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

LANL-FE-308-13

Kathryn A. Berchtold, Rajinder P. Singh, Kevin W. Dudeck, Ganpat J. Dahe, Cynthia F. Welch, and Dali Yang
Carbon Capture and Separations for Energy Applications (CaSEA) Labs,
Material, Physics and Applications Division,
Los Alamos National Laboratory

NETL CO_2 Capture Technology Meeting
10 July 2013, Pittsburgh, PA

Los Alamos National Laboratory is operated by the Operated by Los Alamos National Security, LLC for DOE/NNSA under Contract Contract DE-AC52-06NA25396.

Acknowledgements

Department of Energy/National Energy Technology Laboratory's Carbon Capture Program

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

Los Alamos

Kathryn A. Berchtold

Rajinder P. Singh

Kevin W. Dudeck

Cynthia F. Welch

Dali Yang

Ganpat J. Dahe

PBI Performance Products, Inc.

Mike Gruender

Greg Copeland

Bobby Dawkins

NETL

C. Elaine Everitt

Robie Lewis

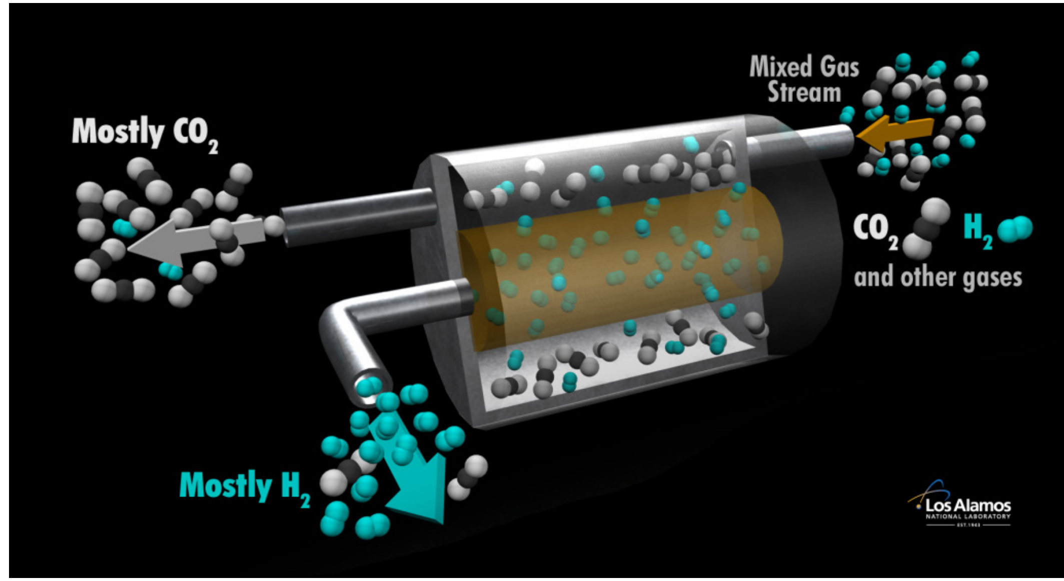
José D. Figueroa

Jared Ciferno

John Marano

Los Alamos National Laboratory is operated by the Operated by Los Alamos National Security, LLC for DOE/NNSA under Contract DE-AC52-06NA25396.

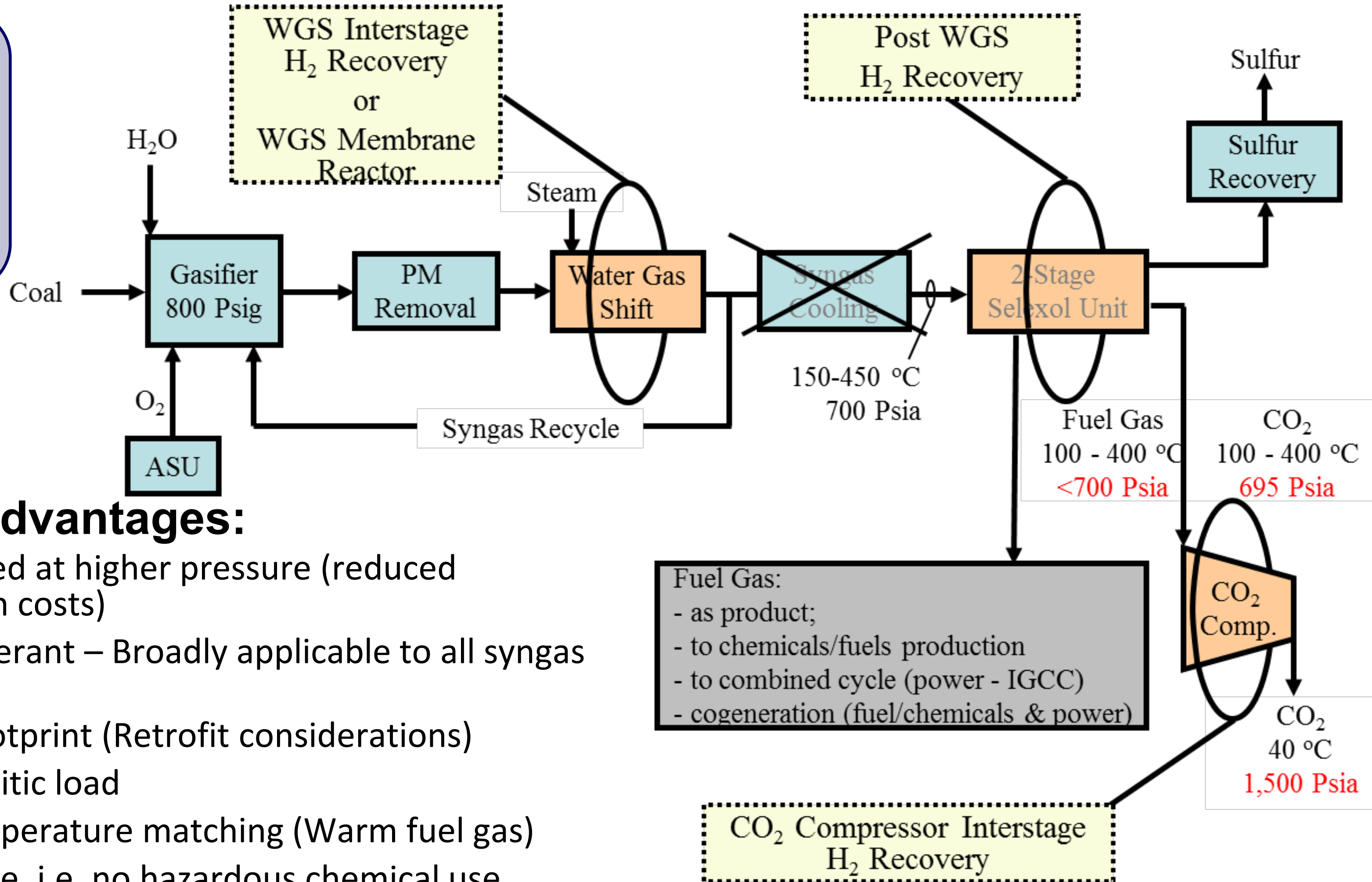
Overarching Objective



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



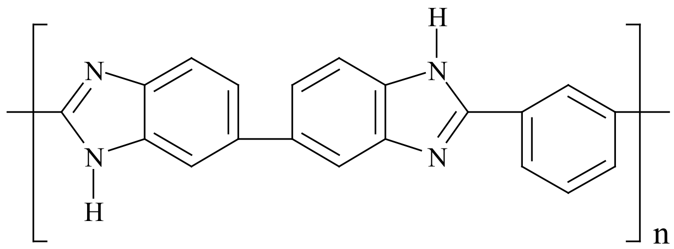
Membrane Advantages:

