Report Title:

A Novel Membrane Reactor for Direct Hydrogen Production from Coal

Type of Report: Quarterly Report

Reporting Period Start Date: 1/1/2005

Reporting Period End Date: 3/31/2005

Principal Authors:
Shain Doong, Estela Ong, Mike Atroshenko, Francis Lau, Mike Roberts

Date Report Issued: April 28, 2005

DOE Award Number: DE-FC26-03NT41851

Submitting Organization:
Gas Technology Institute
1700 South Mount Prospect Road
Des Plaines, IL 60018

DISCLAIMER

ABSTRACT

Gas Technology Institute is developing a novel concept of membrane reactor coupled with a gasifier for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal-derived synthesis gases. The objective of this project is to determine the technical and economic feasibility of this concept by screening, testing and identifying potential candidate membranes under high temperature, high pressure, and harsh environments of the coal gasification conditions. The best performing membranes will be selected for preliminary reactor design and cost estimates.

To evaluate the performances of the candidate membranes under the gasification conditions, a high temperature/high pressure hydrogen permeation unit has been constructed in this project. The unit is designed to operate at temperatures up to 1100^{o}C and pressures to 60 atm for evaluation of ceramic membranes such as mixed protonic-electronic conducting membrane. Several perovskite membranes based on the formulations of BCN ($BaCe_{0.8}Nd_{0.2}O_{3-x}$), BCY ($BaCe_{0.8}Y_{0.2}O_{3-x}$), Eu-doped $SrCeO_3$ (SCE) and $SrCe_{0.95}Tm_{0.05}O_3$ (SCTm) were successfully tested in the new permeation unit.

During this reporting period, a thin BCN membrane supported on a porous BCN layer was fabricated. The objective was to increase the hydrogen flux with a further reduction of the thickness of the active membrane layer. The thinnest dense layer that could be achieved in our laboratory currently was about 0.2 mm. Nevertheless, the membrane was tested in the permeation unit and showed reasonable flux compared to the previous BCN samples of the same thickness.

A long term durability test was conducted for a SCTm membrane with pure hydrogen in the feed side and nitrogen in the sweep side. The pressure was 1 bar and the temperature was around 1010^{o}C. No decline of hydrogen flux was observed after continuous running of over 250 hours. This long term test indicates that the perovskite membrane has good thermal stability under the reducing conditions of the hydrogen atmosphere.

A conceptual design of the membrane reactor configuration for a 1000 tons-per-day (TPD) coal gasifier was completed. The design considered a tubular membrane module located within the freeboard area of a fluidized bed gasifier. The membrane ambipolar conductivity was based on the value calculated from the measured permeation data. A membrane thickness of 25 micron was assumed in the calculation. The GTI's gasification model combined with a membrane reactor model were used to determine the dimensions of the membrane module. It appears that a membrane module can be configured within a fluidized bed gasifier without substantial increase of the gasifier dimensions.

TABLE OF CONTENTS

LIST OF GRAPHICAL MATERIALS

INTRODUCTION

The objective of this project is to develop a novel membrane reactor for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. This concept has the potential of significantly increasing the thermal efficiency of producing hydrogen, simplifying the processing steps and reducing the cost of hydrogen production from coal. The specific objective of the project is to determine the technical and economic feasibility of using the membrane reactor to produce hydrogen from coal. GTI and our project team (Arizona State University, University of Florida and American Electric Power (AEP)) have identified potential membranes (ceramic and metal) suitable for high temperature, high pressure, and harsh coal gas environments. The best performing membranes will be selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with other hydrogen production technologies from coal.

Our approach to membrane material screening and testing is to first identify the materials that have good thermal stability under the conditions of gasification temperatures. The candidate membranes are then evaluated for their hydrogen flux in a laboratory permeation unit. The acquired data will provide the basis for a preliminary membrane gasifier design, process development and economic analysis. In the next stage of the material screening, chemical stability of the membranes with the syngas and the contaminants generated from coal gasification will be evaluated. The trade-off between the hydrogen permeability and the chemical stability will be determined.

