Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels (ITM Syngas)

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Objectives

- Research, develop and demonstrate Ion Transport Membrane (ITM) Syngas ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas
- Scale-up the ITM Syngas reactor technology through three levels of pilot-scale testing and precommercial demonstration
- Obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the ITM Syngas technology

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 R,D&D Plan:

- A. Fuel Processor Capital Costs
- D. Carbon Dioxide Emissions
- AA.Oxygen Separation Technology

This project also addresses DOE Office of Fossil Energy objectives to develop lower cost methods to produce hydrogen from natural gas.

Approach

This project is in Phase 2 of a three-phase program. The approach in Phase 2 includes:

- Task 2.1 Commercial Plant Economic Evaluation
- Task 2.2 Materials and Seals Development and Evaluation
- Task 2.3 ITM Syngas Membrane and Module Design and Fabrication
- Task 2.4 Nominal 24,000 SCFD ITM Syngas Process Development Unit
- Task 2.5 Nominal 330,000 SCFD ITM Syngas Subscale Engineering Prototype

Accomplishments

- Process design and economic evaluation of a 150 million SCFD hydrogen plant with CO_2 separation to provide a carbon-free "clean fuel" showed the potential for 30% capital cost savings in the synthesis gas production step
- Projected hydrogen production costs for a distributed-scale hydrogen process (500,000 SCFD hydrogen, 100 units/year) are more than 25% below the DOE targets for 2005
- Demonstrated good performance stability of tubular membranes and seals at 250 psig and 825°C for 6 month individual test durations
- Achieved the project's Phase 1 oxygen flux targets with catalyzed, supported thin-film planar membranes
- Achieved a three-fold increase in pilot-scale membrane fabrication yields over one year ago
- Selected catalysts for scale-up testing in the Process Development Unit (PDU)
- Demonstrated leak-tight performance of PDU module seals at 425 psig and 850-900°C under static conditions and multiple pressure and thermal cycles
- Tested second-generation pilot-scale membrane modules in the PDU at elevated temperature and pressure with a synthesis gas environment
- Fabricated commercial-size ceramic membranes

Future Directions

- Fabricate multi-wafer membrane module for PDU test
- Test catalyzed planar membranes in PDU
- Fabricate balance of ceramic components for Subscale Engineering Prototype (SEP) module with commercial-size membranes
- Initiate tests to validate commercial-size membrane design
- Conduct tests to determine kinetic parameters for membrane and catalysis performance models

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Introduction

Ion Transport Membranes (ITMs) are a revolutionary platform technology for producing hydrogen and synthesis gas for applications in power generation, transportation fuels, and chemicals. The ITM Syngas process provides a lower-cost method for converting natural gas to hydrogen and synthesis gas by combining air separation and natural gas partial oxidation in a single-step ceramic membrane reactor, with the potential for capital cost savings of over 30%. When successful, this technology will be important to emerging hydrogen markets, such as hydrogen-based fuel cells for transportation and centralized hydrogen production facilities with CO_2 capture.

The new technology utilizes non-porous ceramic ITM membranes fabricated from multi-component metallic oxides that have both high electronic and oxygen ion conductivity at high temperatures (greater than approximately 700°C). In operation, oxygen from a hot air stream is reduced at one surface of the ITM membrane to oxygen ions, which diffuse through the membrane under a chemical potential gradient. At the opposite surface of the membrane, the oxygen partially oxidizes a pre-reformed mixture of hot natural gas and steam to form synthesis gas, a mixture of hydrogen and carbon monoxide. The ratio of hydrogen to carbon monoxide is in part dependent upon the amount of steam. The membrane material must show long-term stability in reducing and oxidizing atmospheres, and long-term compatibility with any oxygen reduction and partial oxidation/reforming catalysts that are in contact with its surface.