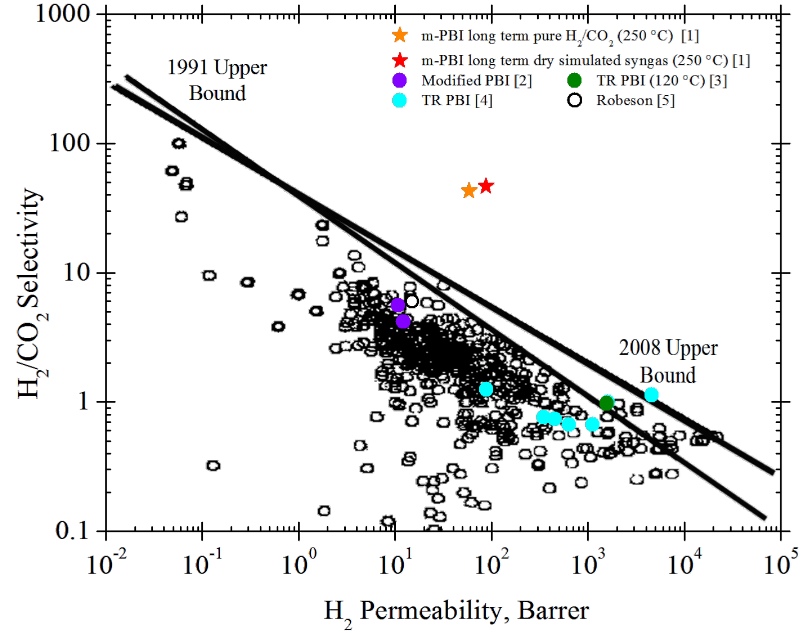
- CO_2 produced at higher pressure (reduced compression costs)
- Impurity tolerant – Broadly applicable to all syngas feedstocks
- Reduced footprint (Retrofit considerations)
- Lower parasitic load
- Process temperature matching (Warm fuel gas)
- Emission free, i.e. no hazardous chemical use
- Decreased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

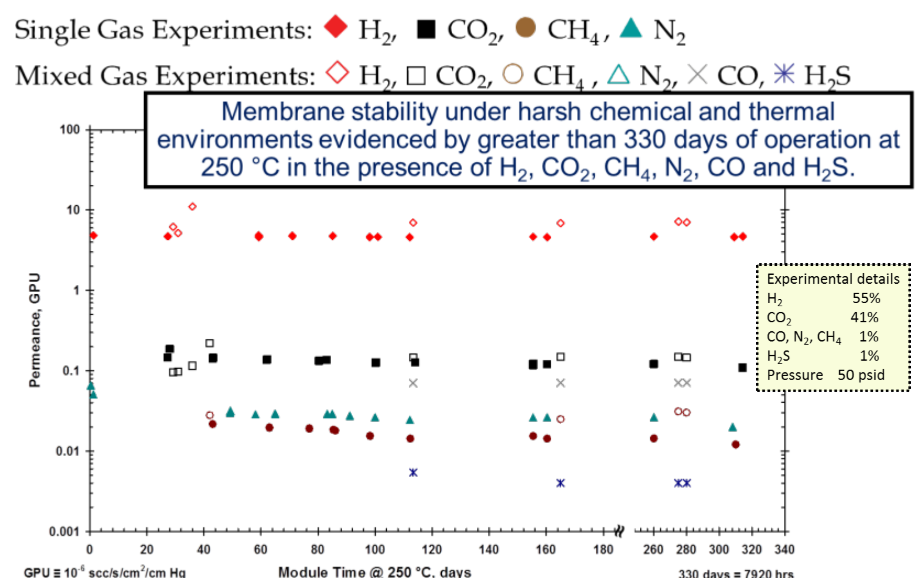
Background: PBI Membranes: Permselectivity/Durability





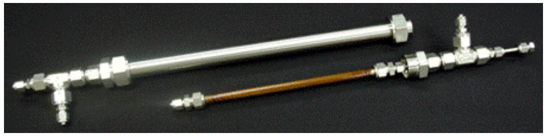
[1] Berchtold and Singh *et.al.* JMS, 415 (2012) **[2]** Kumbharkar et.al., 286 (2006) **[3]** Park et.al., 259 (2010) **[4]** Han et.al., 357 (2010) **[5]** Robeson, 320 (2008)

- 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 hollow fiber (HF) 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 and high surface area membrane deployment platforms such as HFs.
  - See *Refs. For economic analysis: Krishnan, et al. ,Energy Procedia*, 1(1) (2009) 4079 and reports for project DE-FC26-07NE43090.



Ref: Berchtold and Singh *et.al.* JMS, 415 (2012) 265-270.

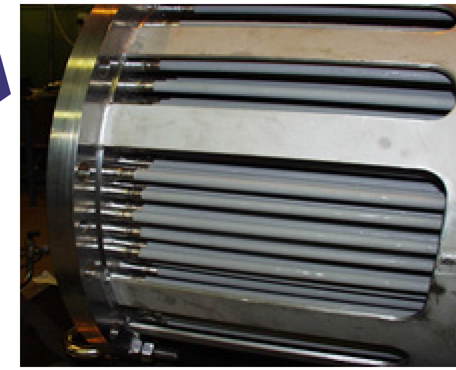
Scale-Up and Optimization: Transition to Hollow Fiber Platform



~30-80 cm²

- **Thin selective layer mandated for high throughput**
- **Defect mitigation required for selectivity retention**
- **High area density hollow fiber configuration desirable for large volume carbon capture applications**

Hundreds of cm²



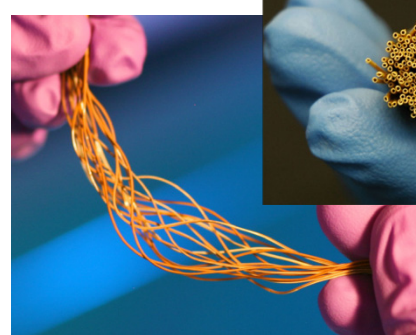
Hundreds of m²

~250 m^2/m^3
@ 75% packing density

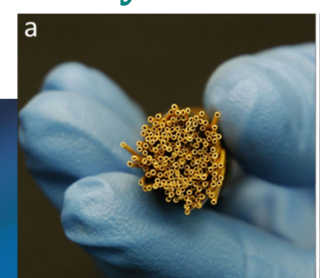
Additional Hollow Fiber Advantages

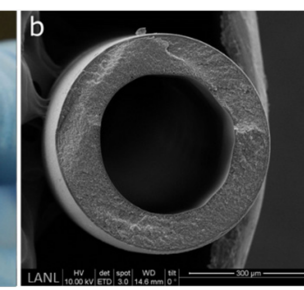
- Large mass transfer interface – efficiency advantages
- Opportunity for improved permeance – Increased capacity with a reduced footprint
- Easily scaled-up with versatile process design
- Widely used in commercial gas separation and water purification applications

High Area Density Hollow Fiber Platform



hundreds of cm²



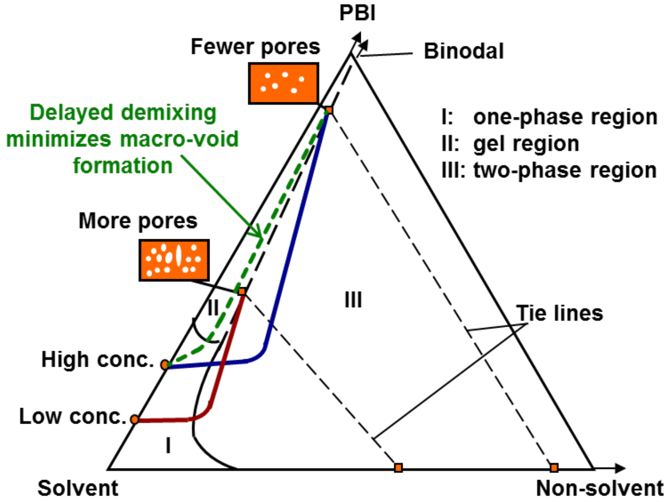


2K–20K+ m^2/m^3
@ ≤≤75% packing density

HF Membrane Fabrication: 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 MW and MW distribution
- Dope 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 T & P
- Spinning speed & take-up velocity
- Drying conditions
- Post-processing protocols



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

Understanding this complex interplay of process parameters was a primary focus of our preceding effort