As coal gasification for hydrogen production occurs at temperatures above 900^{o}C and pressures above 20 atm, it is critically important to evaluate the hydrogen flux of the candidate membrane materials under these operational conditions. To this end, a high pressure/high temperature permeation unit has been constructed. The unit is capable of operating at temperatures and pressures up to 1100^{o}C and 60 atm respectively. The unit allows screening and testing of the membrane materials at more realistic gasification temperature and pressure conditions. Furthermore, it will be able to demonstrate much higher hydrogen flux from the membranes than what have been reported in the literature.

The mixed proton-electron conducting membranes of the perovskite have been identified as one group of the candidate membranes for the membrane gasification reactor applications. The perovskite membrane is 100% selective to hydrogen at high temperatures, >600^{o}C. BCN ($BaCe_{0.8}Nd_{0.2}O_{3-x}$) and BCY ($BaCe_{0.8}Y_{0.2}O_{3-x}$) were first selected for evaluation because they were shown in the literature to have the highest proton conductivity among the perovskite materials. Several perovskite membranes based on the formulations of BCN and BCY were prepared by GTI and successfully tested in the new permeation unit, as reported in the previous quarters. Eu-doped $SrCeO_3$ (SCE) supplied by Dr. Eric Wachsman of the University of Florida and $SrCe_{0.95}Tm_{0.05}O_3$ (SCTm) fabricated by Dr. Jerry Lin of Arizona State University were also tested in the high pressure permeation unit. Among the perovskite membranes tested to date, the

SCTm membrane with a thickness of 1.7 mm shows the highest flux of 0.6 STP $cc/cm^2/min$ at 4 bar of hydrogen feed pressure and 950^oC.

One approach to increase the flux of the membrane is to reduce its thickness. A very thin membrane would require support layer(s) to increase its overall mechanical strength. Previously, a BCN membrane made by pressing a dense BCN layer between two porous BCN layers with NiO as a pore former was fabricated and sucessfully tested in the permeation unit. Another supported BCN membrane with a different pore former was also made in this quarter.

The perovskite membranes can be reduced partially by hydrogen during the permeation, as reported previously. To assess the durability of the membrane under the hydrogen environment, a fresh sample of SCTm membrane was characterized using SEM and compared with the tested sample after permeation. A long term permeation testing was also conducted for the SCTm membrane.

The feasibility of configuring a membrane module within a gasifier was also investigated in this quarter. The preliminary conceptual design considered a 1000 TPD coal gasifier using the fluidization bed technology.

EXECUTIVE SUMMARY

During this reporting period, a thin BCN membrane supported on a porous BCN layer was fabricated. The objective was to increase the hydrogen flux with a further reduction of the thickness of the active membrane layer. Currently, the thinnest dense layer that could be achieved in our laboratory was about 0.2 mm. The membrane was tested in the permeation unit and showed reasonable flux compared to the previous BCN samples of the same thickness. The hydrogen flux at a hydrogen feed pressure of 4 bar was about 0.5 STP CC/min/cm^2 at 950^oC.

A fresh sample of SCTm membrane was characterized using SEM to compare with the previous analysis for the tested sample after hydrogen permeation. The fresh sample shows much clearer grain boundary than the tested sample, indicating further sintering of the membrane during the permeation testing. The mechanical strength of the membrane could be enhanced if further densification actually occurred.

A long term durability test was conducted for a SCTm membrane with pure hydrogen in the feed side and nitrogen in the sweep side. The pressure was 1 bar and the temperature was around 1010^oC. No decline of hydrogen flux was observed after continuous running of over 250 hours. This long term test indicates that the perovskite membrane have good thermal stability under reducing conditions in the hydrogen atmosphere.

A conceptual design of the membrane reactor configuration for a 1000 TPD coal gasifier was completed. The design considered a tubular membrane module located within the freeboard area of a fluidized bed gasifier. The membrane ambipolar conductivity was based on the value calculated from the measured permeation data. A membrane thickness of 25 micron was assumed. The GTI's gasification model combined with a membrane reactor model were used to determine the dimensions of the membrane module. It appears that a membrane module can be configured within a fluidized bed gasifier without substantial increase of the gasifier dimensions.

