# 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

**Los Alamos**

**Kathryn A. Berchtold**

**Rajinder P. Singh**

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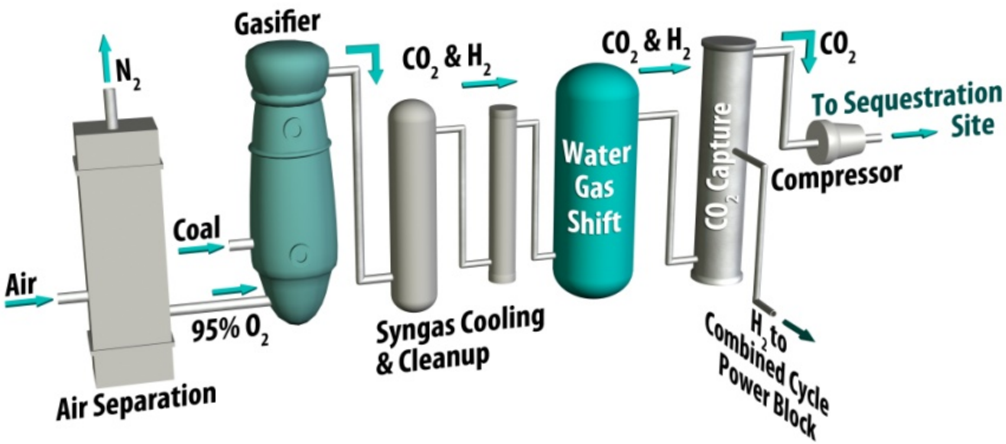
# Project Summary

- Award Name:
  - Polymer-Based Carbon Dioxide Capture Membrane Systems
- Award Number:
  - FE-308-13
- Performance Period:
  - 03/2013-08/2016
- Current Budget Period:
  - BP3 of 3 (04/15-08/16)
- Project Cost (DOE):
  - $1,972K
- DOE NETL Project Manager:
  - David A. Lang
  - C. Elaine Everitt

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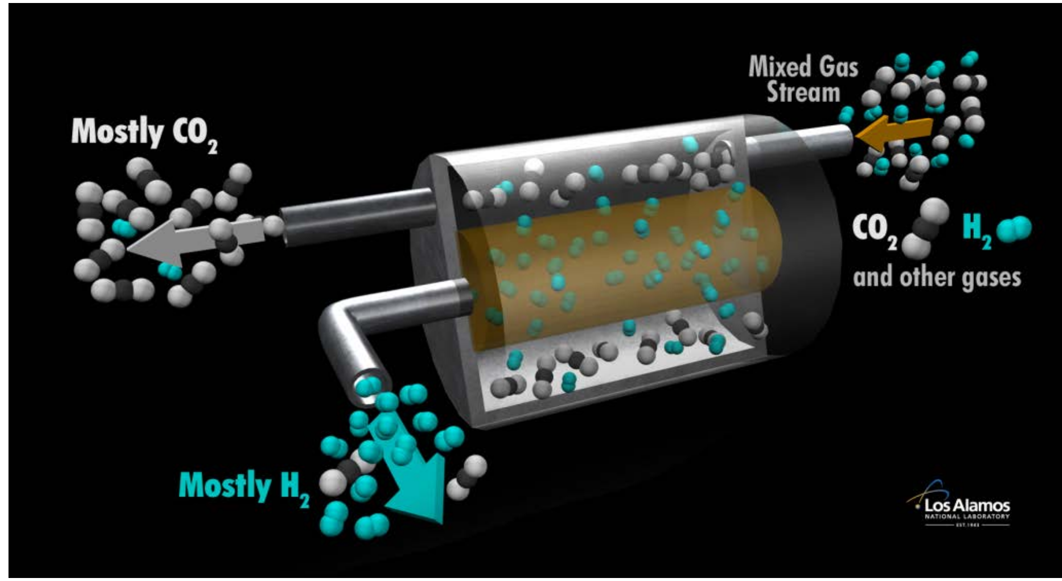
# Overarching Objective