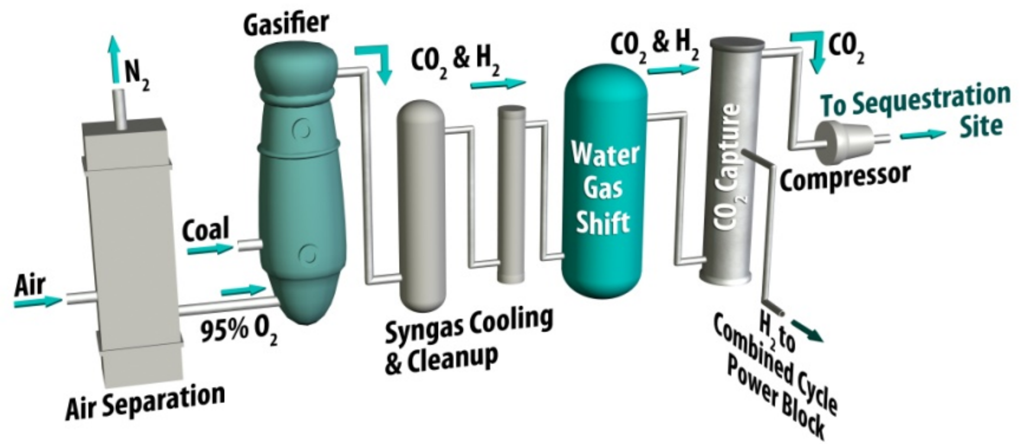
Background Summary

- Highest demonstrated operating temperature of a polymer-based membrane with commercially viable permselectivity.
  - Successful testing of the polymeric-based membrane in environments containing H_2, CO_2, CH_4, N_2, CO, and H_2S from 25 to 400 °C.
  - Long-term demonstration of membrane thermal stability via 330+ days in operation at 250 °C.
  - Successful testing of the membrane on a steam saturated shifted NG reformate up to 400 ° C with no performance degradation
- Early techno-economic evaluations demonstrated the commercial potential of the technology AND the need for a higher area density platform.
- Successfully translated the technology to a HF membrane platform with a solid understanding of the underlying phase inversion system(s) and process parameter influences.
  - Successful demonstration of PBI HF membranes with permselectivity characteristics mimicking those of PBI shell and tube composite membranes.

PROJECT OVERVIEW & STATUS

Project Overview

- Award Name:
  - Polymer-Based Carbon Dioxide Capture Membrane Systems
- Award Number:
  - FE-308-13
- Project Start:
  - 03/2013
- Project Cost (DOE):
  - $600K (BP1 of 3 proposed)
- DOE NETL Project Manager:
  - C. Elaine Everitt



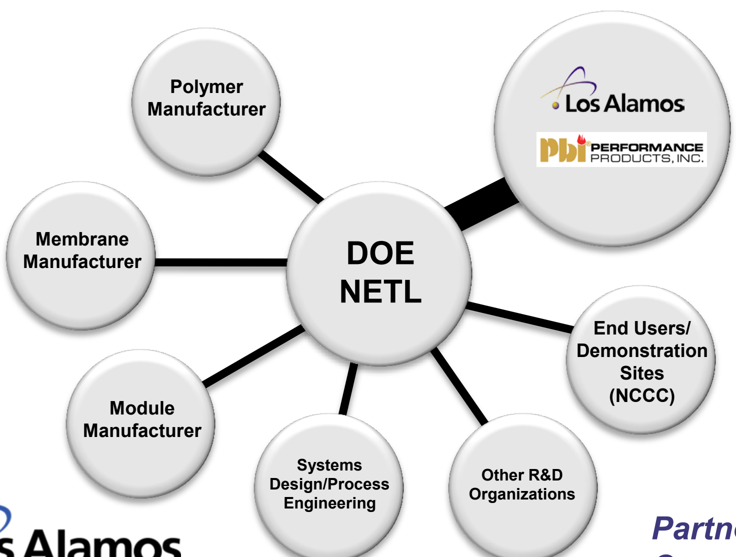
Project Team

Los Alamos NATIONAL LABORATORY

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

Pbi PERFORMANCE PRODUCTS, INC.

- 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

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

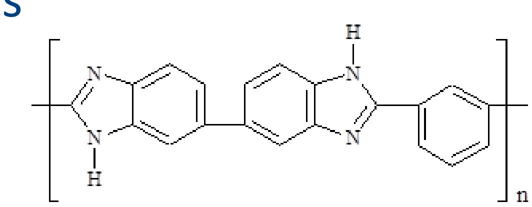
Project Focus Areas: Tasks

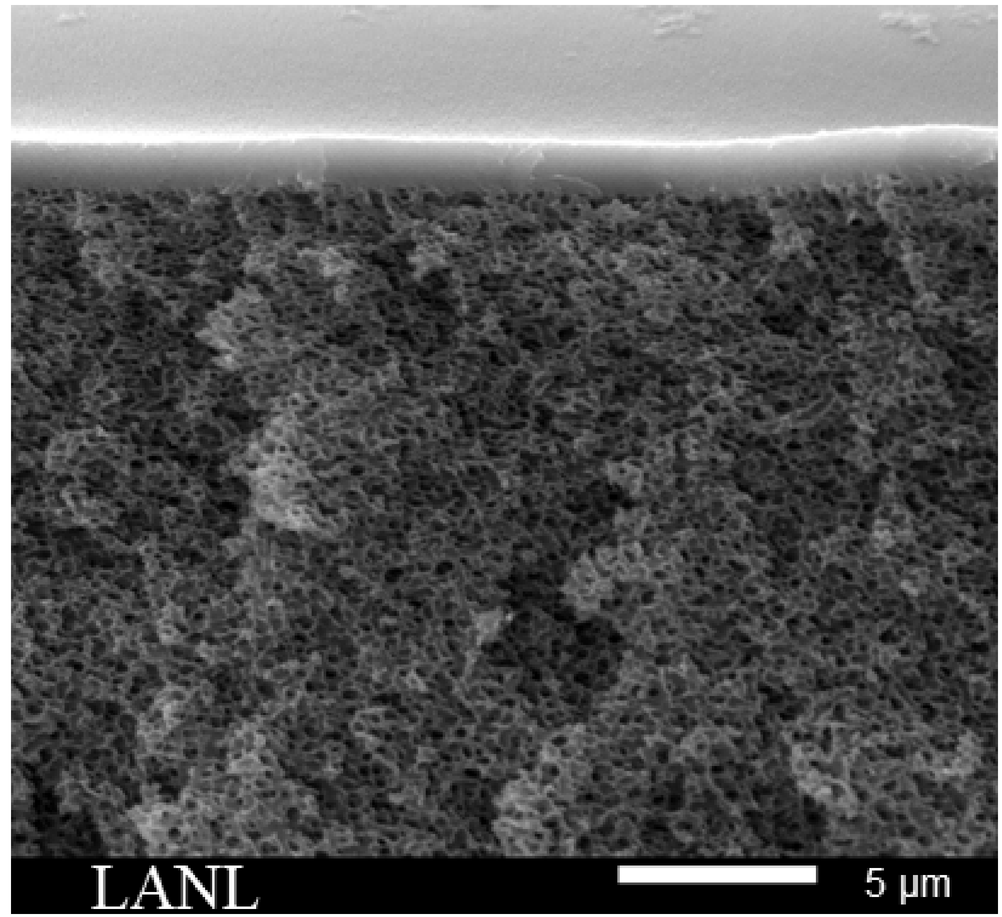
- **PBI-based material, morphology & high area density membrane development**
  - Hollow Fiber Fabrication
  - Module Fabrication
  - Demonstration and Validation of Developed Materials and Methods
- **Membrane defect mitigation materials and methods development**
  - Sealing Layer Development & Implementation
  - Demonstration and Validation of Developed Materials and Methods

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

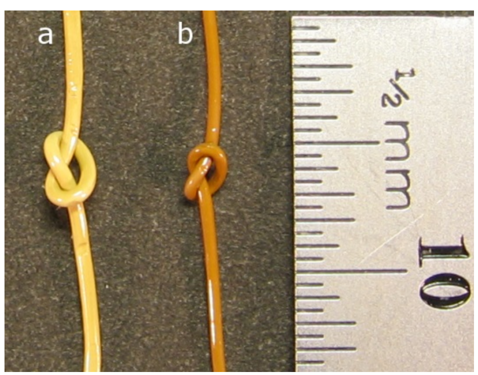
Working Towards Optimized (application Driven) HF Morphology

