Sorption-Enhanced Mixed Matrix Membranes for Hydrogen Purification and Carbon Dioxide Capture

primary project goal

This work focused on combining crosslinked polymers having molecular size-sieving ability, and palladium (Pd)-based nanomaterials with very high hydrogen (H_2)/carbon dioxide (CO_2) solubility selectivity, to achieve membranes with superior gas-separation performance relative to stand-alone polymeric membranes. The primary goal was to advance the new generation of membrane materials that combine robust performance with good processability to significantly decrease the cost of CO_2 capture, utilization, and storage (CCUS), enabling environmentally responsible energy production from abundant domestic coal.

technical goals

- Identify mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 at 150 to 200°C with simulated syngas.
- Prepare thin-film mixed matrix composite membranes with H_2 permeance of 500 gas permeation units (GPU) and H_2/CO_2 selectivity of 30 at 150 to 200°C and perform parametric testing of these membranes using simulated syngas in the laboratory.
- Conduct a 20-day field test of membrane stamps with real syngas from a gasifier, providing duration testing as well as assessing effects of exposure to syngas contaminants.

technical content

The State University of New York (SUNY) developed membrane technology as an energy-efficient and low-cost approach for pre-combustion CO_2 capture and H_2 purification in integrated gasification combined cycle processes. The key advancement of this technology was a series of novel sorption-enhanced mixed matrix membranes (MMMs) with high H_2 permeance (500 GPU) and high H_2/CO_2 selectivity (30) at temperatures up to 200°C. The approach combined highly crosslinked polymers with strong molecular size-sieving ability and Pd-based nanomaterials with high H_2/CO_2 selectivity to achieve membranes with performance superior to stand-alone polymeric membranes.

The working hypothesis explored in this technology development was that Pd nanoparticles exhibit extraordinary H_2 sorption, and therefore would confer favorable H_2/CO_2 solubility selectivity to thin-film composite (TFC) membranes into which they are incorporated (allowing H_2 to "hop" along the particle array). Such membranes, consisting of metallic Pd particles dispersed in a polymer matrix, are termed MMMs. Figure 1 depicts this approach, in which an MMM should improve both permeance and selectivity for H_2 separation above those typical of base polymer membranes.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-combustion Power Generation PSC

key technology:
Membranes

project focus:
Mixed Matrix Membranes with Coal Syngas

participant:
State University of New York (SUNY)–Buffalo

project number:
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predecessor projects:
N/A

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partners:
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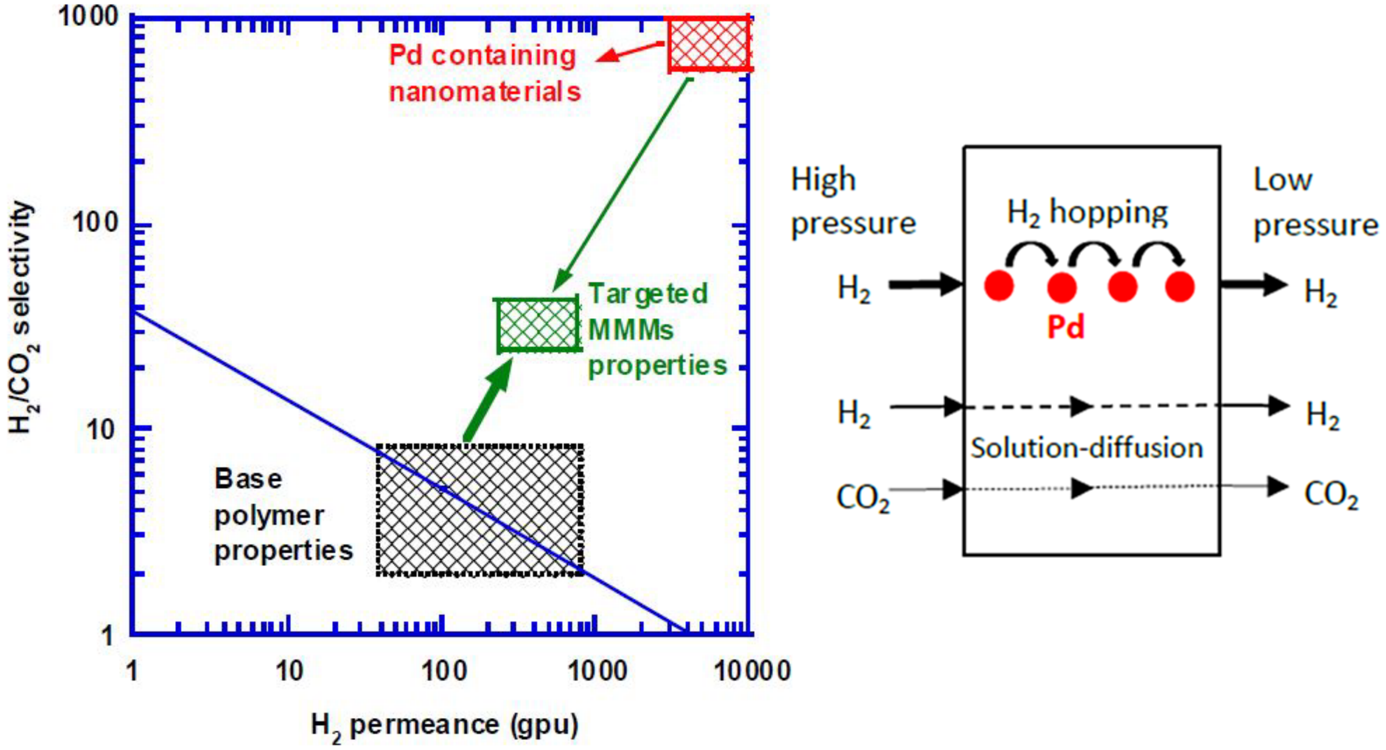