Approach

The objective of this program is to research, develop and demonstrate a novel ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas: the ITM Syngas process. Through a 9½ year, three-phase program, the ITM Syngas technology will be developed and scaled up to obtain the technical, engineering, and operating and economic data necessary for the final step to full commercialization of the hydrogen and synthesis gas generation technology. Phase 2 of the program was initiated in FY 2000 and will extend for 4½ years. Process concepts and performance will be validated in two stages of scale-up in Phase 2: the Process Development Unit (PDU), which began operation in 2002, and the Subscale Engineering Prototype (SEP), which will operate in 2004-2005.

In Task 2.1, "Commercial Plant Economic Evaluation," advanced ITM Syngas processes will be developed, and the economics of operation at the commercial plant scale will be evaluated based on the results of the Phase 2 program. In Task 2.2, "Materials and Seals Development and Evaluation," membrane materials and seals will be tested at the laboratory scale under process conditions to obtain statistical performance and lifetime data. In Task 2.3, "ITM Syngas Membrane and Module Design and Fabrication," membrane reactors will be designed for the ITM Syngas process at the PDU, SEP and commercial scales. Pilot-scale membrane modules will be fabricated for testing in the PDU. Fabrication of the membrane reactor modules will be scaled up in a Production Development Facility (PDF) to supply the requirements of the SEP.

In Task 2.4, "Nominal 24,000 SCFD ITM Syngas PDU," the components of the ITM Syngas technology will be demonstrated in a laboratory Process Development Unit (PDU). The PDU will operate at an equivalent of 24,000 SCFD of synthesis gas capacity and will performance test pilot-scale planar membranes under commercial process conditions. In Task 2.5, "Nominal 330,000 SCFD ITM Syngas SEP", a Sub-Scale Engineering Prototype (SEP) unit will be built to demonstrate the ITM Syngas technology using commercial-size membranes in sub-scale modules. The SEP will demonstrate the operation of the ITM Syngas process at up to an equivalent of 330,000 SCFD of synthesis gas capacity.

Results

Conventional methods for producing hydrogen from natural gas typically require external sources of heat (e.g. steam methane reformers) or a separate pure oxygen stream (e.g. oxygen-fired autothermal reformers). Steam methane reformers (SMR) use natural gas as fuel in reformer furnaces to generate heat, which is transferred to the reforming catalyst packed in high-pressure tubes, resulting in a significant fraction of the carbon emitted to the atmosphere as CO_2 in the low-pressure flue gas. Oxygen-fired autothermal reformers (ATR) use oxygen to partially oxidize natural gas internally in the reactor and retain nearly all the carbon in the high pressure synthesis gas, thus facilitating removal of CO_2 for carbon capture. However, the ATR requires a separate air separation unit (ASU) to produce high purity, high-pressure oxygen - thus adding complexity and capital and operating cost to the overall process. The ITM Syngas process offers the advantages of partial oxidation of the natural gas and the concomitant retention of carbon in the high-pressure synthesis gas, while simultaneously permeating pure oxygen across the ceramic membrane from a low-pressure air supply (Figure 1).

In an evaluation of advanced process concepts, an ITM Syngas process was developed for a centralized hydrogen production plant with CO_2 removal, producing 150 million SCFD of fuel-grade hydrogen. For this application, the ITM Syngas process was compared to a conventional oxygen-blown ATR with a cryogenic ASU to supply oxygen. Economic evaluation of the ITM Syngas process showed the potential for 30% capital cost savings in

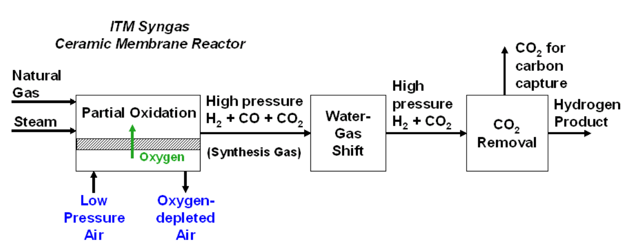

Figure 1. ITM Syngas Process to Produce Hydrogen and Capture CO_2

the synthesis gas generation process area and over 20% capital cost savings for the overall hydrogen and CO_2 production process. The ITM Syngas process also has a higher thermal efficiency of 74% compared to 71% for the oxygen-blown ATR process. The hydrogen product is a "clean" fuel suitable for centralized power generation and for distribution to local stationary or mobile applications, including fuel cells.