- 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

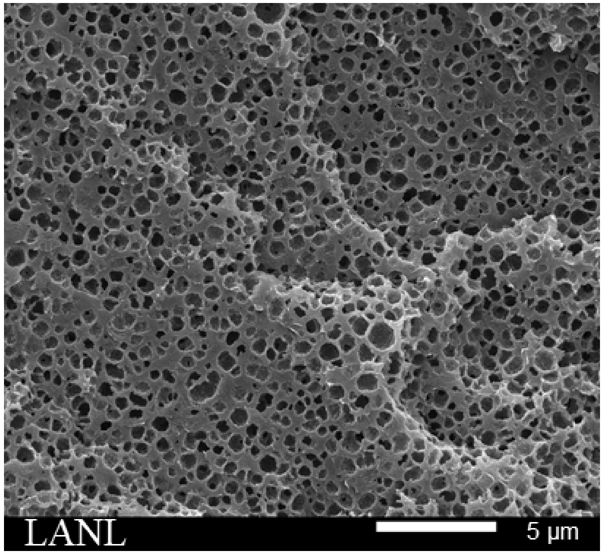


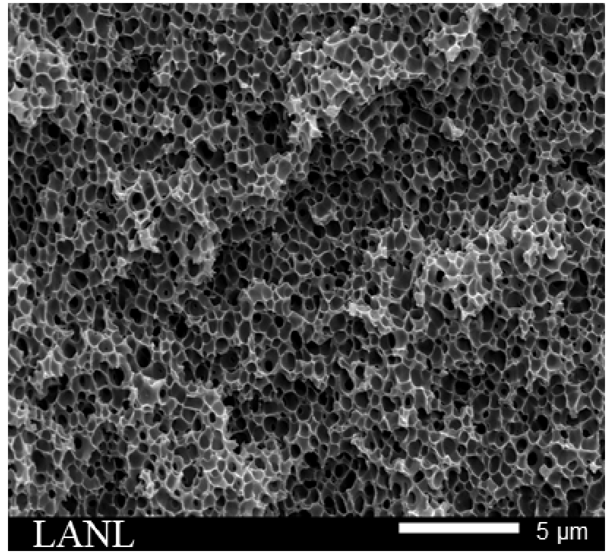


- Fiber morphology thermo-mechanical stabilty and ductility optimization
  - Maximize strength and toughness with minimized permselectivity impact
  - Minimize macrovoid formation in support structure

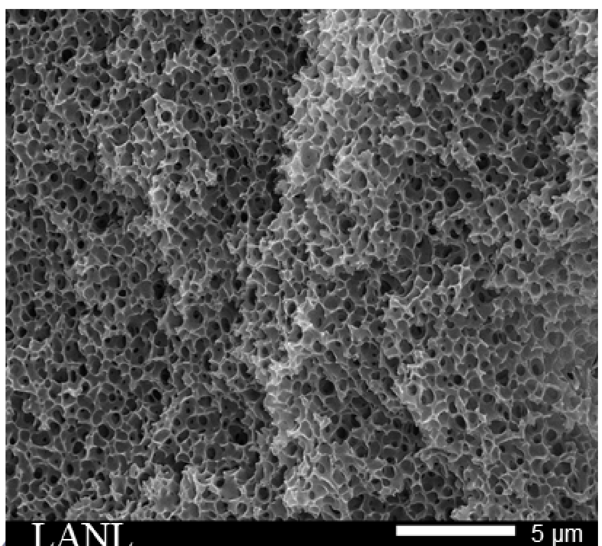


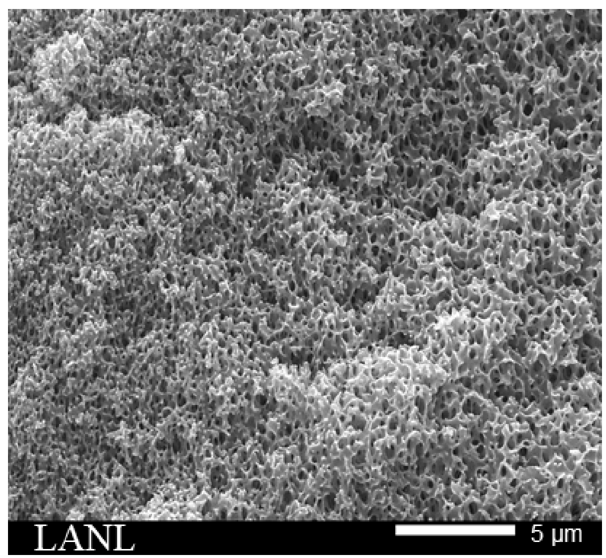
Tailoring of Phase Inversion Dynamics for Material Property Optimization

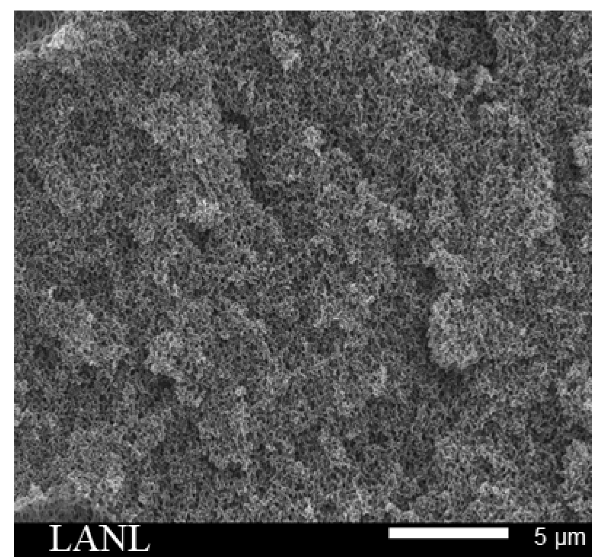




Phase inversion dynamics strongly influence pore structure and correspondingly mechanical & transport properties