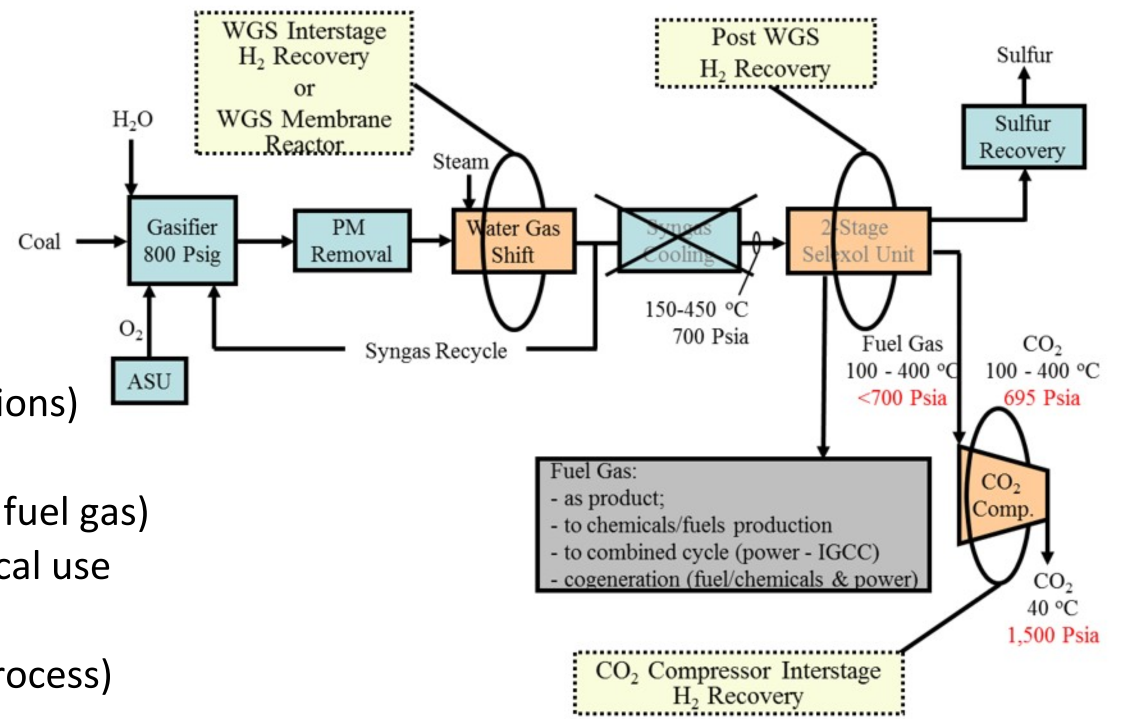

**Development and demonstration of an innovative polymer-based membrane separation technology aimed at improving the economics and performance of hydrogen separation and carbon capture from synthesis (syn) gas, enabling more-efficient and cleaner energy production from coal.**

# Technology Benefits: Pre-combustion Capture

- Carbon capture in integrated gasification combined cycle power (IGCC) systems
  - Economic outcome of $H_2/CO_2$ separation system is strongly tied to process and separation operating temperatures
  - High temperature membrane system provides process intensification opportunities in the vicinity of water gas shift reactors and/or as membrane reactor

**Membrane Advantages for Pre-combustion Carbon Capture:**

- $CO_2$ 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

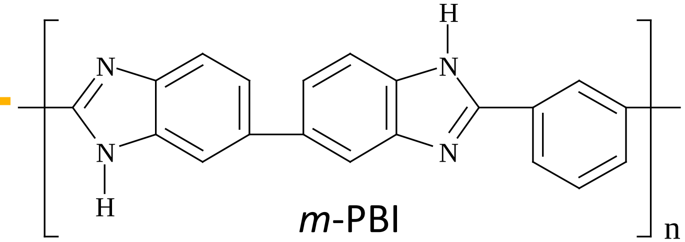


# Technology Challenges & Opportunities

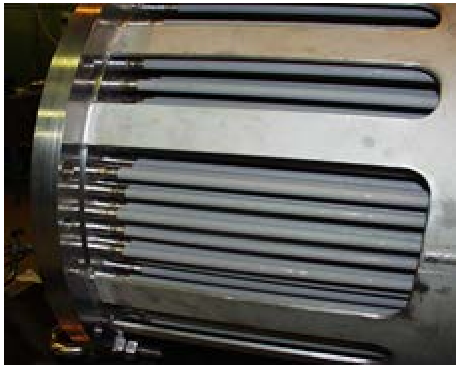
- **Commercial polymer membranes and module manufacture/sealing technologies are limited to $T_{operation}$ ~150 °C.**
  - Separation process economics are strongly tied to process/separation temperature.
- **Membrane materials and systems capable of withstanding IGCC syngas process conditions are required.**
  - 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).