Figure 1: Mixed matrix materials approach.

One of the most suitable choices of polymeric material for membranes intended for H_2 separation from hot syngas is poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (m-PBI), a rigid polymer with strong size-sieving ability, and which has been widely investigated for elevated temperature H_2/CO_2 separation. One of the strategies to enhance the size-sieving ability in m-PBI is to crosslink the polymer chains to increase chain rigidity and/or decrease free volume, and in this work, the m-PBI was crosslinked using terephthaloyl chloride. SUNY also discovered that by doping with phosphoric acid (H_3PO_4), the PBI is favorably modified toward greater H_2/CO_2 selectivity while decreasing H_2 permeability. The H_3PO_4 tightens the polymer structure and increases size-sieving ability while exhibiting stability up to 200°C. The improvement in PBI polymer properties thus demonstrated is depicted in Figure 2.

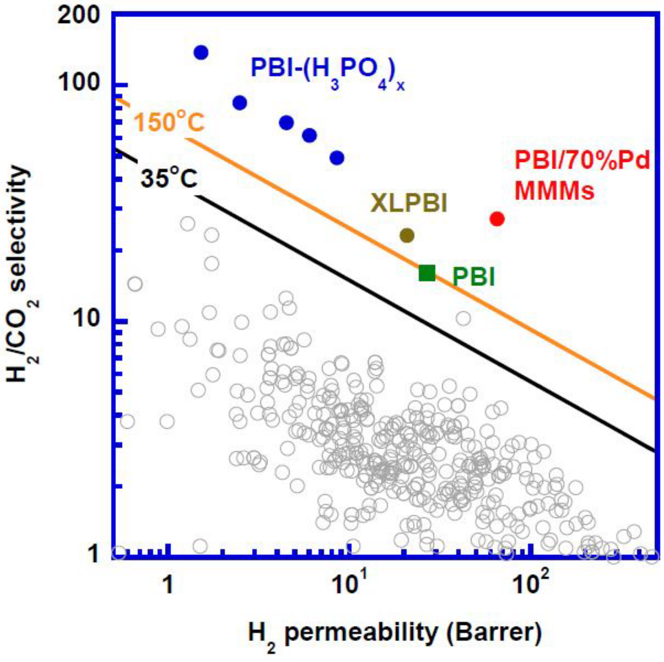

Figure 2: Polymer development and scale-up.

An important aspect of development of this technology was synthesis of the Pd nanoparticles for incorporation in the MMMs. Both solution-phase (colloidal) synthesis and gas-phase (aerosol) synthesis using a high-temperature reducing jet (HTRJ) reactor developed by SUNY were investigated. This reactor is depicted in Figure 3. The solution-phase synthesis directly provides nanoparticles that are dispersible in common organic solvents, including those from which the polymer membranes are cast. However, the HTRJ process can more readily produce alloy nanoparticles and is likely to be a more scalable and cost-effective process at larger scale. Pd-copper (Cu) (60/40) alloy nanoparticles with typical size of 4 to 8 nm were successfully prepared using the HTRJ reactor; when tested, these evidenced extremely high H_2/CO_2 solubility selectivity (≈840), and H_2 chemisorption independent of gas pressure.

