IV.C.7 Development of Mixed-Conducting Dense Ceramic Membranes for Hydrogen Separation

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Objectives

- Identify and develop materials with suitable hydrogen permeability (a minimum flux of 50 $cm^3/min\text{-}cm^2$), which are chemically inert in the gasifier operating environment and are mechanically robust to thermal and pressure differentials in the same environment.
- Prove the utility of these membranes by manufacturing them using conventional manufacturing techniques and validating their performance in a simulated syngas environment typical of coal-based gasifiers.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- L. Durability
- M. Impurities
- N. Defects
- O. Selectivity
- P. Operating Temperature
- Q. Flux
- S. Cost

The project also addresses Section 5.1.5.1., Technical Barriers – Central Production Pathway in the Hydrogen from Coal – Research, Development, and Demonstration Plan of the DOE Office of Fossil Energy. This includes water-gas-shift reaction barriers and hydrogen separation barriers.

Technical Targets

Table 1 lists the targets that the project will attempt to meet during its implementation.

Table 1. Technical Targets: Ion Transfer Membranes for Hydrogen Separation and Purification

Performance Criteria	Units	2003 Status	2005 Target	2010 Target	2015 Target
Flux Rate	scfh/ft^2	60	100	150	200[a]
Cost	$/ft^2	>1,000	$500	$200	<$100
Durability	Hours	<8,760	8,760	26,280	>43,800
ΔP Operating Capability	psi	200	300	400	400-1000
Hydrogen Recovery	% of total gas	Data Not Available	80	90	100
Hydrogen Purity	% of total (dry) gas	>90%	95%	99.5%	99.99%

[a] Flux upper limit for ion transport membranes.

Approach

- Develop pure mixed proton-electron conductors, e.g., acceptor-doped cerates and zirconates, cermets (i.e., ceramic-metal composites) that contain mixed conductors and a metal that enhances the membrane's ambipolar conductivity and flux, and cermets composed of mechanically durable ceramic and a metal/alloy with high hydrogen permeability.
- Select/fabricate candidate materials based on fundamental principles of defect chemistry and mass transport.
- Optimize fabrication methods to reduce membrane thickness and maximize flux.
- Test long-term (1000 h) chemical stability in simulated coal gasification atmospheres.
- Under guidance from National Energy Technology Laboratory (NETL) program managers, transfer membrane technology through industrial collaborations.

Accomplishments

- Demonstrated membranes meet DOE target for flux rates.
- Demonstrated chemical stability of membranes for ≈1200 h in atmospheres typical of coal-based gasifiers.

Future Directions

- Test longer-term (thousands of hours) chemical stability of selected membranes in atmospheres typical of coal-based gasifiers.
- Evaluate the microstructures of the membrane both before and after the long-term exposure to atmospheres that are typical of a coal-based gasifier.
- Continue developing new high-temperature membranes (HTMs) to reduce cost, increase flux, and improve mechanical/chemical stability.
- Evaluate HTM mechanical properties (fracture strength, creep) before and after exposure to hydrogen.

Introduction

The development of cost-effective membrane-based reactor and separation technologies is of considerable interest for applications in advanced coal-based power and fuel production technologies. In the long term, hydrogen is considered the fuel of choice for both power and transportation industries. In the interim, fossil-based technologies will be utilized to generate hydrogen using chemical fixation of carbon dioxide to value-added products of commerce. A cost-effective hydrogen separation technology is integral to successful fossil-based hydrogen production technologies. Thin, dense ceramic membranes fabricated from mixed protonic and electronic conductors may provide a simple, efficient means for separating hydrogen from gas streams.

This project will investigate the development of ceramic membranes that separate hydrogen in a non-galvanic mode from hydrogen-containing gaseous mixtures from coal gasification and methane reforming. These membranes will consist of either dual-phase ceramic/metal composites or monolithic mixed protonic and electronic conductors. The work involves identifying materials with suitable hydrogen permeability followed by the development of methods for fabricating thin, dense membranes. Chemical, mechanical, and thermal stabilities of the membranes will also be examined in this research effort.

Approach

The first step was to develop pure mixed proton-electron conductors, cermets (i.e., ceramic-metal composites) that contain mixed conductors and a metal that enhances the membrane's ambipolar conductivity and flux, and cermets composed of mechanically durable ceramic and a metal/alloy with high hydrogen permeability. Then, candidate materials could be selected based on fundamental principles of defect chemistry and mass transport. Finally, testing of long-term (1000 h) chemical stability in simulated coal gasification atmospheres could be conducted, and the membranes could be transferred into industrial processes.

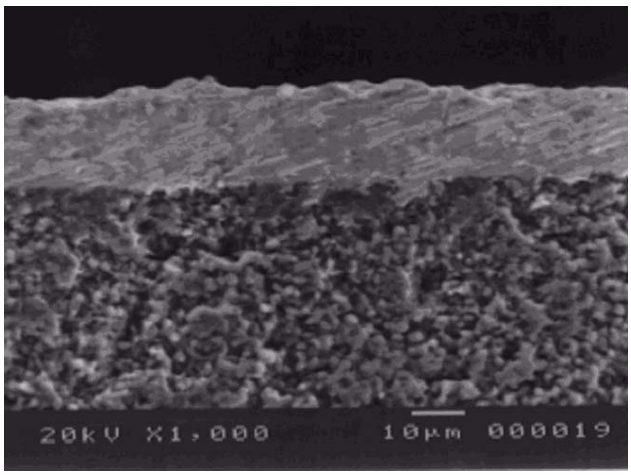

Figure 1. ANL-3e Thin Film on Porous Support

Results

Argonne National Laboratory has developed dual-phase dense membranes (see Figure 1) that are able to separate hydrogen in a non-galvanic manner. It was found that the flux is proportional to the difference in the square roots of hydrogen partial pressure on the two sides of the membrane. The highest H_2 flux (66 scfh/ft^2 at 900°C and 42 scfh/ft^2 at 500°C) was measured on an 15-µm-thick HTM using a feed stream at 1 atm. Flux of >400 scfh/ft^2 can be achieved with a hydrogen partial pressure of 300 psi in the feed gas. Short-term measurements showed stable flux in feed streams that contained CO, CO_2, CH_4, H_2O, and H_2S, and the flux was stable for 1200 h in a feed stream with 400 ppm H_2S.