the ENERGY lab

PROJECT FACTS

Fuels

Integrated Water Gas Shift Membrane Reactors Utilizing Novel, Non-precious Metal Mixed Matrix Membranes

Background

The U.S. Department of Energy (DOE) promotes development of novel hydrogen (H_2) production technology for electricity generation and development of fuels to meet energy needs in an environmentally sustainable manner. Clean co-production of electricity, chemicals, and hydrogen (H_2) using gasification, integrated with carbon capture and storage, will help reduce environmental concerns associated with fossil fuel use.

Historically, separation membranes employed in H_2 production have contained precious metals. However, these metals are expensive and subject to poisoning (deactivation) by contaminants. DOE is partnering with the University of Texas at Dallas (UT Dallas) to develop non-precious metal membranes for H_2 separation. A qualified team at UT Dallas is exploring a novel H_2 separation membrane technology. The team will research and develop innovative membrane materials, concepts, and strategies for effective separation of H_2 from products of coal gasification.

Project Description

UT Dallas will prepare mixed matrix membranes (MMMs) utilizing a family of additives known as zeolitic imidazolate frameworks (ZIFs) in polymer composites. ZIFs are known as molecular sieves for their ability to allow passage of molecules of a certain size while retaining larger size molecules. The intent is to exploit the sieving capabilities, high surface areas, and adsorption capacities of ZIFs to achieve selective transport of H_2 at the high temperatures and pressures found in water gas shift (WGS) reactors used in the coal gasification process.

UT Dallas will develop thermally and chemically stable ZIFs and will conduct tests to evaluate their use in separating H_2 from coal-derived synthesis gas (syngas). Pure gases will be used for preliminary membrane testing, followed by binary mixtures of H_2 and carbon dioxide (CO_2) and H_2 and carbon monoxide (CO). Finally, the membranes will be tested with gas mixtures that simulate the input and output gas compositions, as well as the temperature and pressure conditions in WGS reactors. Promising candidate membranes will be tested under industrial pressure, temperature, and feed composition conditions in an integrated membrane WGS reactor containing a commercial catalyst. Membranes will be characterized both pre- and post-operation via appropriate analytical techniques to determine the effects of long term operation and contaminants. UT Dallas investigators will use these results to better understand the structure-property relationships for target separations.

CONTACTS

Jenny Tennant
Gasification Systems
Technology Manager
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4830
Jenny.Tennant@netl.doe.gov

Arun Bose
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4467
arun.bose@netl.doe.gov

John Ferraris, PhD
Principal Investigator
Kenneth J. Balkus, Jr., PhD
Inga H. Musselman, PhD
Co-principal Investigators
University of Texas at Dallas
800 W Campbell, BE26
Richardson, TX 75080
972-883-2901
john.ferraris@utdallas.edu

PARTNERS

Santa Fe Science and Technology

PROJECT DURATION

Start Date	End Date
10/01/2009	09/30/2013

COST

Total Project Value
$1,250,000

DOE/Non-DOE Share
$1,000,000/ $250,000

Goals and Objectives

The goal of this project is to facilitate the co-production of power and H_2 from coal by improving selective transport of H_2 from syngas under operating conditions as defined by 2015 DOE targets.

The overall objective of the project is to prepare novel, non-precious metal MMMs and advance the understanding of relationships between membrane structures and their properties. This understanding will be useful in designing membranes incorporating nanoparticles to achieve the target separations.

Specific objectives of the project include preparation and characterization of ZIF materials; fabrication of MMMs in flat, tubular, and hollow fiber geometries; characterization of membranes by a battery of physical techniques; and membrane testing to determine permeability of pure H_2, CO, and CO_2 gases, mixed gas pairs of H_2/CO_2 and H_2/CO, and syngas stimulants. In addition, the team will conduct long-term stability and permeability studies to assess the reliability of these MMMs in the presence of water and hydrogen sulfide (H_2S) and at temperatures and pressures consistent with those in WGS membrane reactors.

