

# PROJECT facts

U.S. DEPARTMENT OF ENERGY  
OFFICE OF FOSSIL ENERGY  
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

4/2008



## THERMALLY OPTIMIZED MEMBRANES FOR SEPARATION AND CAPTURE OF CARBON DIOXIDE

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### Background

An important component of the DOE Carbon Sequestration Program is to develop carbon capture technologies for power systems. Capturing carbon dioxide (CO<sub>2</sub>) from mixed-gas streams is a first and critical step in carbon sequestration. To be technically and economically viable, a successful separation method must be applicable to industrially relevant gas streams at realistic temperatures and volumes. The effectiveness of current technologies for separating CO<sub>2</sub> is limited. Amine-based technologies work only at low temperatures and pressure-swing absorption and cryogenic distillation have significant energy penalties (up to 35 percent) for separating CO<sub>2</sub>. Polymer-based membrane separations are less energy intensive, requiring no phase change in the process, have been used successfully in a number of industrial applications, and typically provide low-maintenance operations. Successful synthesis gas separation using a polymer membrane requires a membrane that is thermally, chemically, and mechanically stable at high temperature and high pressure. Commercially available polymeric materials currently employed are not stable in such demanding environments. In general, as the glass transition temperature of the polymer is approached, membrane selectivity is significantly reduced and flux decline due to membrane compaction (creep) becomes more significant. In addition, current membrane materials are often subject to chemical degradation by the process stream, a problem that is exacerbated by elevated temperature.

### Primary Project Goal

The overall goal of this project is to develop thermally, chemically, and mechanically stable polymeric-metallic composite membranes that can provide



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effective precombustion CO<sub>2</sub> capture under a broad range of conditions relevant to the power industry while meeting the Carbon Sequestration Program goals of 90 percent CO<sub>2</sub> capture at less than a 10 percent increase in the cost of energy services.

## Objectives

The primary objective of this project was the development of innovative polymeric-metallic composite membrane structures (Figure 1) that achieve the critical combination of high selectivity, high permeability, chemical stability, and mechanical stability all at elevated temperatures (>150 °C). The research team pursued two major pathways to its primary goal. The first involved extending the current PBI-based polymeric-metallic composite membrane to its limits. The second pathway built upon the base PBI framework to develop materials with enhanced gas separation properties (primarily H<sub>2</sub>/CO<sub>2</sub> selectivity and H<sub>2</sub> flux) while maintaining the desirable chemical, mechanical, and thermal stability exhibited by the unmodified PBI and improving polymer solvent solubility.

## Benefits

The base performance of the polymeric-metallic composite membrane structure has been determined from room temperature to 400 °C. The polymer maintains a commercially attractive selectivity between hydrogen (H<sub>2</sub>) and CO<sub>2</sub> even at 400 °C (Figure 2). The PBI-based composite membrane outperforms any polymer-based membrane available commercially or reported in the literature for separations involving hydrogen. This achievement is validated via membrane productivity (separation factor and flux) comparisons. Additionally, the improved performance of this technology in an application such as integrated gasification combined cycle-integrated capture is further substantiated by the accessible operating temperature range and the chemical stability of the composite membrane in challenging operating environments.

## Accomplishments

- Fabrication and testing of the first polybenzimidazole (PBI)-based composite polymeric-metallic membrane structure (in flat disk and tubular formats) that is selective from room temperature to >400 °C than current commercially available polymeric membranes (<150 °C). This achievement represents the highest demonstrated operating temperature at which a polymer-based membrane has successfully functioned.
- Improvements to the intermediate layer on the outside diameter of Pall's AccuSep® tubes resulting in a smooth, high porosity, defect-free surface.
- Successful long-term testing of the polymeric-metallic composite membrane in dry gas environments containing H<sub>2</sub>, CO<sub>2</sub>, methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), carbon monoxide (CO), and hydrogen sulfide (H<sub>2</sub>S) from 25 - 400 °C. Demonstration of the membrane's thermal stability via 300+ days in operation at 250 °C.
- Successful out-of-the-laboratory slip-stream testing of the polymeric-metallic composite membrane on a natural gas fuel processor. The test stream consisted of the fully hydrated natural gas reformat exiting the water gas shift reactor. Testing was conducted from 250 - 400 °C.
- Development and demonstration of an innovative methodology that enables the simultaneous measurements of gas permeation and membrane creep at elevated temperatures. This technique provides a unique approach to the optimization of long-term membrane performance under challenging operating conditions and has been utilized to obtain the first-ever transport-mechanical property dataset for PBI at elevated temperatures.
- Synthesis of a number of new PBI-based compounds by post-polymerization modification.
- Demonstration of commercialization potential.