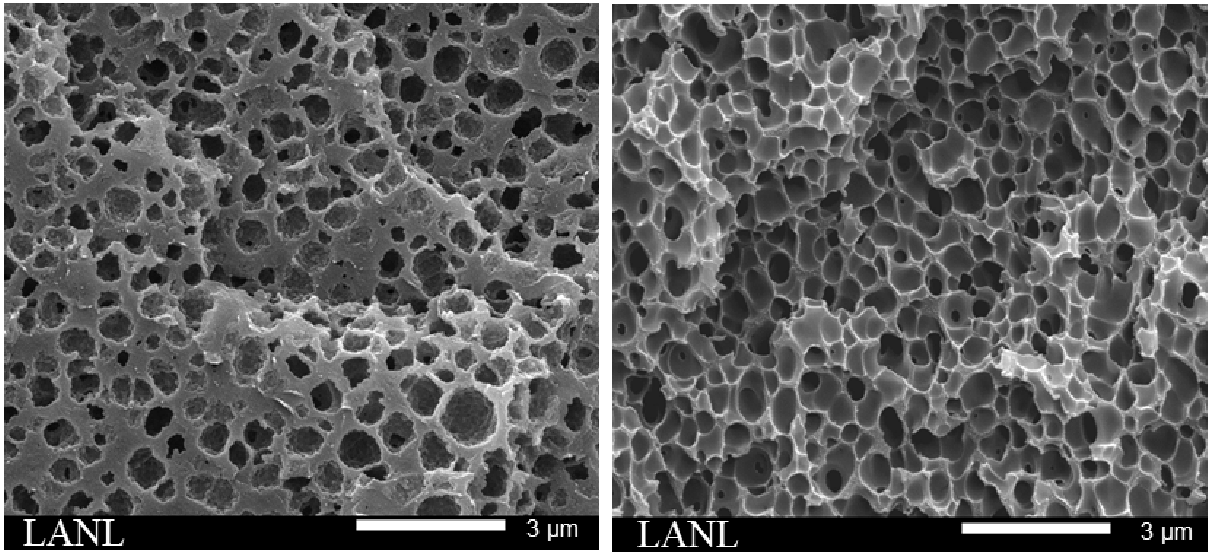




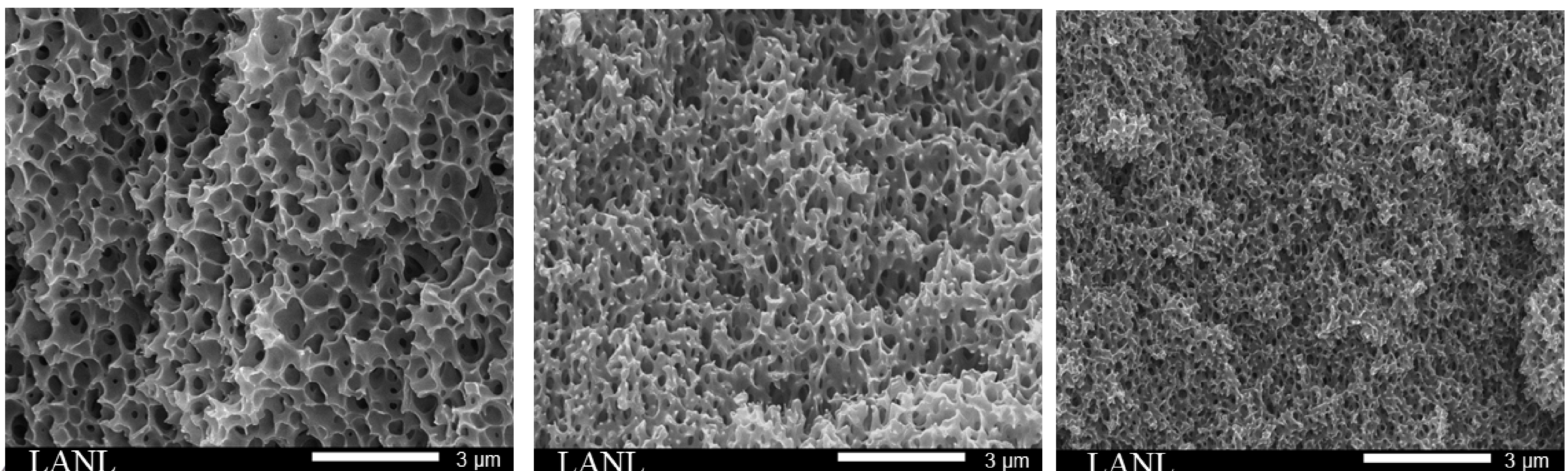


SEM micrographs of HF cores – all taken at the same magnification (12kX)

Tailoring of Phase Inversion Dynamics for Material Property Optimization

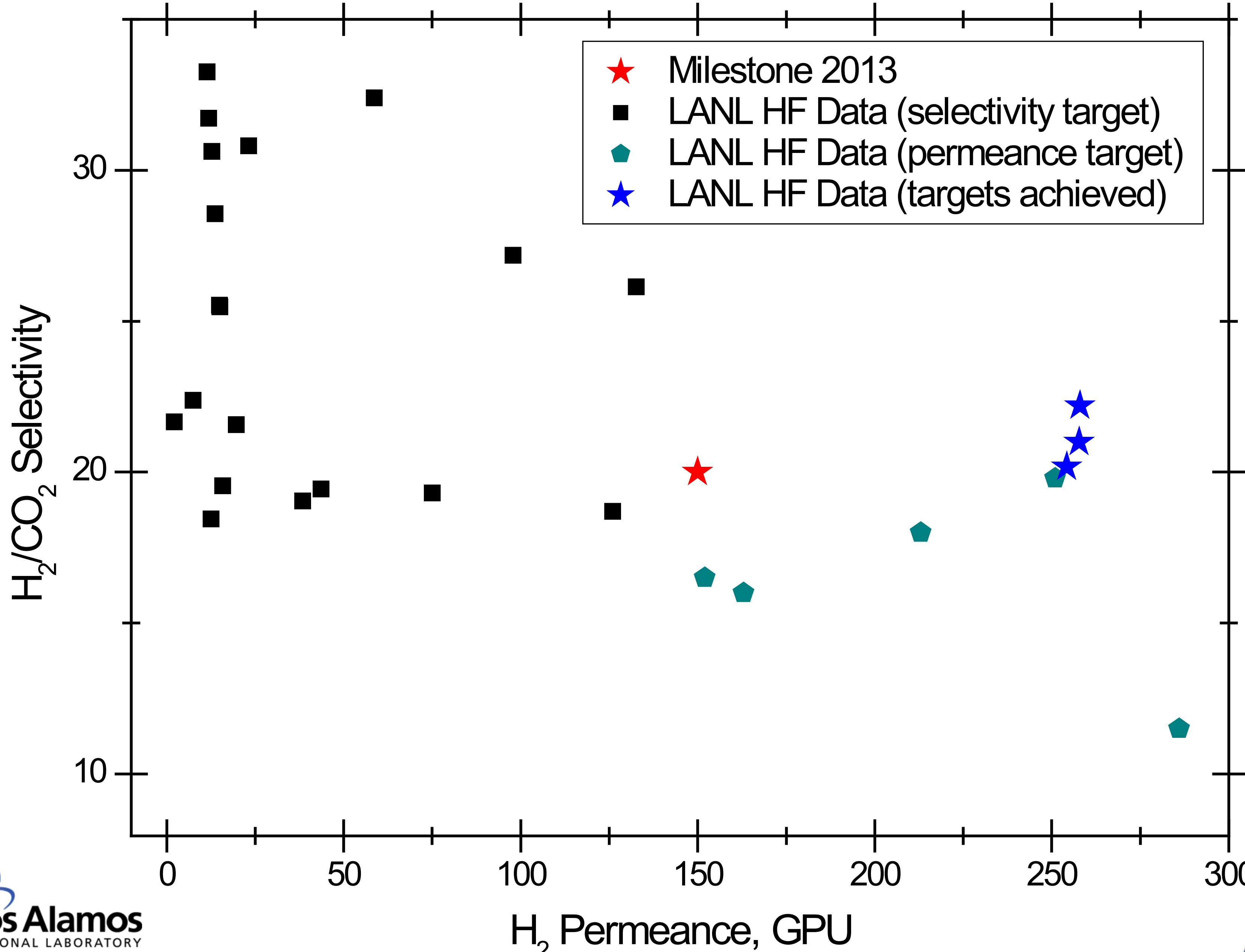


Phase inversion dynamics strongly influence pore structure and correspondingly mechanical & transport properties