EXPERIMENTAL

High Pressure Permeation Unit

The experimental apparatus and the procedure for measuring the hydrogen flux of the candidate membranes were described in the previous reports. The unit was designed to operate at temperatures up to 1100^{o}C and pressures to 60 atm for evaluation of disc membranes with a diameter of about 2 cm. The membrane disc was sealed to the test fixture following the same techniques as described in the previous reports.

RESULTS AND DISCUSSION

Supported BCN Sample

Previously, a BCN ($BaCe_{0.9}Nd_{0.1}O_{3-x}$) membrane made by pressing a dense BCN layer between two porous BCN layers with NiO as a pore former was fabricated and sucessfully tested in the permeation unit. The dense layer of the supported membrane sample was 0.2 mm. In this quarter, another thin BCN membrane supported on a porous BCN layer was also fabricated. A different pore former other than NiO was used for this membrane. The original objective was to increase the hydrogen flux with a further reduction of the thickness of the active membrane layer. However, the thinnest dense layer that could be achieved in our laboratory so far still remained at about 0.2 mm. The total thickness of this membrane including the support layer was 0.5 mm. This supported BCN membrane was tested in the permeation unit for the hydrogen flux.

The test was conducted at 950^{o}C and various pressures from 1 to 12 bar with pure hydrogen as the feed and nitrogen as the sweeping gas. Prior to the hydrogen permeation testing, helium was used as the feed gas to check any leakage across the membrane and the seal. A helium leakage rate of 0.157 STP cc/cm^2/min was detected at 1 bar. Assuming that the gas leakage through the sealing material follows the Knudsen diffusion mechanism, the hydrogen leakage will be about 40% higher due to its lower molecular weight. Consequently, a constant leakage rate of 0.22 cc/cm^2/min was used to correct the measured hydrogen flux.

The results of the corrected hydrogen flux for this membrane are summarized in Figure 1. The hydrogen flux measured for this membrane is close to the previous BCN membrane supported with a porous layer using NiO as a pore former. This may be expected as both membranes have a dense layer thickness of about 0.2 mm. The hydrogen permeation flux first increases with the increasing pressure and then decreases after about 6 bar. The flux and pressure relationship is very similar to all the previous perovskite membranes tested in this project. The pressure probably affects the hydrogen flux through two mechanisms: (1) providing the driving force of the permeation by the hydrogen partial pressure difference across the membrane and (2) affecting the conductivity by the different proton (and perhaps electron) concentration or proton diffusivity inside the perovskite membrane due to the different hydrogen pressures.

Figure 1 also shows that the flux increases with the increasing hydrogen concentration in the feed side. The data were obtained at 7.8 atm pressure with 20% and 60% hydrogen with the balance of helium in the feed side.