The team will characterize these MMMs for their crystallinity using x ray diffraction, membrane morphology using scanning electron microscopy, and thermal stability using thermal gravimetric analysis. The custom-built high-temperature, high-pressure permeameter (HPHT) will be optimized for testing MMMs at a temperature of 300 degrees Celsius (°C) and a pressure of 15 atmospheres (atm).

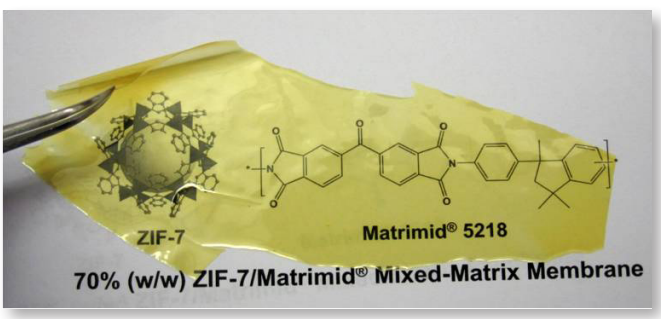

Figure 1. Nanocrystalline Zeolitic Imidazolate Framework incorporated into Matrimid® at high loadings formed flexible and transparent Mixed-Matrix Membranes

Accomplishments

- Researchers fabricated MMMs by incorporating synthesized ZIF nanocrystals, into thermally synthesized and commercially available stable polymers.
- The resultant MMMs were transparent indicating excellent polymer-ZIF interaction.
- ZIF incorporation at 50% w/w increased both H_2 permeability and H_2/CO_2 selectivity.
- The research team completed construction of a permeation apparatus for evaluating the novel membranes at commercially relevant process conditions. The complete installation of a High Pressure Volumetric Analyzer allowed the team to obtain temperature-pressure adsorption isotherms of hydrogen and carbon dioxide from targeted ZIFs up to 15 atm and 300 °C, conditions at which water gas shift reactors operate.
- Hollow fiber membranes of polybenzimidazole (PBI) were spun, assembled into custom-built modules and tested for permeability at 35 °C and 2.5 atm.
- A stainless steel membrane module for a tubular WGS reactor was constructed for operation at 300 °C and 30 atm. Optimization of the module for use at DOE target conditions is currently underway.

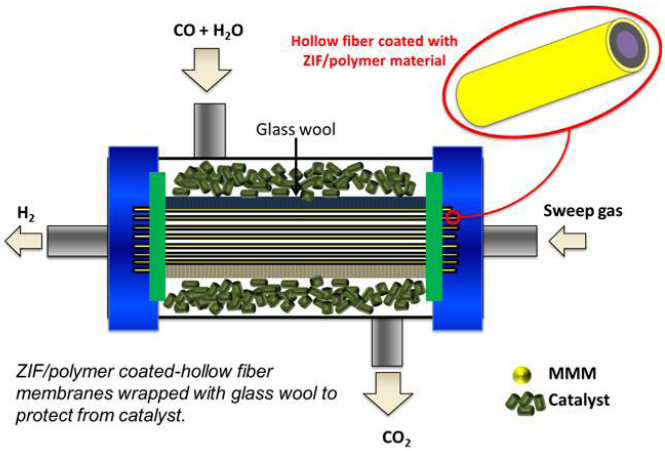

Figure 2. Hollow fiber module for water gas shift reactor

Benefits

This project is aligned with the DOE's objectives of research, development, and demonstration for eventual commercial deployment of near-zero emission clean coal facilities that incorporate carbon capture and storage. This project will contribute to advancing hydrogen separation membrane technology by increasing product flux, reducing separation cost, and improving membrane life and plant reliability. It might also demonstrate to U.S. coal plant operators that practical improvements to existing processes can help existing plants mitigate greenhouse gas emission.