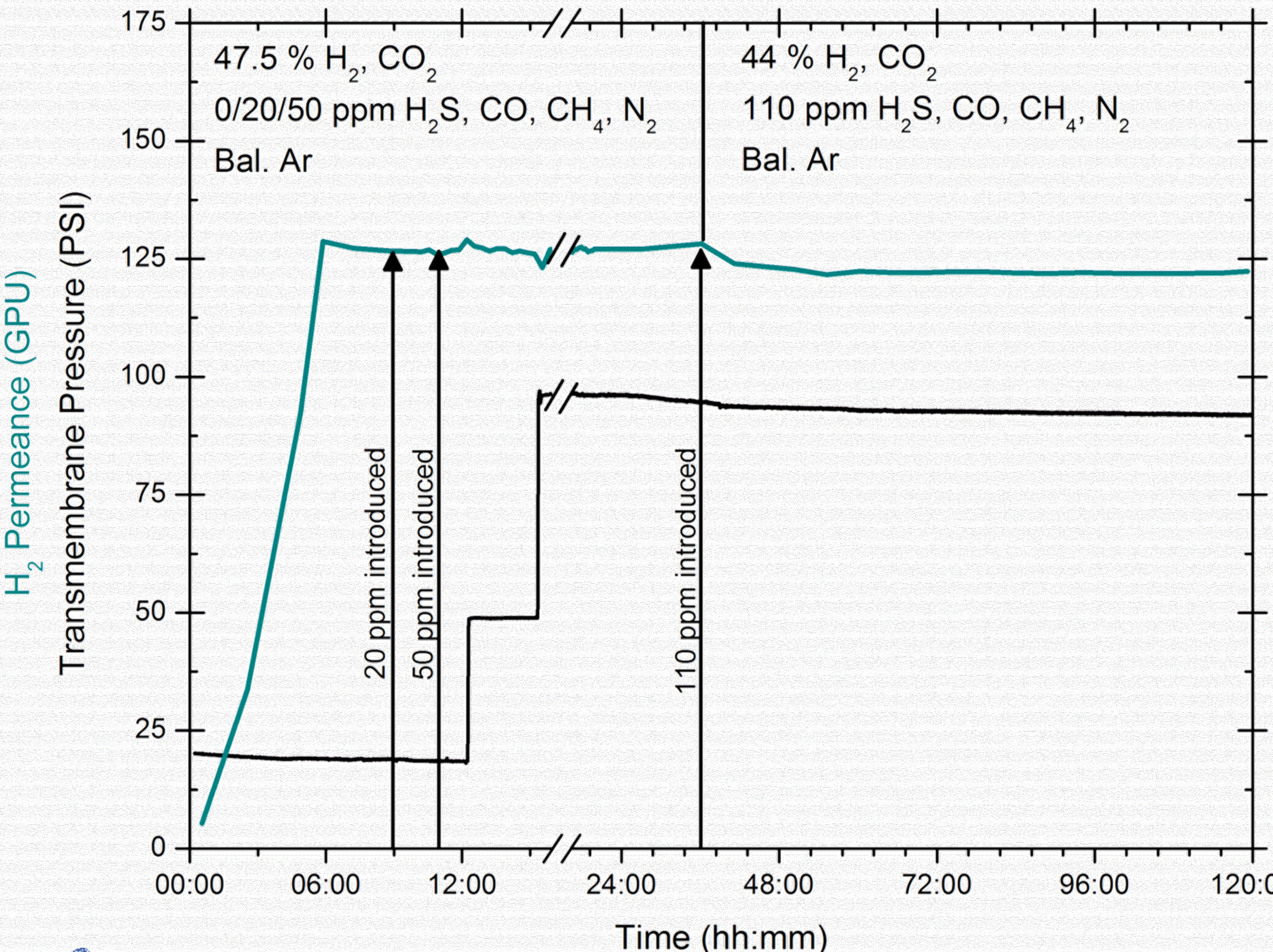
SEM micrographs of HF cores – all taken at the same magnification (25kX)

Achieving Permselectivity Targets: Status



Simulated Syngas Evaluations

Stable performance in the presence of H_2S observed

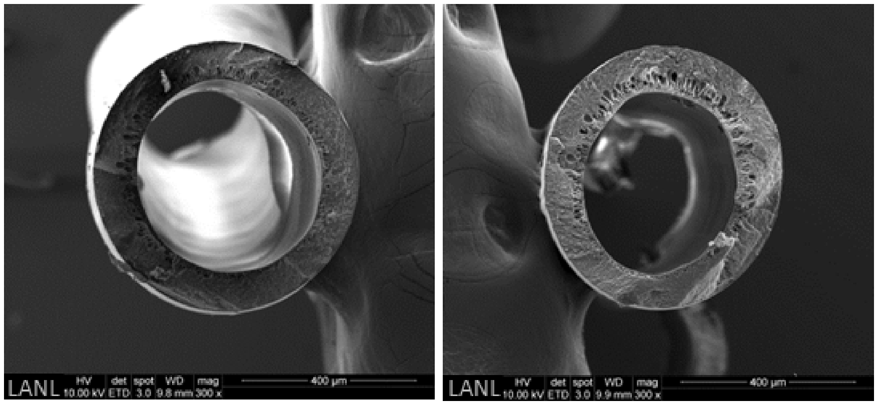


- PBI HF:
  $P(H_2) \rightarrow$ ~124-126 GPU
  $\alpha\ (H_2/CO_2) \rightarrow 19$
- T > 250 °C
- Argon sweep
- TMP 20-100 psid
- Dry conditions with primary syngas components present
- Fibers with varied fabrication protocols evaluated
  - Protocol influences on H_2S tolerance observed and under further investigation
  - H_2S permeance observed in membranes with non-ideal selectivity

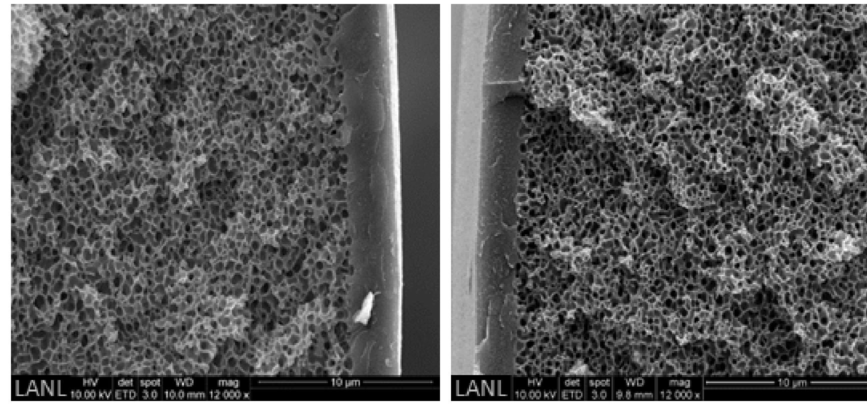
Structural Stability Assessments

SEM Before and After Permeation Testing

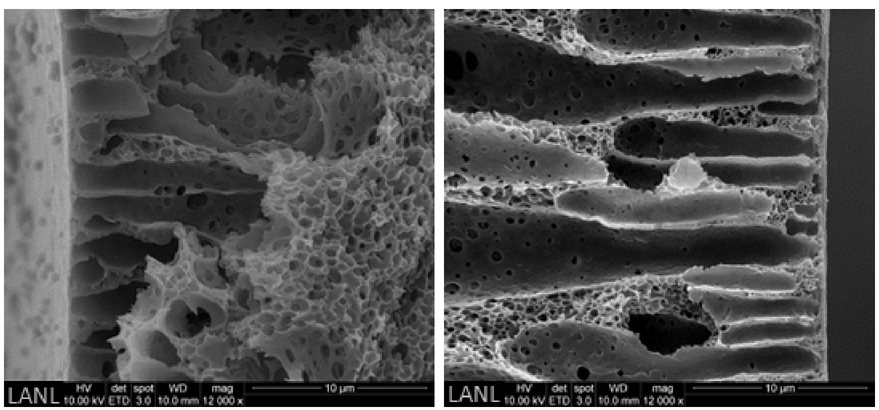
Before **After** **Before** **After**



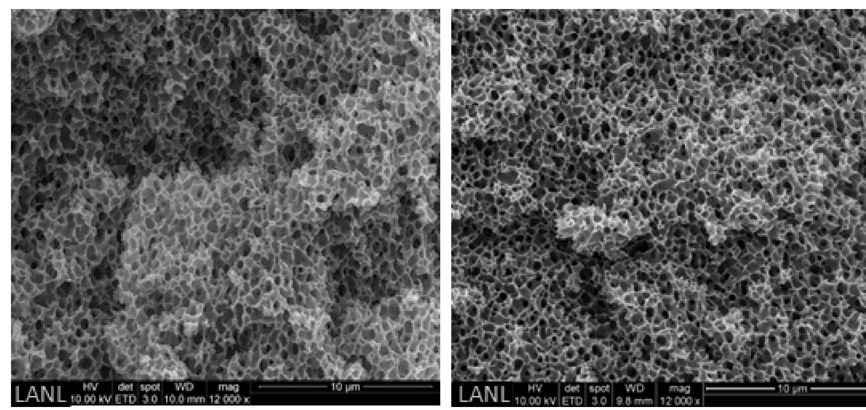
Complete cross-section



Outer edge (SL) cross section



Inner edge (bore) cross section



Central support cross section

- ~ 2 weeks of evaluation at temperatures > 250°C
- Overarching structure and structural integrity retained

Los Alamos NATIONAL LABORATORY EST. 1943

Simulated Syngas Testing

Syngas evaluation capability – dry feed only

- Utilized for evaluation of optimized HF/flat sheet formulations meeting single gas test and mechanical property criteria
- 4 process gases singularly or in combination at up to 100 psig and 100 SCCM each.