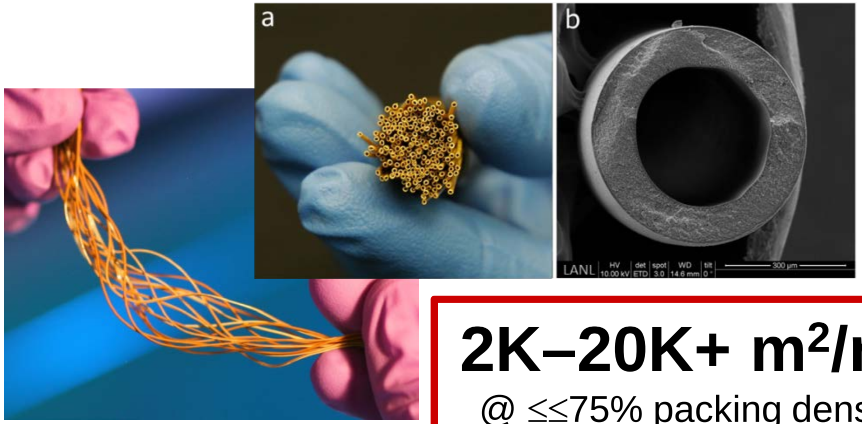

*m*-PBI



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

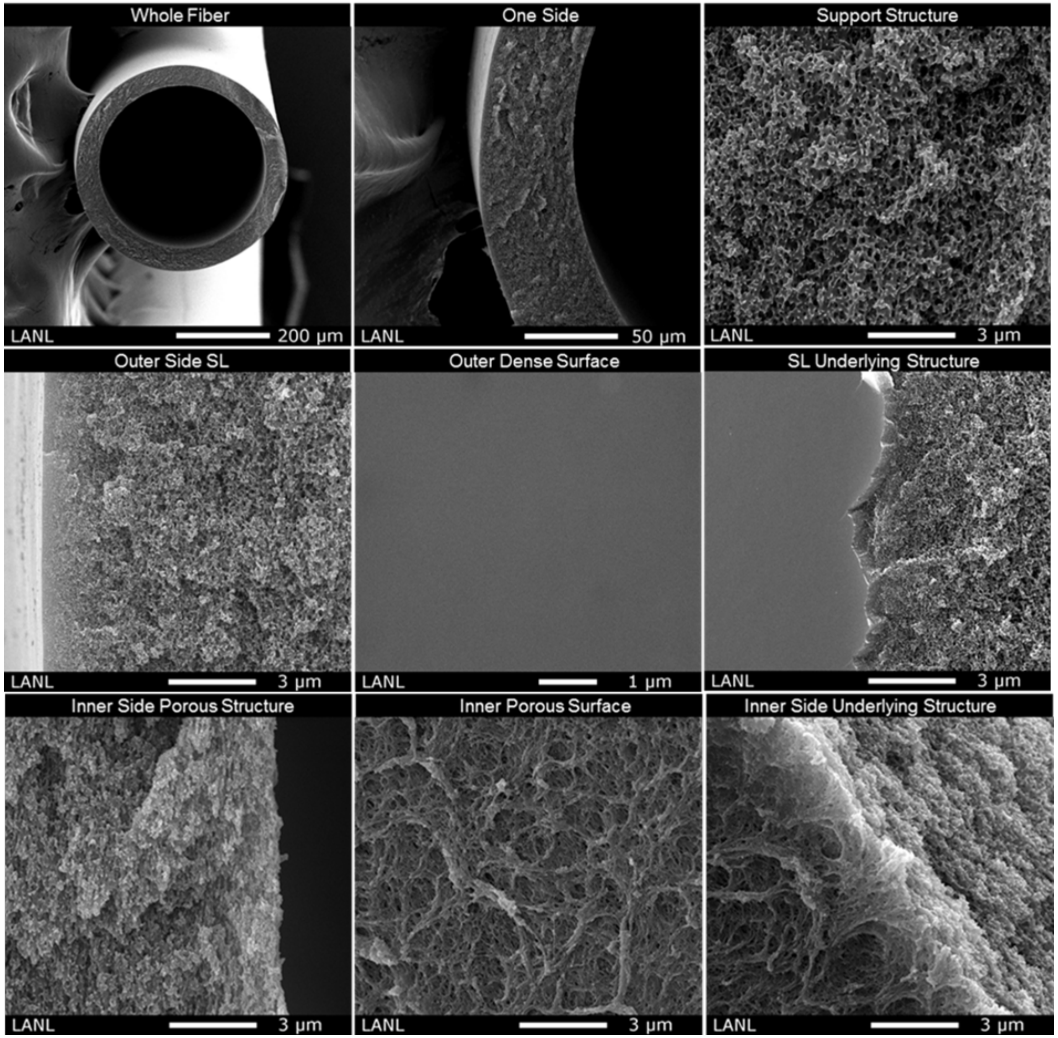
| Milestones/ Decision Points M/D | Project Milestones/Deliverables | Planned/Actual Completion Date |
|---|---|---|
| M-1 | Demonstrate feasibility of coating sealing layer on hollow fibers | COMPLETE BP1Q1 |
| M-2 | Initiate mixed gas hollow fiber testing under realistic syngas conditions | COMPLETE BP1Q1 |
| D-1 | Demonstrate hollow fiber membrane with pure gas $H_2$ permeance of at least 150 GPU and $H_2/CO_2$ 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 |
| M-5 | Report on stage cut influences on membrane performance and module design optimization and fabrication (with NETL). | COMPLETE BP2Q4 |
| M-6 | Report on multi-fiber membrane module performance in simulated syngas environments | 45% |