## PERFORMANCE PERIOD

05/15/2000 to 09/30/2006

## COST

### Total Project Value

\$5,118,000

### DOE/Non-DOE Share

\$3,998,000 / \$1,120,000

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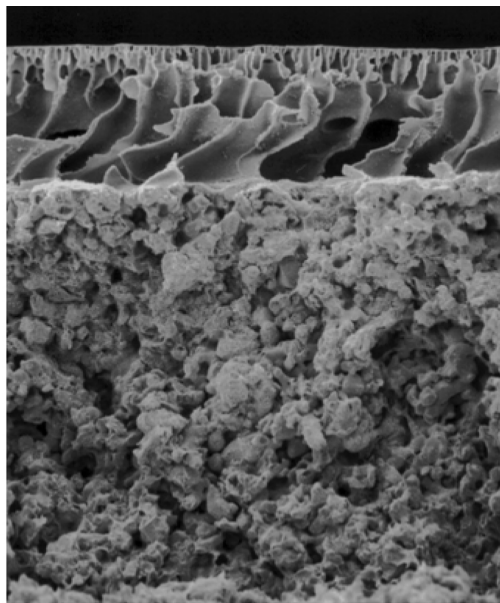


Figure 1. Scanning electron microscopy image of a poly-benzimidazole (PBI)-based polymeric-metallic composite membrane cross-section. The polymeric selective layer is the thin skin at the surface of the composite structure.

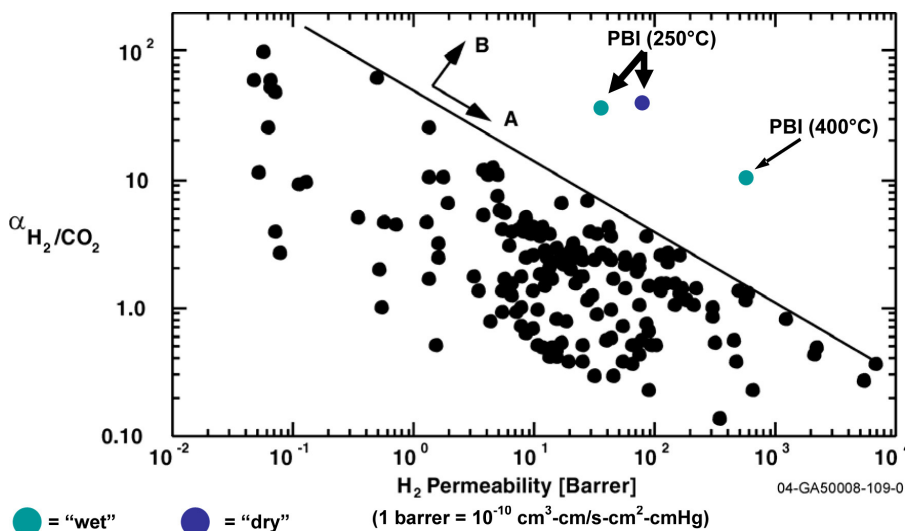


Figure 2. Trade-off plot between  $H_2$  permeability and  $H_2/CO_2$  selectivity in polymers. The data points for PBI reflect measurements made at high temperature. Note the excellent combination of permeability and selectivity.