Tubular membranes and seal assemblies were tested in high-pressure, high-temperature lab-scale units under commercial process conditions. In these tests, pre-reformed natural gas mixtures at process pressure were passed over the outer surface of the tubular membrane, while air at atmospheric pressure was fed to the inner surface of the tube. Multiple tests, each operated continuously for over 6 months at 250 psig and 825°C under process conditions, were completed, and the membranes demonstrated good performance stability. A long-term test of a tubular membrane at high pressure and temperature is shown in Figure 2.

Sub-scale supported thin-film membranes were also tested at atmospheric pressure for periods of over 1200 hours. Tests of advanced catalyzed membranes demonstrated oxygen fluxes that approach the commercial flux target range and meet the Phase 1 flux target (Figure 3).

Rapid progress has been made in scaling up ceramic membrane fabrication using conventional processing methods (Figure 4). Lab-scale disk membranes were developed in 1999 in conjunction with initial materials development. Pilot-scale membranes were developed in 2000-2001 and have a 30-fold increase in membrane area over the lab-scale membranes. The pilot-scale membranes are being used to demonstrate membrane performance at commercial process conditions in the PDU. Fabrication methods that were developed at the pilot-scale were scaled up for commercial-size membranes, which have a 160-fold increase in membrane area over the lab-scale membranes. Fabrication of commercial-size membranes started in 2002.

Pilot-scale membrane modules have been tested in the PDU at elevated temperature and pressure with a synthesis gas environment. The PDU integrates the various components of the ITM Syngas reactor design and is used to confirm the performance of the planar membrane modules and seals under commercial process conditions. Ceramic-to-metal

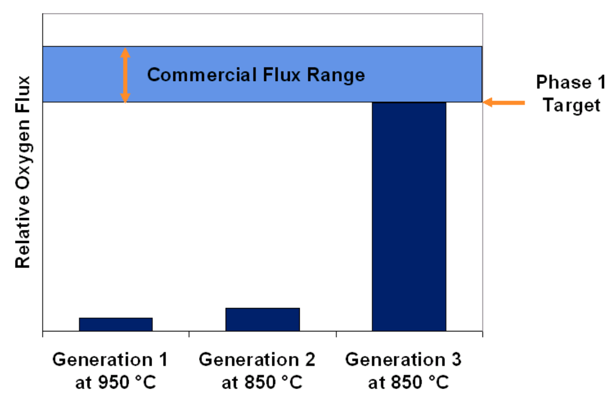

Figure 3. Advanced Catalyzed Membranes Approach Commercial Flux Target

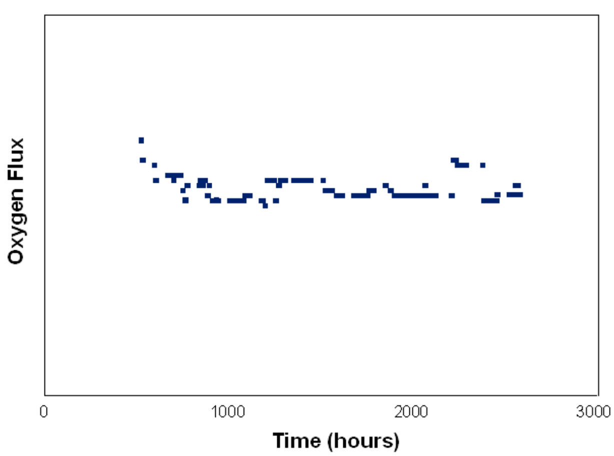

Figure 2. Long-Term High Pressure Test of a Tubular Membrane Shows Stable Oxygen Flux