Simulated syngas evaluation capability

- Utilized for module configurations of any type. Employed for modules comprised of materials down-selected from dry syngas evaluations.
- Supports modules up to 10"x 20" x 30"
- Supports dry or steam saturated operation in both flow-thru and 2 stage pressure rise configurations.
- Switching between operational modes enabled "on the fly" without disruption to the module, flows, or temperatures.
- 6 Process gases singularly or in combination at up to 400 psig and 500 SCCM each.
- Steam generation as low as 1 µL/min and as high as 100% composition at 400 psig and above 230 °C, continuously, using dual pumping stations.
- Systems (all) typically operated between 150-400 °C (broader conditions are accessible).
- Gas flows (all systems) and steam generation are interlocked with gas monitoring systems and exhaust flow in the event of a loss of ventilation or power failure.
- System and data acquisition automated & controlled using NI LabVIEW (all systems).

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

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

Gen1 Seal: Transport Resistance & Thermal Stability Characteristics

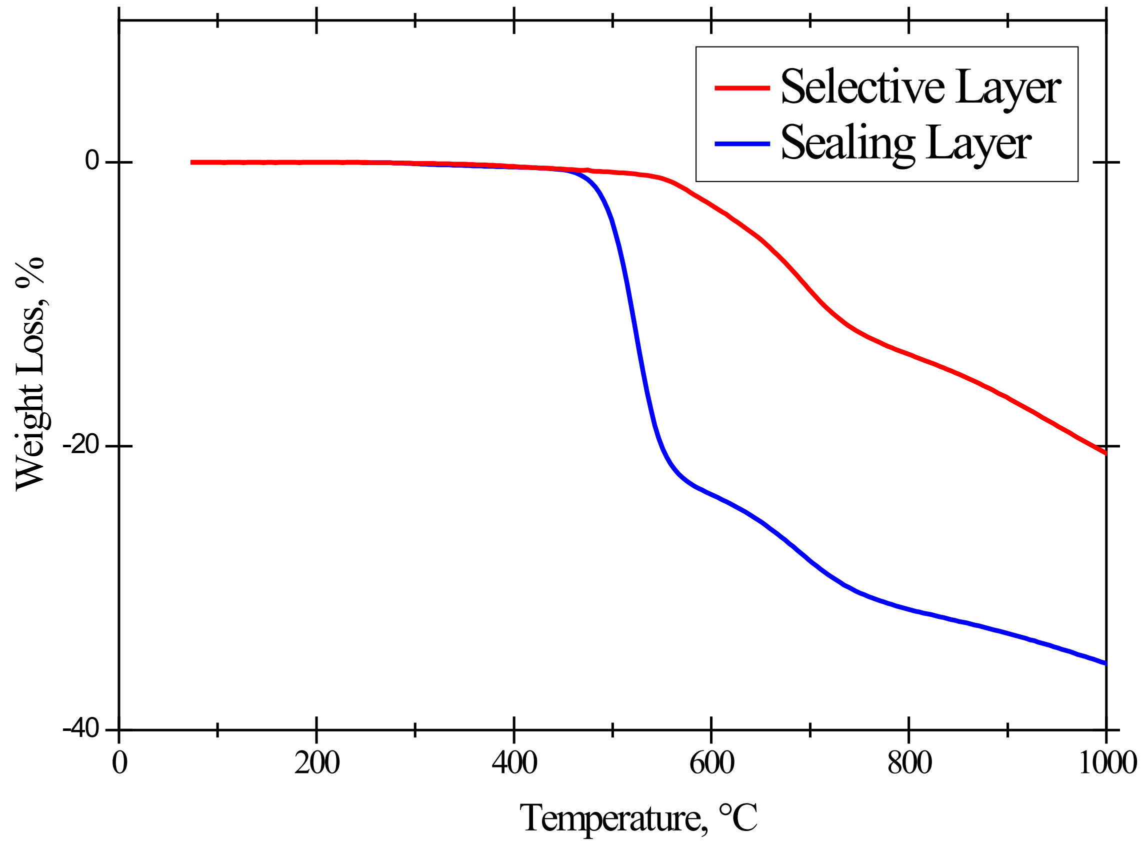
Material	Temperature [°C]	H_2 Permeability [barrer]	H_2/CO_2 Selectivity
HT Seal - 1	250	1008	5.2
PBI SL	250	78	23-43*