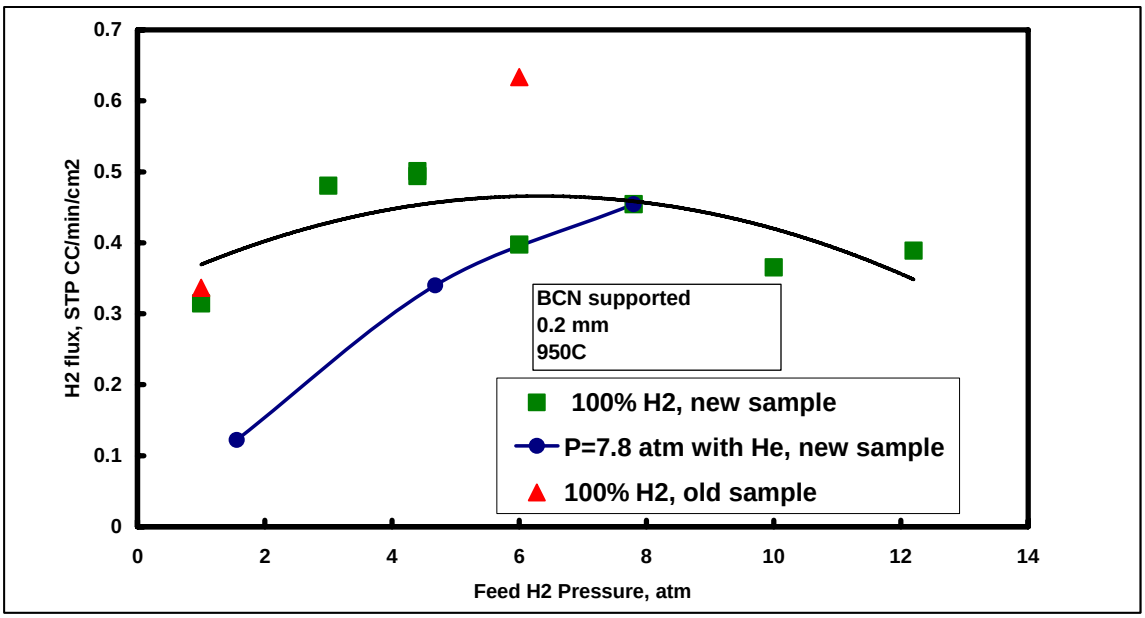


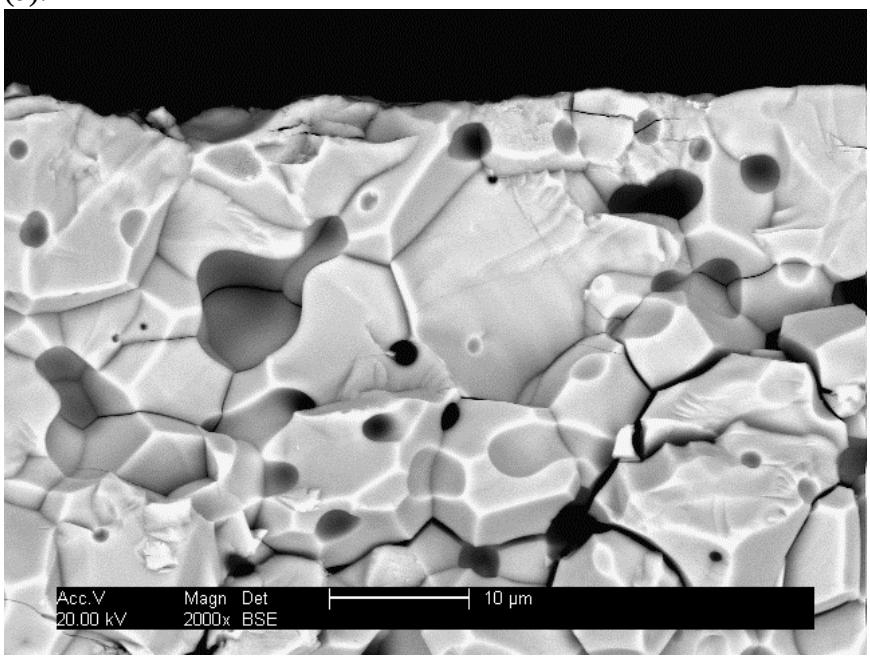
Figure 1. Hydrogen permeation flux for two supported BCN membrane measured from high-pressure permeation unit

SEM Analysis of SCTm Membrane

Two SCTm samples were previously tested and showed quite reproducible hydrogen permeation flux. SEM analysis for the tested sample after permeation showed partial phase separation towards the feed side, as reported last quarter. This probably was due to partial reduction of the SCTm perovskite material by the hydrogen.

A fresh sample of SCTm membrane was examined by Professor J. Lin of Arizona State University. The SEM image of the membrane cross section for the fresh sample is shown in Figure 2(a), compared with the tested sample after the permeation near the feed side in Figure 2(b). SEM micrographs at large magnification show that the fresh sample has much clearer grain boundary and more faceted grain surface, and the permeation-tested sample has almost invisible grain-boundary. This difference could be caused by the additional sintering effects for the permeation-tested sample, which was subjected to elevated temperatures for the permeation test for extended period of time. Although the permeation temperature (around 900^{o}C) may not be as high as the normal sintering temperature (>1200^{o}C), the actual sintering effects during permeation could be more pronounced due to the presence of hydrogen (more like a reactive sintering). This still needs to be verified.