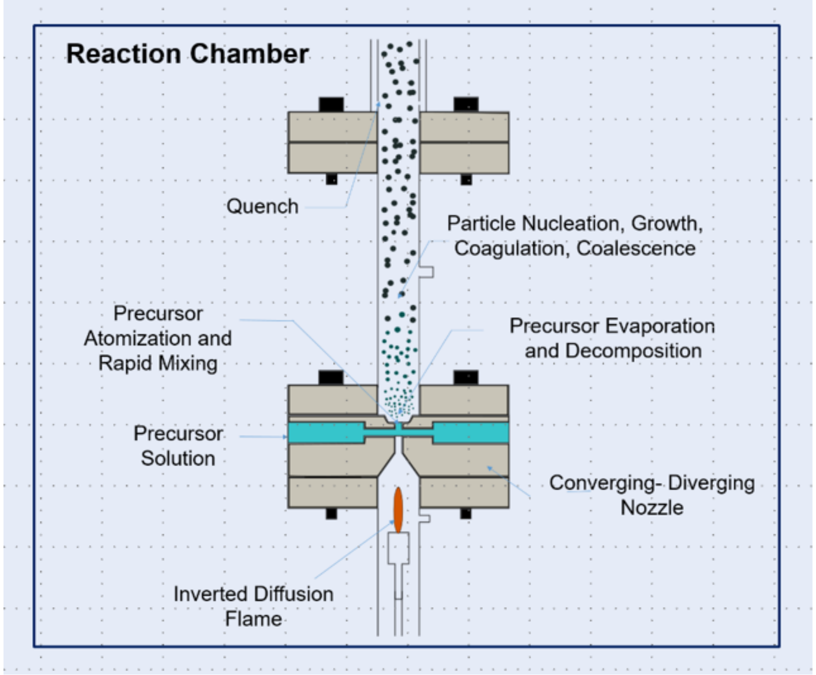

Figure 3: HTRJ reactor.

Particles prepared in the gas phase were collected as dry powders. For incorporation into polymer membranes, these nanoparticles must be stably dispersed in solvents that are also capable of dissolving the polymers of interest. The Pd alloy nanoparticles were suspended in toluene solvent and mixed with 5.0 wt% PBI in dimethylacetamide (DMAc) solvent. The combined dual solvent system incorporating both the dissolved PBI and nanoparticles was sonicated, then placed on a plate or support and allowed to dry at elevated temperature and under vacuum. The mixed matrix PBI/Pd layer was created directly on a support structure of polydimethylsiloxane (PDMS) silicone on pure PBI support, all of which is underlain by stainless steel mesh. In Figure 4, a very thin mixed matrix layer only 900 nm thick with embedded nanoparticles is visible on the silicone gutter layer, with porous PBI support underneath. In this image, the mixed matrix layer is 58 wt% or 13 vol% of Pd nanoparticles (designated PBI-Pd-58/13). Syntheses have increased Pd nanoparticle content up to 70 wt%; the point depicted in red in Figure 2 shows performance properties of the 70 wt% Pd/PBI MMM.