# Hollow Fiber Fabrication & Evaluation

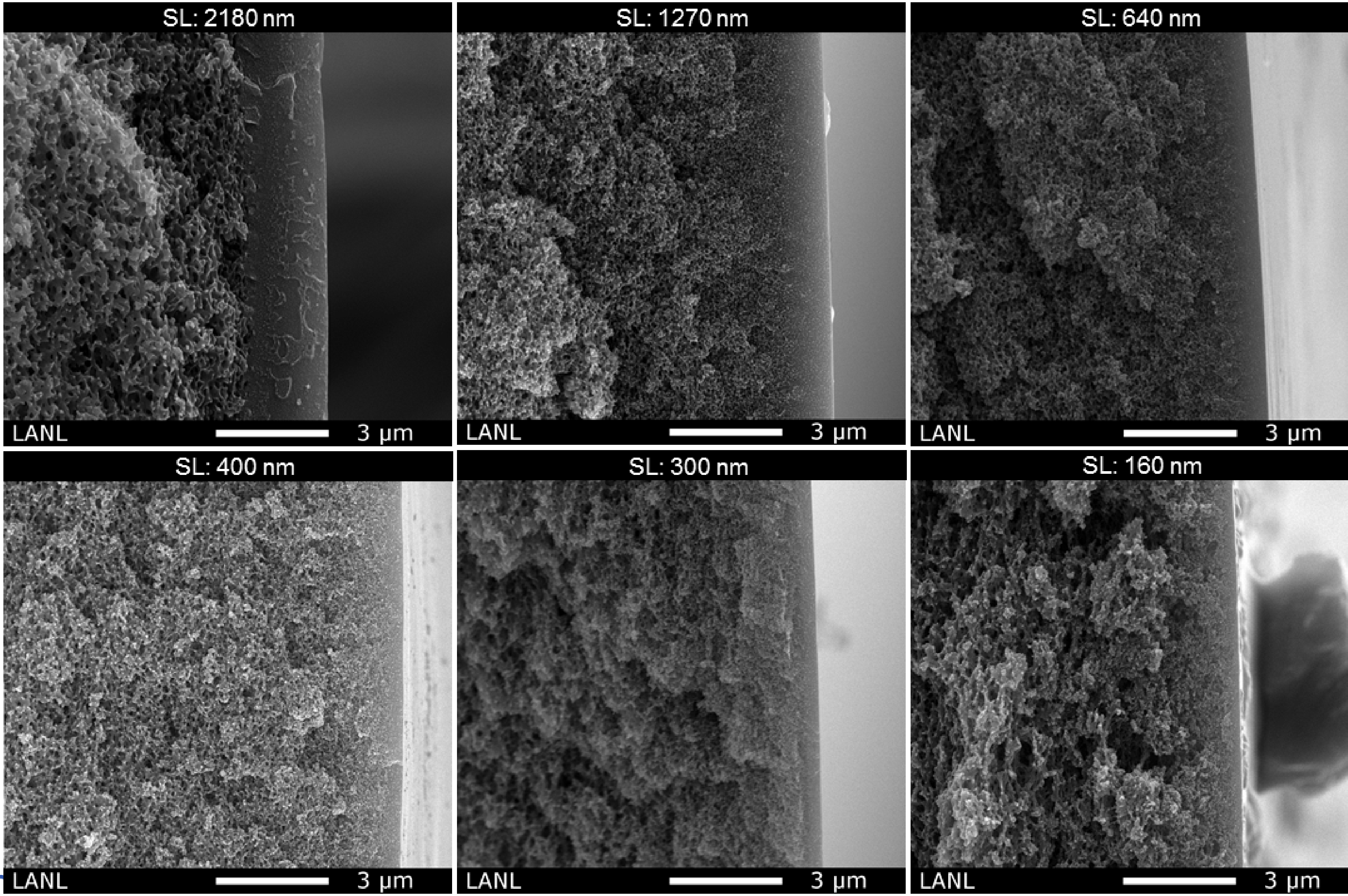
# Key Accomplishments: Hollow Fiber Fabrication

- Developed novel methods for PBI hollow fiber membrane
  - **Industrially attractive fabrication process:** Continuous spinning using commercially available polymer and environmentally benign coagulant
- Exceptional fiber characteristics
  - **Macro-void Free**: Interconnected porous support morphology with porous inner surface layer
  - **Selective Layer**: Nearly defect-free selective layer with thickness controllable between 100 and 3000 nm
  - **Robust Manufacturing process:** Repeatability demonstrated by fabricating multiple batch of fiber under same conditions

Provisional Patent filed: June 2015
Non-provisional Patent filed: June 2016
DOE Docket S133262/L2015020