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

* Thermal conditioning dependent effect on CO_2 permeance

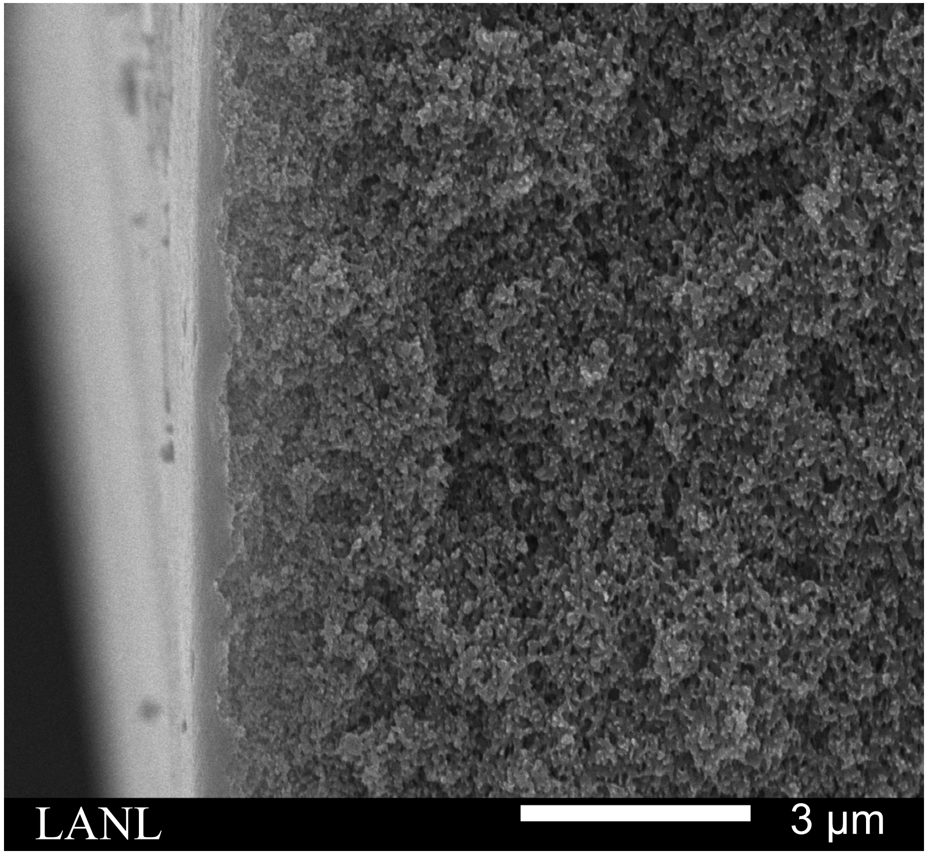
HT Seal-1 / PBI Comparison

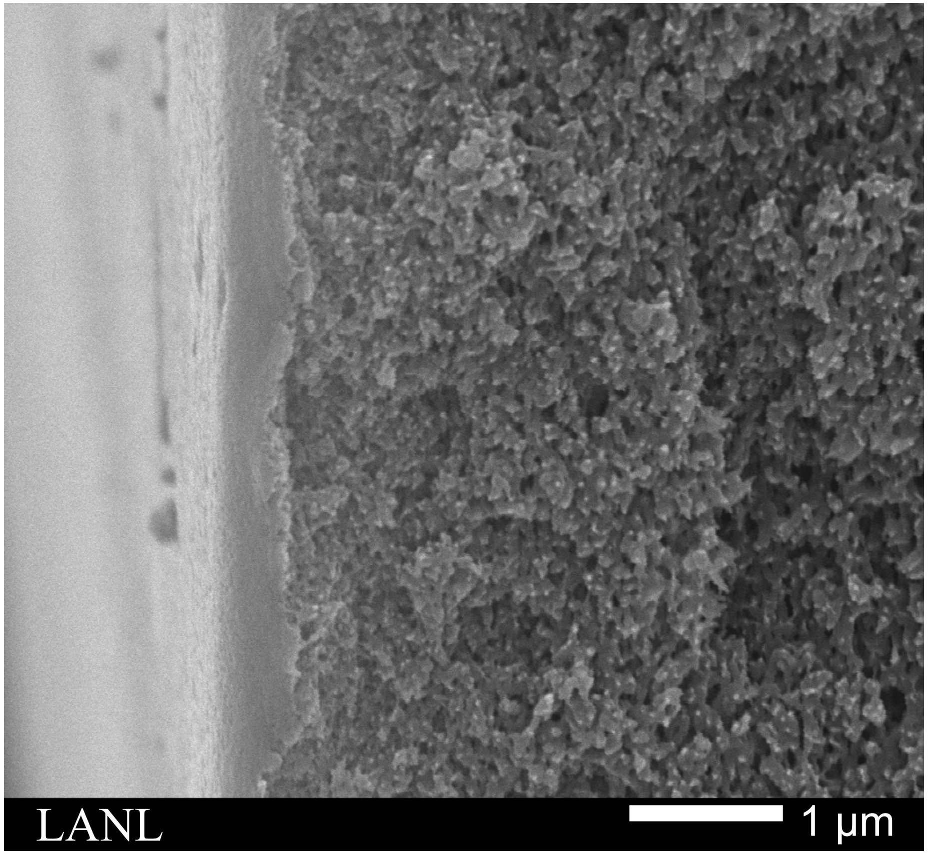
- Large H_2 permeability low selectivity compared to the PBI selective layer material
  - Minimized – but not zero! – transport resistance
- Gen 1 seal thermally stable to ≥ 300 °C
- Initial chemical stability experiments indicate tolerance to anticipated syn gas environment



PBI Hollow Fiber Membranes with Integrated Seal Layer

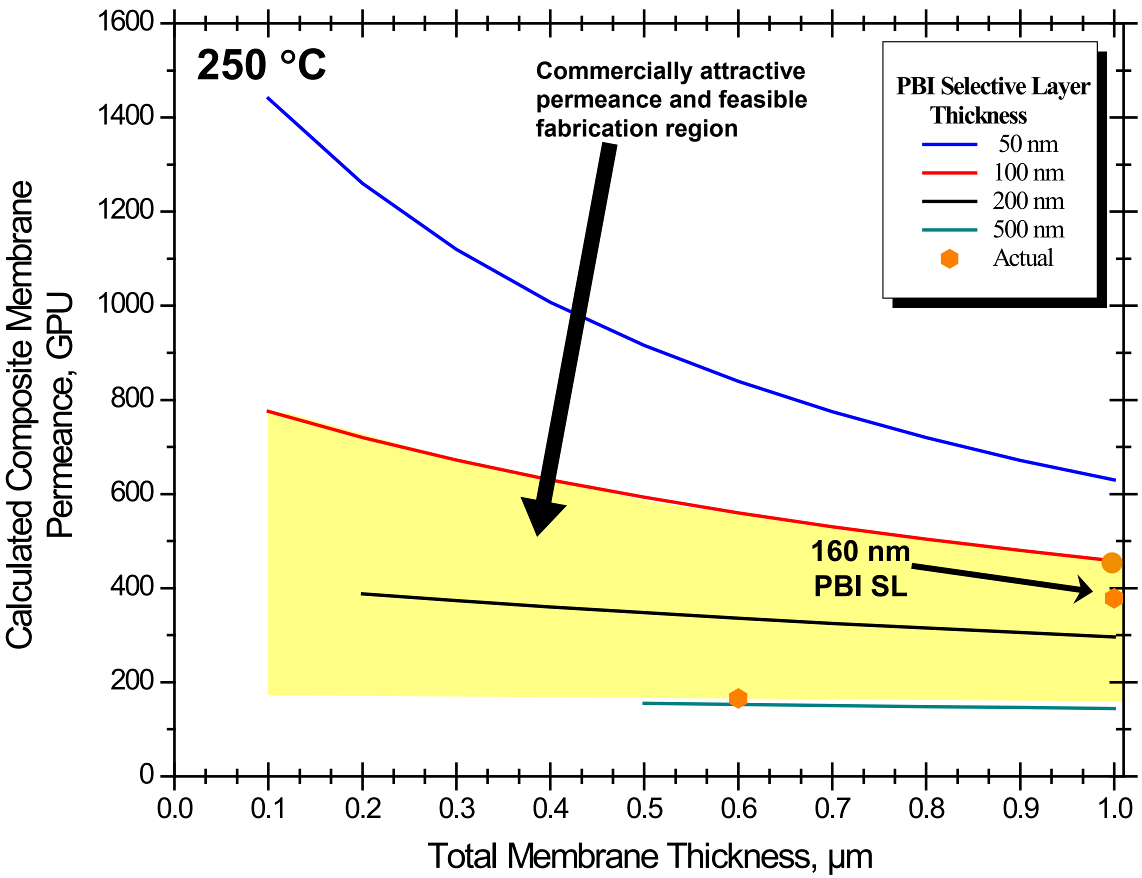
- Integral seal/selective layer interface achieved
- Underlying support unaffected by current seal layer introduction processes





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



Gas transport is controlled by the PBI selective layer

Permselectivity validation achieved on 1 µm composite films 900 nm Seal/100 nm PBI, 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**

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*

BY1 Project Milestones & Decision Point

Milestone/Deliverable Description	Status
Demonstrate feasibility of incorporating sealing layer into hollow fibers	Complete
Initiate mixed gas hollow fiber testing under realistic syngas conditions	Complete
Demonstrate single 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	**In-Progress** **250 GPU and $\alpha(H_2/CO_2)$ 20 achieved** **Evaluations on-going - adapted from the NETL Test Protocol (DOE/NETL-2008/1335)**

Wrap-Up

- **Optimization of a robust, high permeance, hollow fiber based platform on-going**
  - Fundamental understanding of multicomponent phase inversion system developed
  - Translation of those learnings into fiber fabrication protocols established
  - Control of selective layer thickness demonstrated using processing and phase inversion manipulations
- **Developed module fabrication materials and methods enabling HFM evaluation to 400 °C**
  - Fiber and module integrity and performance to 400 °C demonstrated
  - HF performance of >250 GPU H_2 with H_2/CO_2 selectivity > 20 demonstrated
- **Demonstrated success in developing methods for defect sealing**
  - HTSeal1 performance indicates exceptional opportunities for defect mitigation with minimal transport resistance in membrane prototypes
  - Integration of seal layer into HF platform demonstrated
- **Initiated HF module evaluations in simulated syngas environments**
  - Fibers with varied fabrication protocols evaluated – dry gas
  - Protocol influences on apparent H_2S tolerance observed and under further investigation

Path Forward

- **Hollow Fiber Fabrication**
  - Fabrication optimization to achieve high permeance membranes in defect minimized platforms with in-process stability/durability
- **Module Fabrication**
  - Further develop and demonstrate materials and methods for pilot-scale multi-fiber module fabrication
- **Sealing Layer Development & Demonstration**
  - 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 (coupon/small scale module testing in coal derived syngas)
- **Demonstration and Validation of Developed Materials and Methods**
  - Realization of a PBI hollow fiber membrane manufacturing capability for transfer to our industrial partners for scale-up/commercialization
  - Realization of a prototype PBI-based hollow fiber membrane module for 2 lb H_2/day demonstration in 2015 in "real" coal derived IGCC syngas

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

Ph.: 505.663.5565
Fax: 505.663.5550
berchtold@lanl.gov

Los Alamos NATIONAL LABORATORY EST. 1943

Kathryn A. Berchtold, PhD
Project Leader, Carbon Capture &
Separations for Energy Applications (CaSEA)

Materials Physics and Applications Division
Materials Synthesis & Integrated Devices, MS T004
P.O. Box 1663, Los Alamos, NM USA 87545

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

Disclaimer