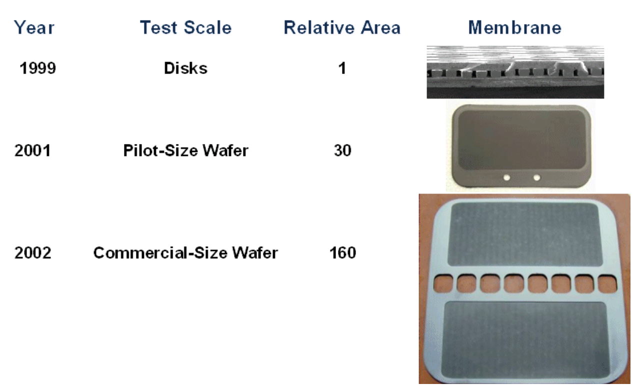

Figure 4. Achieved Rapid Scale-up of ITM Syngas Ceramic Membranes Target

seals are used to connect the ceramic membrane module to metal air feed and vent piping and are a critical element in the membrane reactor system. PDU module seals have demonstrated leak tight performance at 425 psig and 850-900°C under static conditions, and also over 50 thermal cycles and 8 pressure cycles (Figure 5).

Conclusions

Significant progress has been made to develop the ITM Syngas technology. A database is being built of performance data from several six-month duration membrane tests. Membrane modules and seal assemblies have also been fabricated and tested in the PDU at elevated temperature and pressure typical of synthesis gas conditions. Ceramic fabrication scale-up has progressed, and commercial-size membranes are being fabricated. Excellent progress continues to be made against the remaining technical challenges in the demonstration and scale-up of the ITM Syngas technology.

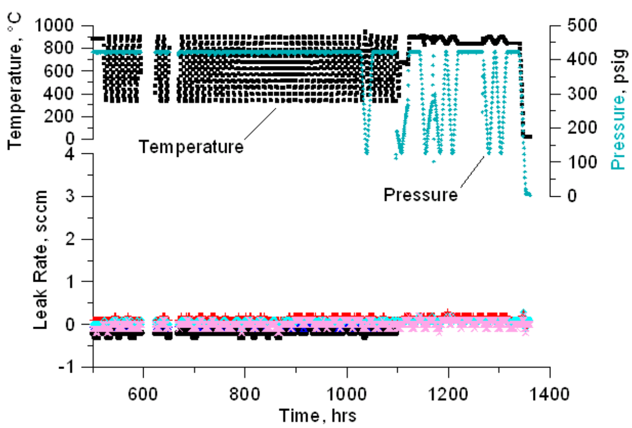

Figure 5. PDU Module Ceramic-To-Metal Seals Demonstrate Leak-Tight Performance at Steady-State and with Thermal and Pressure Cycling

FY 2003 Publications/Presentations

1. "Development of Ceramic to Metal Seals for Ceramic Membrane Applications," 57th Annual Forum of the Pennsylvania Ceramics Association, Sept. 2002

2. "Ion Transport Membranes for Gas Separation," 57th Annual Forum of the Pennsylvania Ceramics Association, Sept. 2002

3. "Development of the Ceramic Membrane ITM Syngas Process," American Chemical Society National Meeting, New Orleans, LA, March 2003

4. "Development of the Ceramic Membrane ITM Syngas Process," American Institute of Chemical Engineers Spring Meeting, New Orleans, LA, March 2003

5. "Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels," US DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Merit Review, Berkeley, CA, May 2003

6. "Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels," US DOE Advanced Synthesis Gas and Clean Fuels Program Merit Review, Houston, TX, June 2003

FY2003 Patents Issued or Applications Filed

1. "Mixed Conducting Membranes for Syngas Production", US Pat #6,492,290

2. Three patent applications filed covering ceramic-ceramic joining methods and the membrane assembly