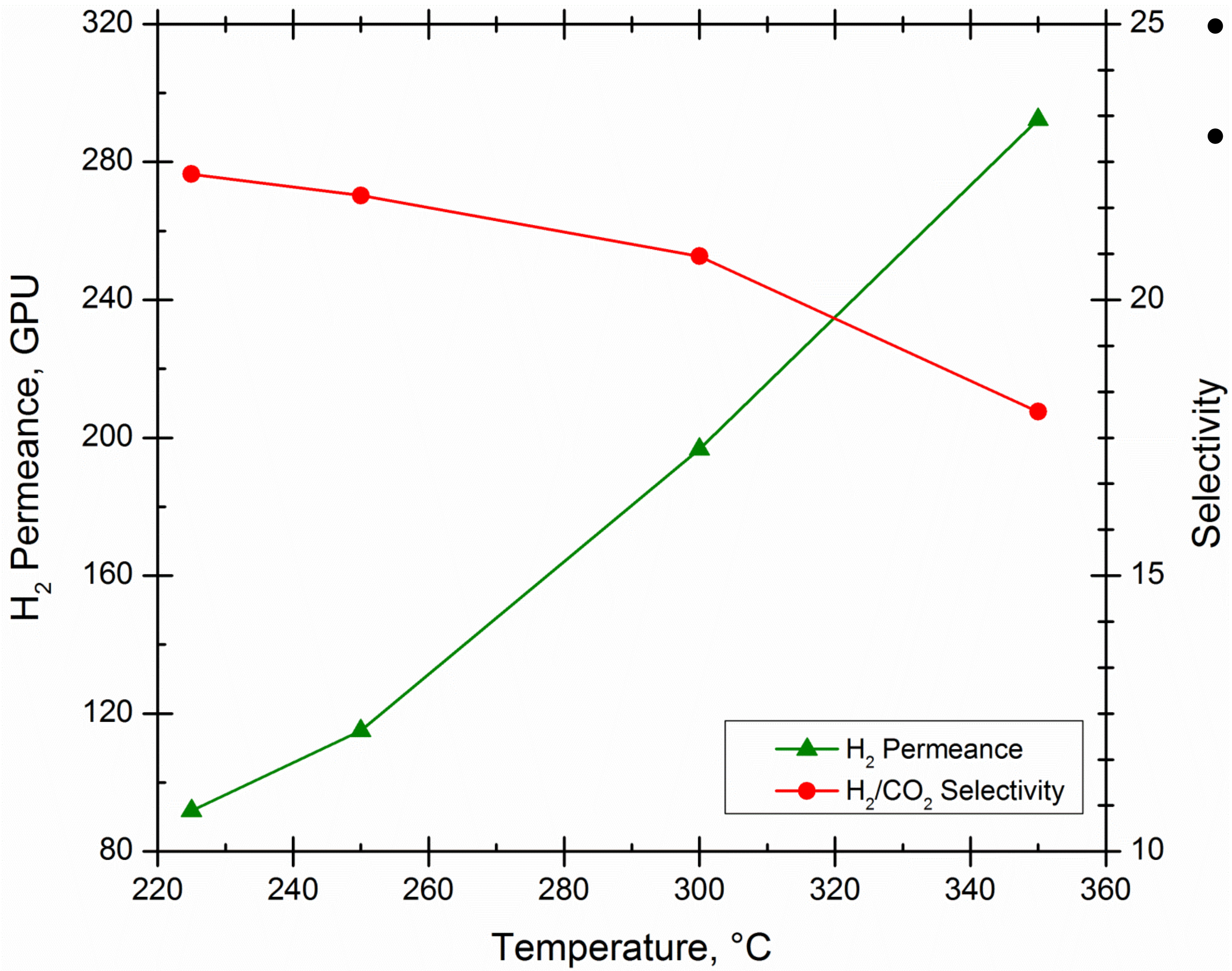
250 °C

Permeate Pressure

20 PSIA

Mixed Gas Testing: Effect of operating conditions

- H_2 permeance significantly increased while H_2/CO_2 selectivity decreased with increase in 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