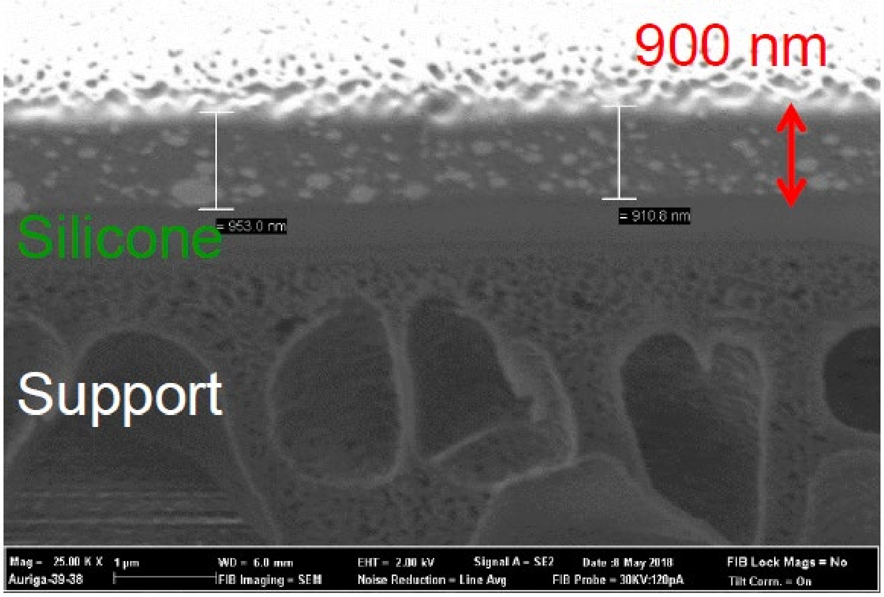

Figure 4: Cross-sectional scanning electron microscopy (SEM) of membranes.

Figure 5 shows the final laboratory-scale testing results for MMM permeability and selectivity for H_2/CO_2 separation. Behavior of optimized membranes at temperatures ranging from 150 to 225°C is shown for three loadings of nanoparticles

(22%, 46%, and 58% nanoparticles by weight). Note that the target performance region was attained with the PBI-PD-58/13 MMM.

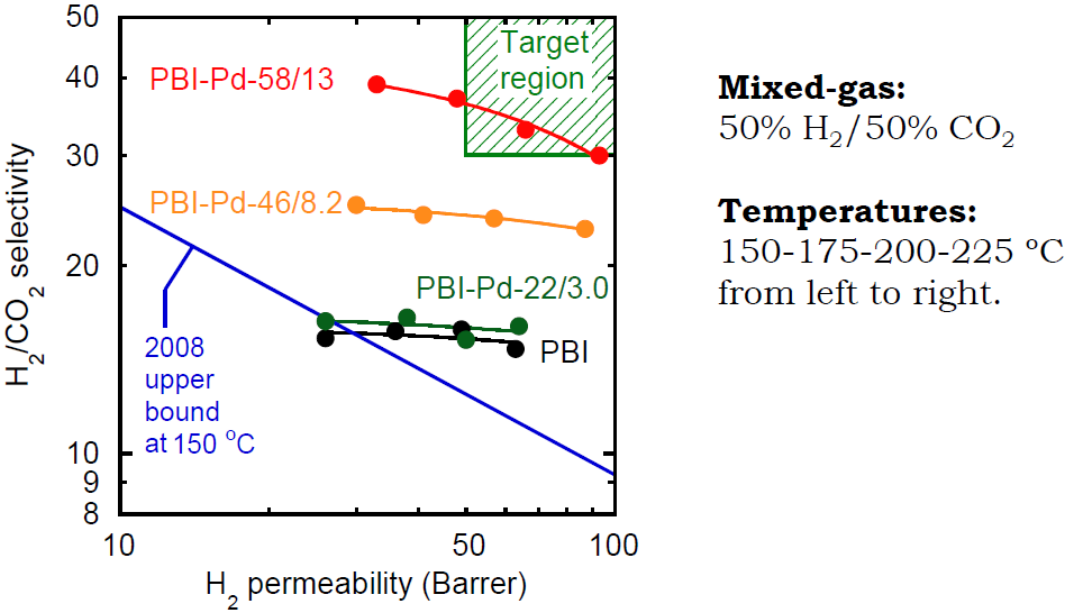

Figure 5: Effect of increasing Pd nanoparticle content on H_2/CO_2 separation in MMMs.

Also, stability of the MMMs in the presence of hydrogen sulfide (H_2S) and water (H_2O) was experimentally evaluated by measuring any changes of membrane permeability and selectivity with and without these species added to the simulated syngas mixtures. Satisfactory stability was observed in long-term laboratory-scale testing.

An important performance target of H_2 permeance of 500 GPU or greater at 150 to 200°C (with selectivity at least 30) had been set for this technology. Figure 6 shows the laboratory-scale permeances attained in this project (red) for a 70-nm thin-film MMM and various other competing H_2 separation membranes' permeance performance for comparison. Note that a thin-film MMM at 230°C would have more than adequate selectivity; however, with permeance of 400 GPU, it does not attain the target field.