(a).



(b).

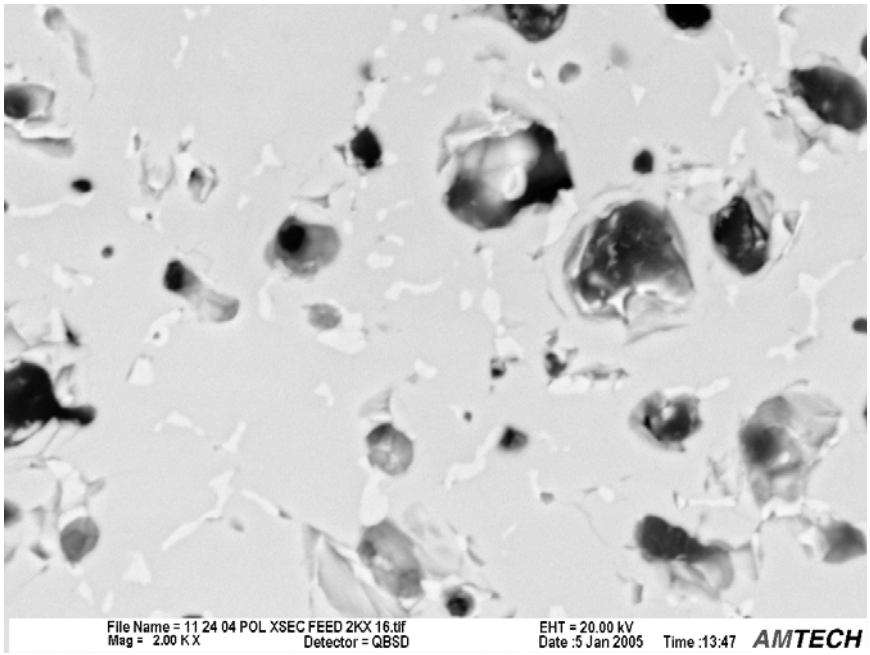


Figure 2 Comparison of microstructure of SCTm membranes at magnification of 2000X, (a) fresh sample, (b) sample after permeation near feed side

The light colored material formed between the grains in the tested sample is not seen in the fresh sample. The color change for the permeation-tested membrane could indicate composition change as a result of the hydrogen permeation test causing reduction and ion segregation. The present results show however that the membrane after the permeation

test still remains in good mechanical integrity with similar microstructure. In fact, the "reactive sintering" during permeation test, if does occur, seems to further densify the membrane and enhance its mechanical strength.

Long term permeation testing

During this quarter, a long term durability test was conducted for the second SCTm sample with pure hydrogen in the feed side and nitrogen in the sweep side. The pressure was 1 bar and the temperature was around 1010C. This continuous testing lasted about 250 hours. However, prior to this testing, the same membrane had been tested for about 2 weeks during the daytime, with the hydrogen feed switched off at nights and weekends while keeping the membrane at about 950^{o}C. The total length of time for this membrane sample in the test unit was about one month.

The long term testing results are shown in Figure 3 for both the flux and the temperature. The hydrogen flux actually drifted upwards because a constant temperature was not exactly maintained. The temperature was between 1010 and 1030^{o}C. After manually decreasing the temperature, the hydrogen flux returned back to about the same value as the beginning. A helium leak checking was also performed at the 120th hour, with an interruption of hydrogen flow of about 2 hours, to verify no deterioration of the leakage. This long term test indicates that the perovskite membrane has good thermal stability under reducing conditions in the hydrogen atmosphere. The chemical stability of the perovskite membrane under coal derived syngas conditions, however, still remains to be tested.

