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INTEGRATED CERAMIC MEMBRANE SYSTEM FOR HYDROGEN PRODUCTION

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Abstract

This paper describes a new technology development program launched by Praxair with Argonne National Laboratory (ANL) as a subcontractor. The proposed program will lead to commercialization of cost-effective and environmentally-friendly hydrogen production systems for use in the transportation sector for fuel-cell vehicle refueling stations and in the industrial sector as a small, on-site hydrogen supply. The proposed system will integrate ceramic membrane based syngas production and hydrogen separation technologies. The Phase 1 activities in the current year will focus on technoeconomic feasibility evaluation and hydrogen separation membrane testing to validate the concept and define the critical development program for subsequent years.

Introduction

Hydrogen is expected to play a vital role in the transportation sector for fuel cells vehicles and in the distributed power generation market for stationary fuel cells. One of the crucial factors for successful introduction of fuel cell vehicles on US roadways is a low-cost supply of hydrogen for refueling. Steam methane reforming (SMR) is a process of choice for large-scale hydrogen production. This process requires several processing steps including reforming, heat recovery/steam generation, shift conversion, further heat recovery and hydrogen purification. The cost of hydrogen from a plant producing 40 - 100 MMscfd H_2 is $6 to $8/MMBtu, of which fuel costs account for 52 - 68 % (Padro 1999). Due to costs of liquefaction, distribution and storage, the cost of liquid hydrogen at the refueling station is estimated to be in the range of $16 to $20/MMBtu (Thomas 1998). A small on-site plant can eliminate the costs associated with liquefaction and distribution. However, when a multi-step process like SMR is scaled down to 3000 scfh capacity, typically anticipated for vehicle fueling stations, capital related charges represent almost 90% of the total product cost which is ~$75/MMBtu (Thomas 1998).

Praxair's vision to lower hydrogen cost is based on reducing the number of processing steps required to produce hydrogen. The reduction in number of pieces of equipment and resulting simplicity of plant layout would significantly reduce the capital cost. Praxair has defined and is in the process of obtaining patent coverage on the concept that involves integration of syngas generation, shift reaction and hydrogen separation into a single membrane-reactor separator. The key elements required to make this possible are an oxygen transport membrane (OTM) and a hydrogen transport membrane (HTM). Both of these membranes are based on ceramic mixed conducting materials and both operate at similar temperatures (800 - 1000 C). The OTM conducts oxygen ions and electrons and has infinite selectivity for oxygen over other gases. Similarly, the HTM conducts only protons and electrons and therefore infinitely selective for hydrogen.

Integrated-Membrane Reactor Concept

A schematic diagram of the integrated-membrane reactor separator is shown in Figure 1. The reactor is divided in three compartments by integrating both OTM and HTM into a single unit.

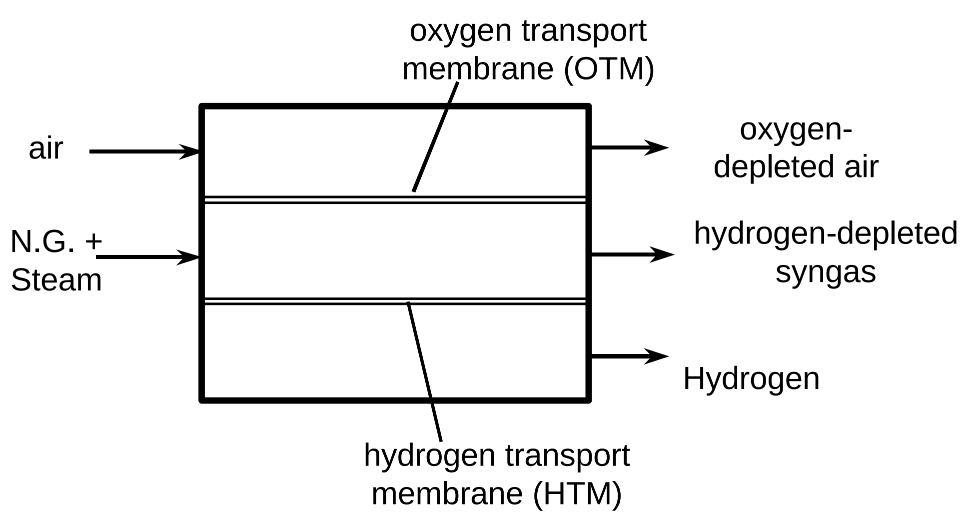

Figure 1. Integrated-Membrane Reactor Separator

Air at low pressure (~25 psia) is passed to the cathode side of the OTM and compressed natural gas (200 - 300 psia) and water/steam are passed to the anode side of OTM. Oxygen is transported across OTM to the anode side, where it reacts with natural gas to form syngas. A portion of natural gas also reacts with steam to form syngas. Catalyst is incorporated in the reactor to promote reforming reaction.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \text{(Partial Oxidation)}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{(Reforming)}$$

The syngas side is also exposed to feed side of HTM. Hydrogen is transported through HTM to the permeate side driven by partial pressure difference. Due to removal of hydrogen from the reaction zone, more hydrogen is formed by the shift reaction:

$$H_2O + CO \rightarrow H_2 + CO_2$$

As much hydrogen as possible is recovered from the reaction zone by its transport through HTM to the permeate side. Eventually, a pinch partial pressure difference between reaction zone and permeate side is reached and no more hydrogen can be recovered.