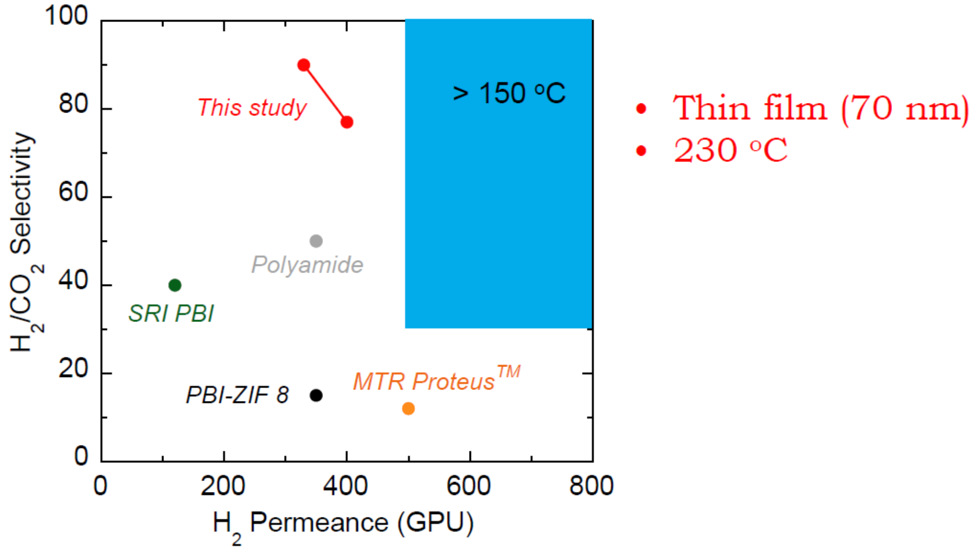

Figure 6: Hydrogen permeance target performance.

SUNY and Membrane Technology and Research Inc. (MTR) investigated behavior of the MMMs in a real syngas environment by testing of field stamps. This testing was conducted at the University of Kentucky's Center for Applied Energy Research (CAER), using syngas from the opposed multi-burner entrained flow coal gasifier at CAER. Samples were of large enough area to allow enough permeate gas flow rate for gas chromatography analysis (e.g., one stamp was about 3 cm^2 in area). Testing syngas flow rate was about 40–50 standard liters per minute (slpm), with test duration ranging from 23–40 hours. Syngas composition and conditions were approximately as follows:

TABLE 1: SYNGAS COMPOSITION FOR FIELD TESTING

		Composition						
Pressure	Temperature	vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S + COS
65-115	104	17	20	0	40	20	2	149

Technical problems limited the field syngas temperature to 40°C (104°F)—a much lower value than intended.

Following exposure to syngas in the field, two samples were evaluated at the laboratory to measure any changes in permeability and selectivity for H_2/CO_2 separation. Gas separation performance of the samples before and after the field test is shown below. All the tests were conducted in mixed gas ($H_2:CO_2$ = 50:50) at 100 pounds per square inch gauge (psig). Significant decreases in gas selectivity were observed, stemming from decreases in H_2 permeance, increase in CO_2 permeance, or both.

TABLE 2: GAS SEPARATION PERFORMANCE OF THE SAMPLES BEFORE AND AFTER FIELD TESTING

Samples	Temp (°C)	H_2 Permeance (GPU)	CO_2 Permeance (GPU)	H_2/CO_2 Selectivity
#32 Before	150	146	3.4	42
#32 After	150	114 9	9.3	12
#23 Before	150	124	2.6	48
#23 After	60	7.5	1.3	5.8

TABLE 3: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polymers	
Materials of Fabrication for Support Layer	—	polysulfone, polyethersulphone, etc.	
Nominal Thickness of Selective Layer	µm	0.1–0.2	0.1
Membrane Geometry	—	Flat sheet or hollow fiber	Flat sheet
Maximum Trans-Membrane Pressure	bar	50	50
Hours Tested without Significant Degradation	—	1 month	3 weeks
Manufacturing Cost for Membrane Material	$\$/m^2$	10-50	20-50
Membrane Performance			
Temperature	°C	100-300	250
H_2 Pressure Normalized Flux	GPU	200	500
H_2/H_2O Selectivity	—	0.1-0.5	—
H_2/CO_2 Selectivity	—	20	30
H_2/H_2S Selectivity	—	10-20	20
Sulfur Tolerance	ppm	50	10
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	spiral-wound modules	
Packing Density	m^2/m^3	1,000-5,000	
Shell-Side Fluid	—	syngas	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
H_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10-6 cm3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10-6 kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Barrer – Gas permeability unit of membrane selective materials, 10^{-10} cm^3 (STP)/(cm^2 s cm Hg).