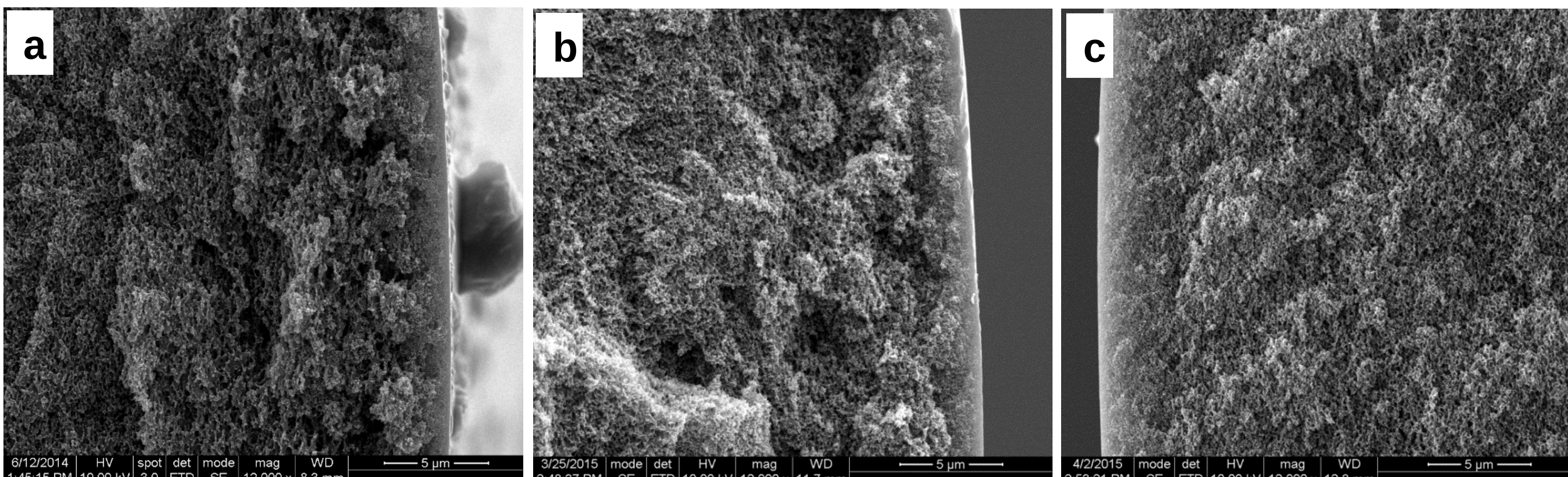
# PBI Hollow Fiber: SL Thickness Variation




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

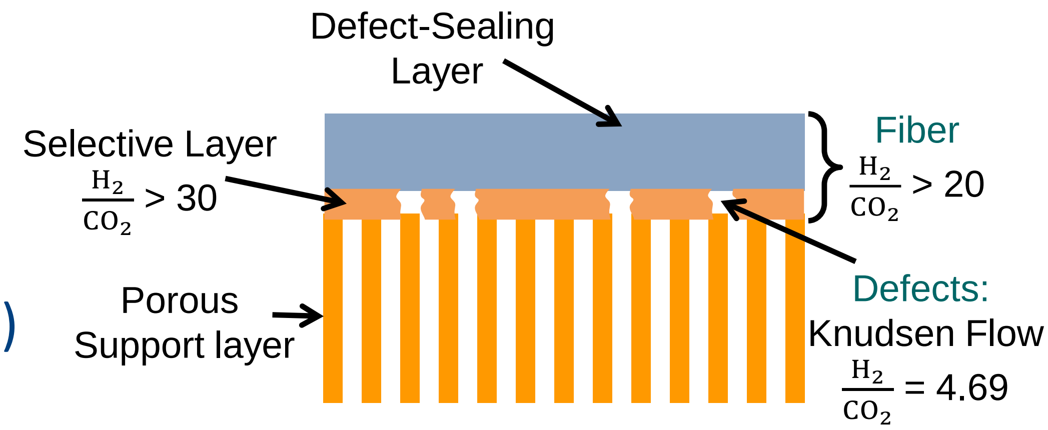
# Robust Spinning Process Demonstration

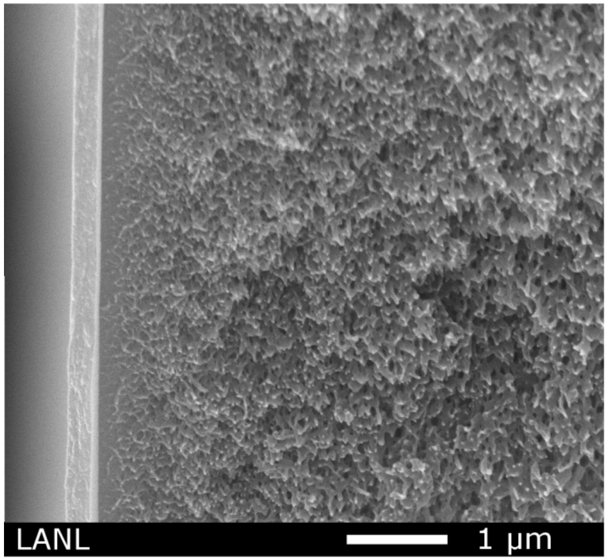
- Demonstrated successful manufacture of multiple batches of our high performance fiber
  - Evaluated fiber manufacturing process reproducibility using the optimized fiber spinning process parameters anticipated for multi-fiber module production
  - Demonstrated consistency of dope preparation and dope stability over extended periods of time (multiple 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 yielding nearly identical wall thickness, overarching geometry, and morphology