Technology Status

Praxair, Inc. is a member of the Oxygen Transport Membrane (OTM) Syngas Alliance, whose other members are BP Amoco, Sasol (South Africa) and Statoil (Norway). The alliance was formed in 1997 to develop a low-cost environmentally friendly technology for the manufacture of syngas. The OTM Syngas Alliance entered Phase II, the pilot demonstration phase, in 2000. The alliance completed Phase I of its program in December 1999. Phase I focused on ceramic membrane materials development, manufacturing technology and bench scale testing of syngas production reactions.

The HTM development is at much earlier stage compared to the OTM technology and significant development efforts will be required to take this technology to commercial scale. Argonne

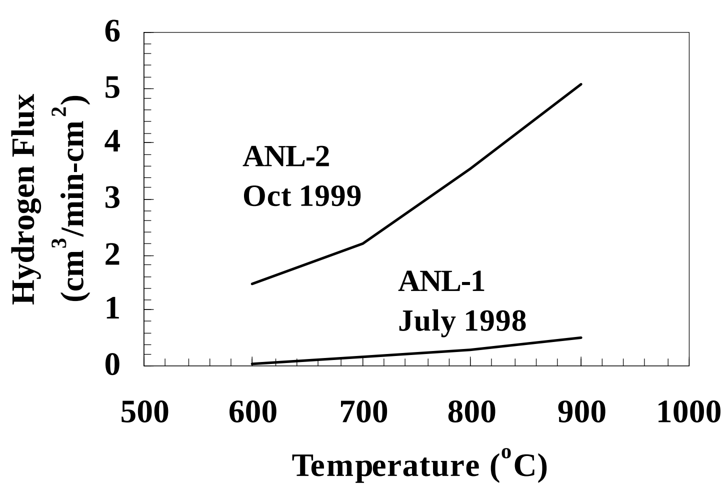

Figure 2. Progress in HTM Materials Development

National Laboratory (ANL) is developing materials for HTM. The proof-of-concept experiments at coupon-scale have demonstrated the feasibility of separating pure hydrogen from hydrogen containing gas mixtures. ANL has developed improved HTM materials with an order of magnitude higher hydrogen flux in last couple of years (Figure 2).

Program Overview

The long-term goal of the program is to commercialize a small-scale cost effective hydrogen production system with the hydrogen cost target of $6-$8/MMBtu. The program will be completed in three phases. Phase 1 spanning one year will focus on technical and economic feasibility studies to validate the concept and screen process schemes, performing experiments to obtain basic information for technoeconomic evaluation and defining a development program that will lead to commercialization. A multi-year Phase 2 program will focus on HTM material development and characterization, lab-scale testing of key components, marketing/business studies, economic analysis and development of a commercialization plan. In Phase 3, a pilot-scale unit will be built, a manufacturing process will be developed and detailed engineering design and cost estimation will be carried out.

Phase 1 Tasks

Technoeconomic feasibility analysis of the proposed concepts and critical experimental tests to support this activity will be the focus of Phase 1. Economic feasibility analysis will be used to compare product costs of the proposed concept with the competitive systems. Business model will be developed to perform profitability analysis.

Initial testing will study the effect of various operating parameters (hydrogen partial pressure, temperature, and membrane thickness) on flux. The data generated from the flux experiments and reaction kinetics for reforming and shift reaction will be used to design an integrated reactor separator.

Endurance and viability tests will be performed for the membrane in the presence of various components (CH_4, CO, CO_2, H_2O, N_2, sulfur compounds) expected to be present in the reactor. This test will identify any problem components for the membrane and will be useful to define future efforts on materials development. Flux studies in the presence of simulated reaction mixtures will also be performed. This study will test viability of membrane in the presence of actual mixtures and generate meaningful data for better reactor-separator design. This information will be recycled to revise the membrane-reactor separator design. Flux and cost targets necessary for both OTM and HTM will be identified to produce hydrogen at a cost of $6-$8/MMBtu.

Technical risks related to the membrane reactor will be evaluated. If OTM-HTM reactor is found to be a viable option then the rest of activities will focus only on this option. If technical risk analysis suggests that the difficulties with an integrated reactor are insurmountable then other alternative concepts will be explored. These options will also go through the same technical risk analysis.

A marketing study will identify potential opportunities for small hydrogen plants in the transportation sector, in the distributed power generation market and in the industrial sector. Assessment will also be made for competing options such as liquid hydrogen and electrolysis. The potential market share that the proposed technology could capture will be estimated based on its competitive position vs. other alternatives. The results of marketing study and the key financial parameters will form the basis for business analysis. Preliminary estimate of future development costs will be made. Financial analysis models will be used to determine viability of the proposed program. If a commercially viable hydrogen production system is unattainable, the program will be terminated.

Assuming that the business is viable and consistent with Praxair's business strategies, the project team (Praxair-ANL) will prepare a detailed plan and proposal for Phase 2 and provide an overview of Phase 3 activities.

Future Plans

Phase 2 efforts will ultimately lead to bench-scale testing units of key subsystems such as HTM separator, and integrated HTM-shift conversion reactor. Praxair's experience in development of OTM syngas reactor will be very useful in expediting the development work for this program. Some of the technical goals for the HTM will be to achieve specific flux targets and desirable operating characteristic with respect to tolerance for various components. Bench scale testing unit will be useful in generating flux data under actual operating conditions. If the performance targets for membrane matches Praxair's expectation and if business profitability analysis is still favorable then we will proceed to Phase 3.

The primary goal of Phase 3 will be to build a pilot-scale unit. This will be useful to generate key technical data necessary for engineering design and economic analysis for a commercial unit. It is anticipated that present development of cost-effective manufacturing of OTM elements will be also applicable to HTM elements.

Acknowledgement

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