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Resistant to water, high-pressure CO_2. However, the effects of sulfur and carbon monoxide (CO) on gas separation properties are to be determined.

Syngas Pretreatment Requirements – Sulfur removal and temperature adjustment.

Membrane Replacement Requirements – Not determined.

Waste Streams Generated – None identified.

Process Design Concept – Not determined.

technology advantages

- Synergism created by incorporating Pd in a polymer membrane, taking advantage of the well-understood properties and performance of PBI in membrane gas separations with the extremely high H_2 selectivity and permeability of Pd.
- Cost savings over pure Pd membranes, using relatively little expensive Pd metal, but still taking advantage of its H_2 sorption properties and stability against sulfur compounds.
- Good processability derived from polymer-based materials for the fabrication of the industrial thin-film composite membranes.

R&D challenges

- Membrane stability at operating conditions (elevated pressure and temperature).
- Loss of gas separation performance of membranes after exposure to sulfur-containing syngas.
- Fabrication of thin-film composite membranes consistently to specification and without defects.
- Scaled-up production of high-purity Pd nanoparticles and improving process yield.
- Attaining target region of selectivity versus permeability in MMMs.
- Particulate matter needs to be controlled to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

The project was completed at the end of 2019. Mixed matrix materials with superior H_2/CO_2 separation properties, and polymers and nanomaterials with promising H_2/CO_2 separation properties, were identified and prepared. Laboratory-scale testing of MMM-based membranes was completed, from which adequate H_2/CO_2 selectivity, targeted gas permeability, and stability in the presence of simulated syngas was confirmed. Field testing of membrane samples in actual coal syngas was completed, with before and after gas separation performance quantified; H_2/CO_2 selectivity fell by at least a factor of 4, suggesting challenges remain with membrane durability in exposure to realistic syngas conditions.

available reports/technical papers/presentations

"Sorption Enhanced Mixed Matrix Membranes for Hydrogen (H_2) Purification and Carbon Dioxide (CO_2) Capture," Final Report, Haiqing Lin, Ph.D. and Associate Professor, The U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, April 23, 2020. *https://www.osti.gov/servlets/purl/1603097*

"Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture," presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Mixed-Matrix-Membranes.pdf*

"Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture," presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-SUNY-Sorption-Enhanced-Mixed-Matrix-Membranes.pdf*

"Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture," presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/2018-01/H-Lin-UB-Enhanced-Mixed-Matrix-Membranes.pdf*

"Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture," presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File Library/Events/2016/c02 cap review/3-Wednesday/H-Lin-UBuffalo-Sorption-Enhanced-Mixed-Matrix-Membranes.pdf*

"Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture," project kickoff meeting presentation, Pittsburgh, PA, October 5, 2015.

L. Zhu, M. Swihart and H. Lin, Unprecedented size-sieving ability in polybenzimidazole doped with polyprotic acids for membrane H_2/CO_2 separation, Energy & Environmental Science, 2018, DOI: 10.1039/c7ee02865b

L. Zhu, M. Swihart and H. Lin, Tightening nanostructure of PBI for membrane H_2/CO_2 separation, Journal of Materials Chemistry A, 5, 19914-19923, 2017, DOI: 10.1039/C7TA03874G

Lingxiang Zhu, Maryam Omidvar and Haiqing Lin. "Manipulating Polyimide Nanostructures via Crosslinking for Membrane Gas Separation," Chapter 6 in Membranes for Gas Separation, pp. 243-270, World Scientific, Aug 11, 2017.

H. Lin, "Molecularly Engineering Membrane Materials for Separations through Enhanced Interactions: A Road Less Traveled," Department of Chemical and Materials Engineering and Center of Membrane Science, University of Kentucky, Lexington, KY, March 1, 2017.

H. Lin et al., "CO2-selective membranes for hydrogen production and CO2 capture – Part I: Membrane development," Journal of Membrane Science, Volume 457, 149-161 (2014).