Wrap-Up & Path Forward

BP1 & BP2 Milestones & Decision Points

Milestones/ Decision Points M/D	Milestone/Deliverable Description	Planned/Actual Completion Date
M-1	Demonstrate feasibility of coating sealing layer on hollow fibers	COMPLETE BP1Q1 (CY13Mar)
M-2	Initiate mixed gas hollow fiber testing under realistic syngas conditions	COMPLETE BP1Q1 (CY13Mar)
D-1	Demonstrate hollow fiber membrane with pure gas H_2 permeance of at least 150 GPU and H_2/CO_2 selectivity of at least 20 under realistic process conditions	COMPLETE BP1Q3 (CY13Q4)
M-3	Demonstrate ability to control the selective layer thickness	COMPLETE BP2Q1 (CY14Q2)
M-4	Demonstrate sealing layer efficacy and composite structure tolerance to syngas operating environments	BP2Q3 (CY14Q4)
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	BP2Q4 (CY15Q1)

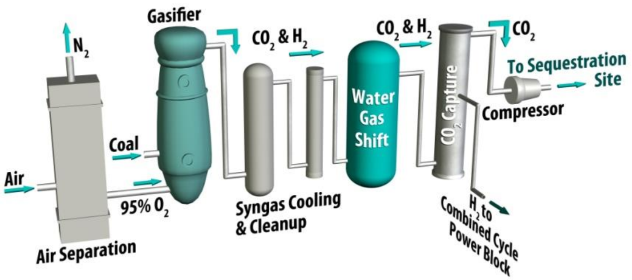
Wrap-Up

- **Optimization of a robust, high permeance, hollow fiber based platform on-going**
  - Develop fabrication protocols leading to high H_2 permeance, macrovoid-free, mechanically robust HFMs with defect minimized selective layers
- **Demonstrated success in developing methods for defect sealing**
  - Integration of seal layer into HF platform demonstrated – *All membranes presented here have an integrated seal layer*
  - HF performance w/seal indicates exceptional opportunities for defect mitigation with minimal transport resistance in HFM application
  - Initial sulfur tolerance and steam tolerance demonstrated in HF format.
- **Developed module fabrication materials and methods enabling HFM evaluation to 400 °C in simulated syngas environments**
  - Fiber and module integrity and performance to in simulated syngas demonstrated
- **Initiated HF module evaluations in simulated syngas environments**
  - Fibers with varied fabrication protocols evaluated – dry gas, wet gas
  - Long-term HF performance of >150 GPU H_2 with H_2/CO_2 selectivity > 20 demonstrated
  - No reduction in H_2 perm-selectivity performance demonstrated for PBI hollow fiber membrane at 250 °C for approximately 1000 hours.

Path Forward

- **Hollow Fiber Fabrication**
  - Fabrication optimization to achieve high permeance defect minimized membranes with in-process stability/durability - Further optimization around SL thickness of 100-200 nm
  - 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 (Demonstration task)
- **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 HFM performance of >250 GPU H_2 with H_2/CO_2 selectivity > 25
  - Development and protection of PBI hollow fiber membrane manufacturing protocols for transfer/licensing to industry for scale-up/commercialization
  - In-house HFM demonstrations: 1000+hr campaigns, no-sulfur syngas, low sulfur (20ppm) syngas, high sulfur (100+ppm) syngas, upset conditions (T, P, steam composition)

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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Carbon Capture Program

Disclaimer

Membrane Terminology

- **Permeability** is a ***material*** **property: describes rate of permeation of a solute through a material, normalized by its thickness and the pressure driving force (typical unit ≡ barrer)**

$$P_A \equiv \frac{J_A}{(p_2 - p_1)/l} = \frac{J_A}{-\Delta p / l}$$

- **Permeance** is a ***membrane*** **property: calculated as solute flux through the membrane normalized by the pressure driving force (but not thickness) (typical unit ≡ GPU)**
- **Ideal selectivity describes separation factor: the ratio of permeability (or permeance) of two different components in a membrane, and is a** ***material*** **property**
- **High membrane permeance is achieved by both:**

Material selection/design **(high permeability)**

&

Membrane design **(minimized selective layer thickness)**