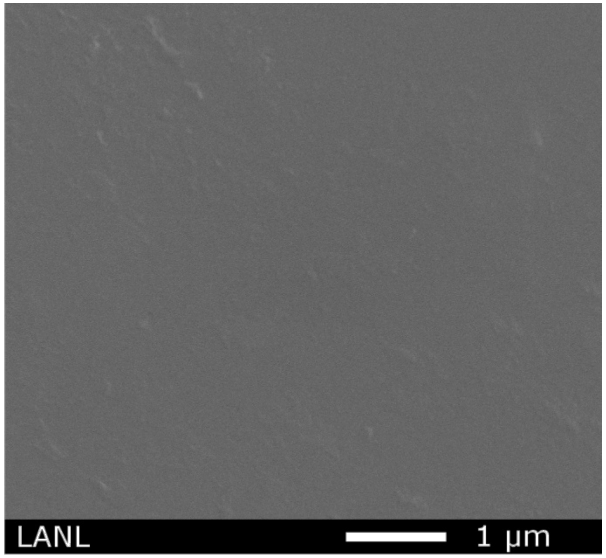


# Key Accomplishment: Defect Sealing Layer

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

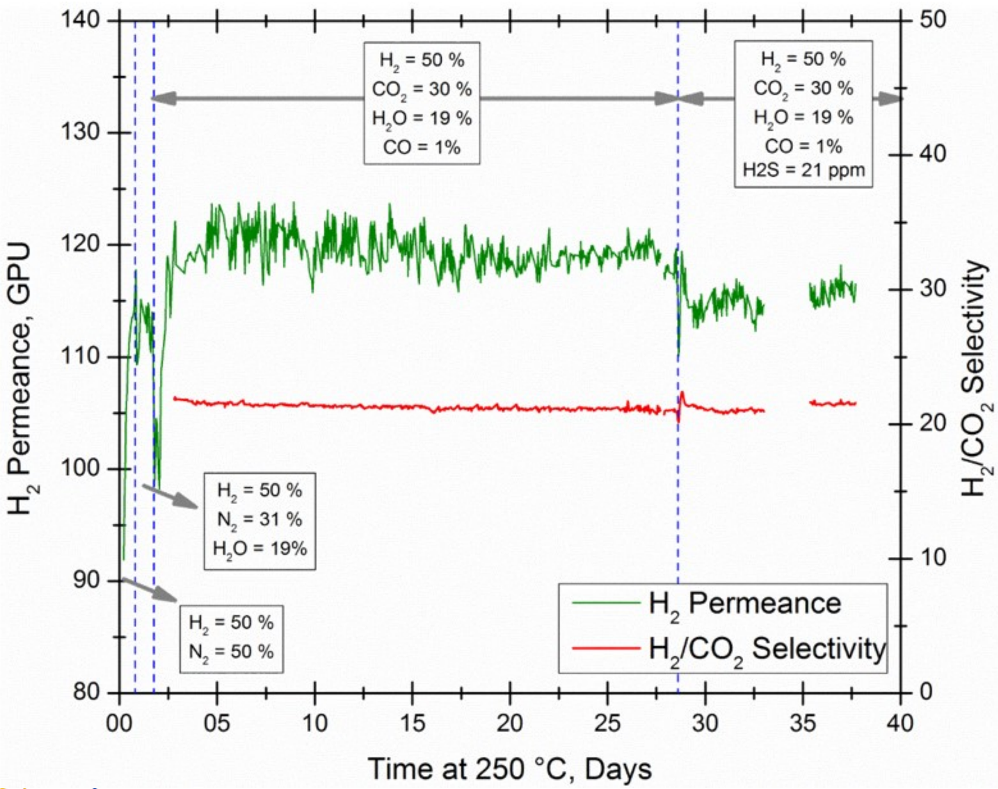


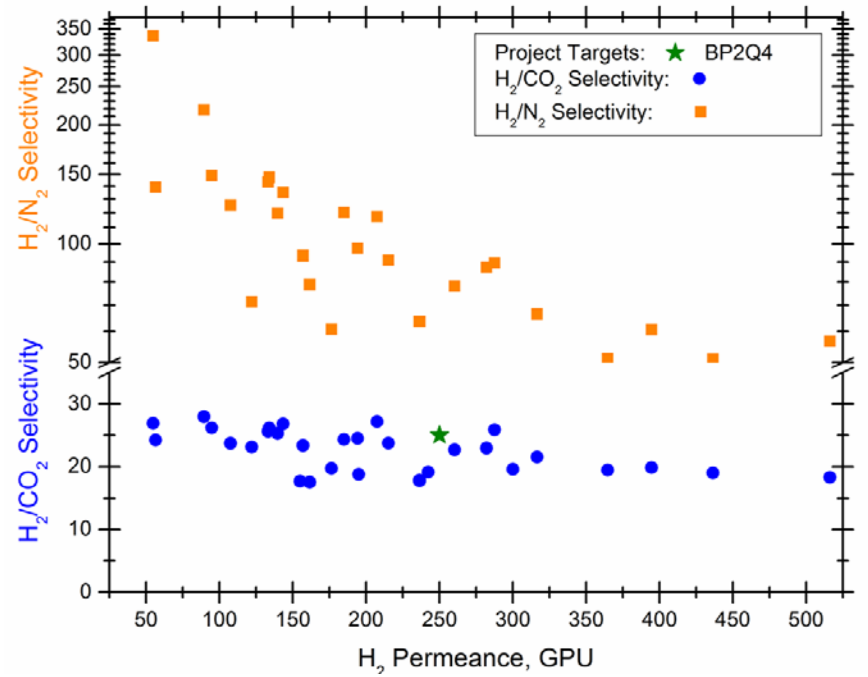



# Key Accomplishment: Separation Performance

- Industrially attractive performance with high $H_2$ permeance (50 to 500 GPU) and $H_2/CO_2$ (19 to 30) at 250 to 350 °C
- Demonstrated exceptional thermo-chemical robustness
  - Tolerance to CO, steam and $H_2S$ at realistic process conditions




- Exceptional thermo-mechanical robustness
  - Fibers tested in simulated syngas at high differential pressure (200 PSI) and 200 to 350 °C

# Multi-Fiber Module Fabrication & Evaluation

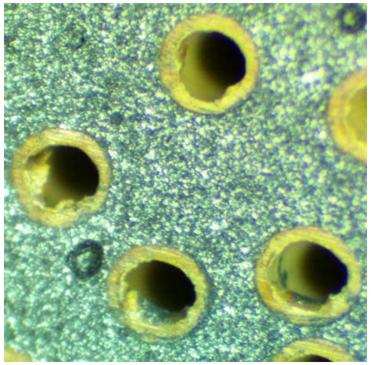
# Module Fabrication & Evaluation

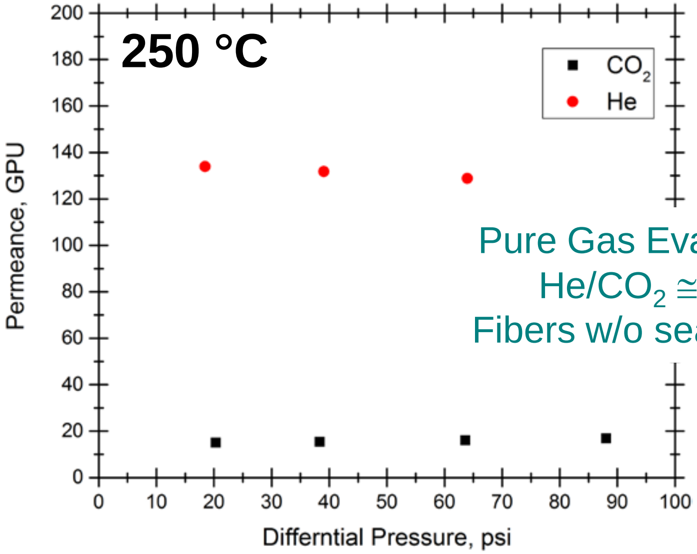
- **Goal**: Develop laboratory scale multi-fiber module to enable module design and potting materials & methods assessment at realistic pre-combustion carbon capture conditions
- Potting material is a significant challenge for industrial deployment of PBI membrane technology for pre-combustion carbon capture
  - Long term hydrothermal stability at process conditions of commercial potting materials (e.g. silicones, epoxies) unknown
  - Lab scale modules enables down-selection of a suitable high temperature potting material for long-term evaluation under realistic conditions
- Small scale module fabrication has additional challenges including the need for minimization of potting material wicking and defects in the seal ends
  - High viscosity potting material desirable to minimize wicking but creates fiber ends encapsulation issues
  - High temperature potting materials require extensive heat treatment to minimize shrinkage and mechanical failure due to evolving gases during curing and use

# PBI Multi-fiber Module Development

- Fabricated laboratory scale PBI multi-fiber modules
  - Identified commercial potting material to enable evaluation at elevated temperature
  - Optimized fabrication protocol to minimize capillary wicking while achieving defect-free interface between potting material and fibers
  - $<$ 0.1%/24 hr weight loss measured for the down-selected potting material at 250 °C in inert conditions.
  - Optimized curing and heat-treatment protocols