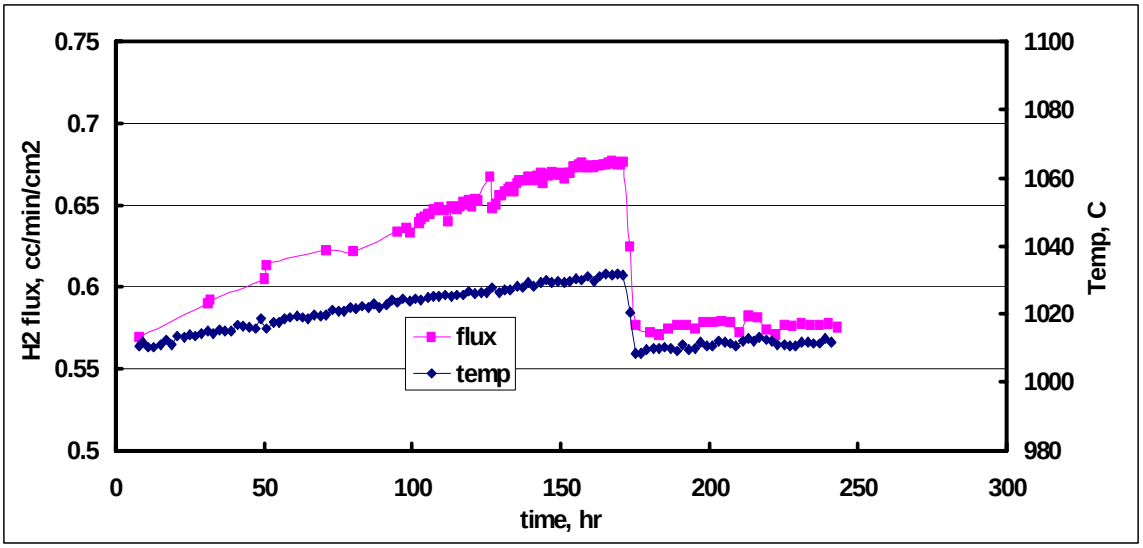


Figure 3. Hydrogen permeation testing for the SCTm membrane at 1 atm with pure hydrogen in the feed and nitrogen sweep in the permeate side

Conceptual Design of Membrane Gasification Reactor

A conceptual design of the membrane reactor configuration for a 1000 TPD coal gasifier was conducted to investigate the feasibility of placing a membrane reactor within a gasifier. A tubular membrane module is located within the freeboard area of a fluidized bed gasifier was shown in Figure 4. The coal syngas generated in the gasification zone at the lower section of the fluidized bed enters the membrane reactor module. To further protect the membrane material from the solid particles, each membrane tube, as a provision, can be enclosed within a ceramic filter tube as shown in Figure 5. Thus, only gas species can enter the annual section of the tube. As the filter tubes are sealed at the bottom, the syngas will continue traveling upwards inside the annular part. Due to the perm selective property of the membrane material, hydrogen will permeate through the inner membrane tube and flow upwards to the top plenum chamber before exiting the gasifier. The non-permeate gas or retentate will be collected at another plenum chamber below the hydrogen chamber and exit through the side ports of the gasifier.

In this preliminary study, gas contaminants generated from coal gasification are not considered. In reality, a stable, durable and robust membrane material and the reactor module must be developed.

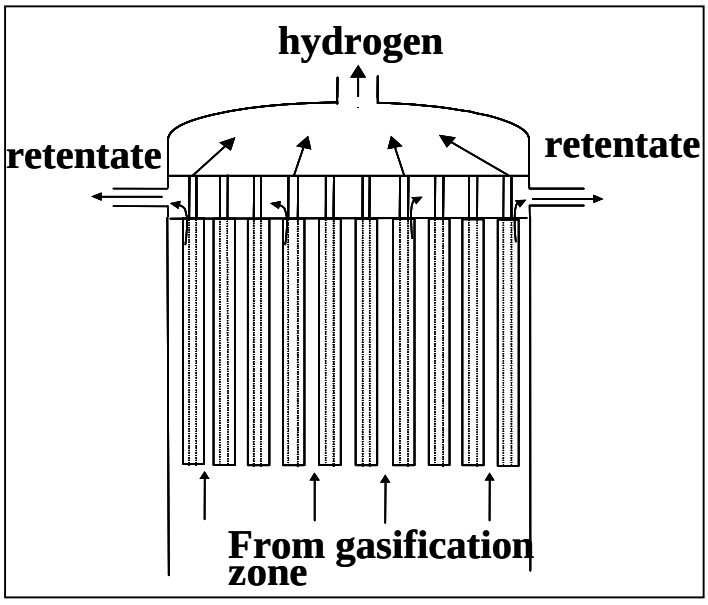


Figure 4. Schematic diagram of a tubular membrane module within a fluidized bed gasifier

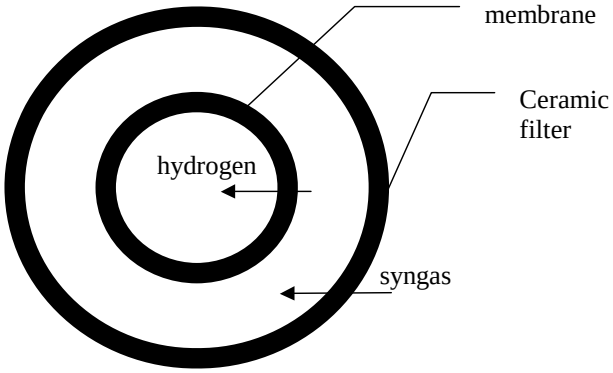


Figure 5. Enlarged cross section of a membrane tube

A mass balance for the feed side of the membrane tube yields

$$\frac{\partial F_i}{\partial x} - R_i + J_i = 0 \qquad (1)$$

where F_i is the molar flow rate of component i, x is the length of the membrane tube, R_i is the reaction rate for forming component i, and J_i is the permeation rate of component i.

To evaluate R_i, chemical kinetics was employed to describe the rates of gas reactions in the feed side of the membrane. This approach was used by Karim and Metwally[1] satisfactorily for modeling of the reforming of natural gas. A reaction scheme comprising 14 chemical species and 32 elemental reaction steps has been employed. The chemical species considered are six major gas components in the gasifier: CH_4, O_2, CO, H_2, CO_2, and H_2O, and eight radicals: OH, CH_3, H, O, HO_2, H_2O_2, CH_2O, and CHO. Because reforming reactions without catalysts are not expected to occur even at the gasification temperature of 1000^{o}C, catalytic reaction kinetics was used in the model calculations.

In a simplified form, the hydrogen flux can be expressed in the form of the Wagner equation [2,3]:

$$J_{H_2} = -\frac{RT}{4F^2 L}\frac{(\sigma_{H^+})(\sigma_{el})}{\sigma_{H^+} + \sigma_{el}}\left(\ln(p_{H_2}^f) - \ln(p_{H_2}^p)\right) \qquad (2)$$

where R is the gas constant, F is the Faraday constant, L is the membrane thickness, σ_{H^+} is the proton conductivity, σ_{el} is the electronic conductivity, $p_{H_2}^f$ is the partial pressure of hydrogen in the feed side of the membrane and $p_{H_2}^p$ is the partial pressure of hydrogen in the permeate side. The membrane ambipolar conductivity was determined from the hydrogen permeation data measured in this project. The ambipolar conductivity

values calculated from Eq. (2) based on the hydrogen flux of the SCTm membrane are shown in Figure 6. Although the conductivities vary with the pressure, a constant value of 0.05 S/cm was used for the calculation. The membrane thickness was assumed to be 25 micron, which is considered achievable with the current fabrication technologies.