Good adhesion between fiber and potting material

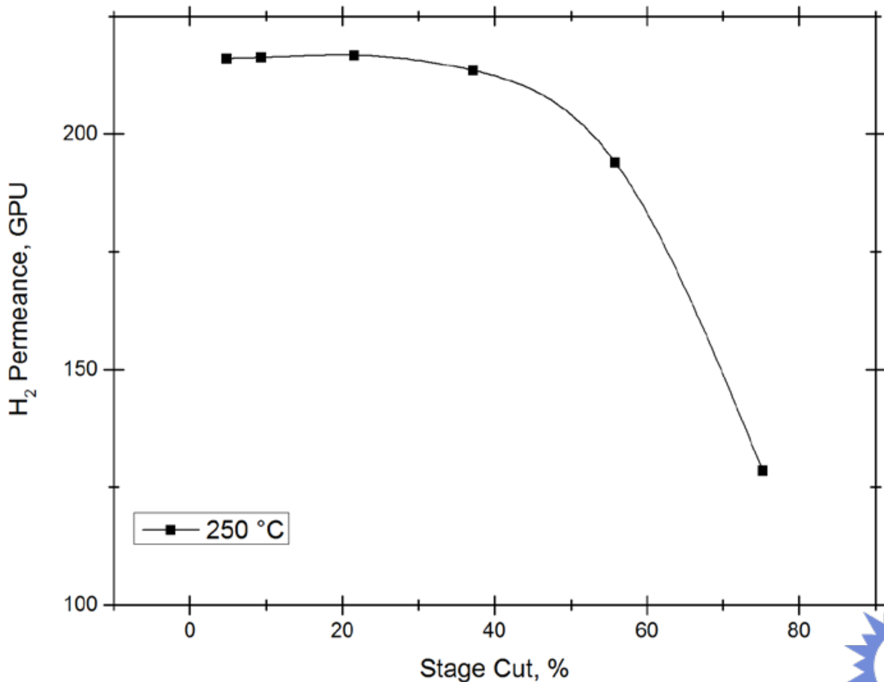


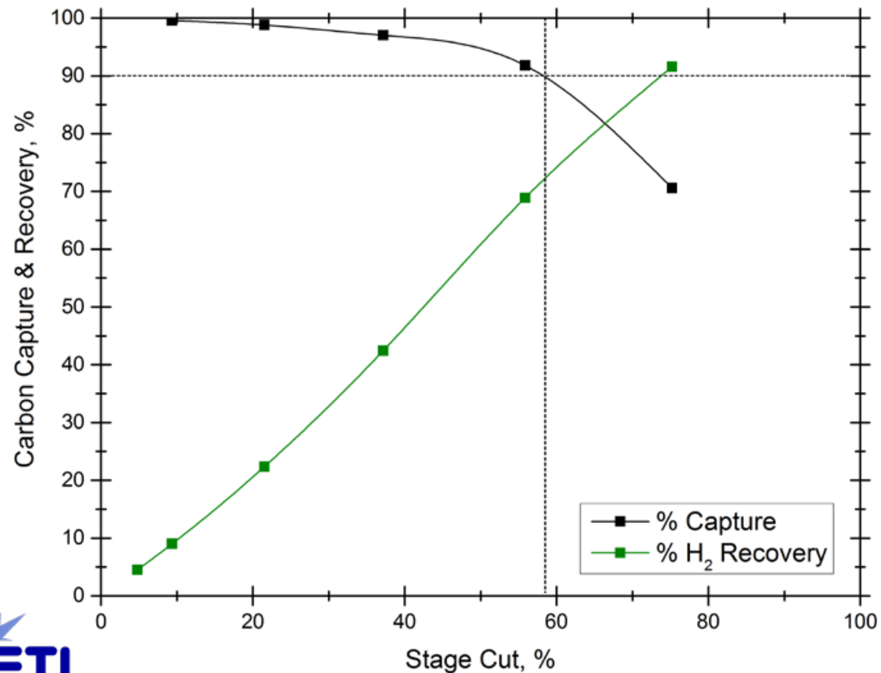



# Membrane Simulations

# Performance Assessment

- Influence of stage cut on PBI membrane performance simulated using Computation Fluid Dynamic (CFD) model based on single fiber data
  - Stage cut reduces the effective $H_2$ permeance
  - Difficult to achieve 90% $H_2$ recovery and 90% carbon capture using <u>single stage</u> membrane operation
  - Additional downstream purification step or improved $H_2/CO_2$ selectivity required to meet CCS targets
    - Multi-stage membrane operation further improves performance



# Conclusions & Path Forward

## Project Accomplishments:

- Novel methods to spin high permeance, $H_2$ selective continuous PBI hollow fibers developed
- Membrane defect mitigation materials and methods developed
- Long-term stability of developed PBI hollow fibers demonstrated in simulated syngas environments
- Lab-scale multi-fiber modules developed
- Developed intellectual property protected

## Technology Path Forward and Next Phase Efforts:

- Development & Demonstration
  - Demonstration of multi-fiber modules in real syngas at National Carbon Capture Center
  - Need to further improve $H_2/CO_2$ separation performance to minimize the need for downstream processing
- Scale-up & Commercialization
  - Discussions with industry on-going: next-phase PBI membrane technology development and demonstration planning

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