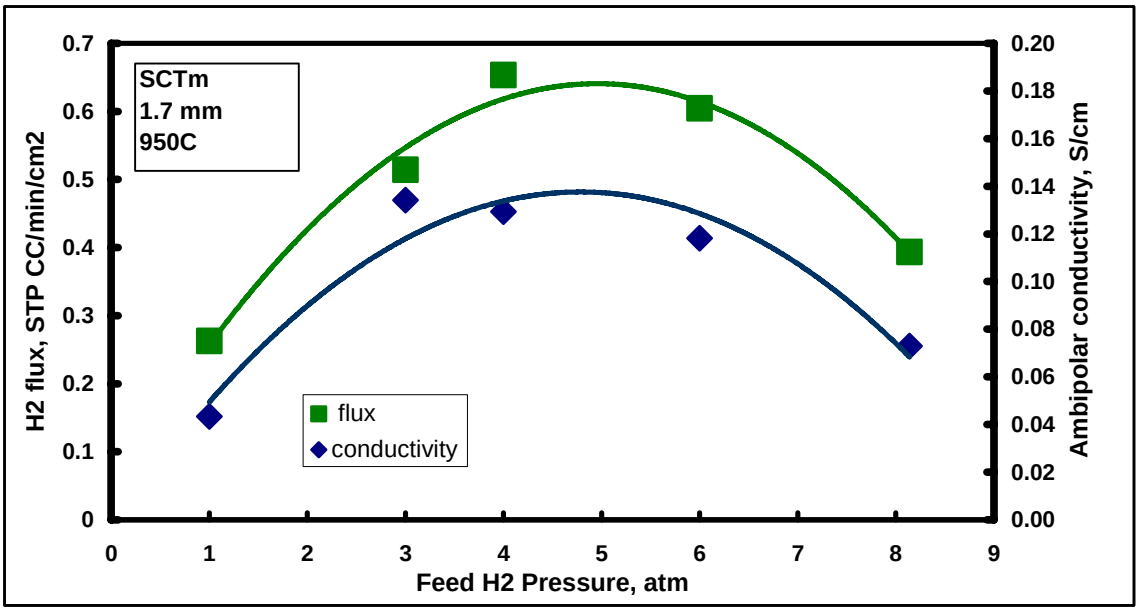


Figure 6. Hydrogen flux and calculated ambipolar conductivity for the SCTm membrane

Equation (1) can be solved with the typical numerical techniques. The required boundary conditions are the flow rates and the compositions of the coal syngas entering the membrane tubes. A GTI gasification model U-GAS® was used to estimate the gas flow rates and the compositions from a fluidized bed gasifier, which are listed in Table 1 along with other operating conditions and parameters. The Illinois #6 coal was used for this example.

The gasifier diameter without the membrane module calculated from the GTI's gasification model was about 2.5 meter. To accommodate the membrane unit, the upper section of the gasifier was increased to 3.3 meter in diameter. It appears that a membrane module can be configured within a fluidized bed gasifier without substantial increase of the gasifier dimensions. If multi-train of gasifiers are used for the 1000 TPD coal to hydrogen plant, the gasifier diameter and the associated number of membrane tubes will be reduced.

In this design example, the membrane gasification reactor produces 44240 Nm^3/hr of hydrogen and 46610 Nm^3/hr of non-permeable syngas with the following compositions: 4% H_2, 0.8% CH_4, 39% CO, 40% CO_2, and 16% H_2O. Further optimization and process options for recovering more hydrogen from the non-permeable syngas stream will need to be developed. The performance of this membrane configuration will be used in the simulation for the overall coal to hydrogen processes employing the membrane reactor.

Table 1. Summary of design parameters for the conceptual membrane gasification reactor

coal feed, TPD	1000	temperature, C	1100
oxygen feed, TPD	600	pressure, atm	60
steam feed to gasifer, TPD	595	gasifier diameter, cm	330
steam feed to shift reactor,TPD	270	membrane tube diameter, cm	1.25
coal syngas flow rates, Nm/hr	97125	membrane thickness, cm	0.0025
coal syngas composition		membrane tube length, cm	900
H2	0.280	number of membrane tubes	21300
CH4	0.042	membrae area, m2	7550
CO	0.297	ambipolar conductivity, S/cm	0.05
CO2	0.146	gas residence time of mem., sec	8
H2O	0.236	enclosing filter tube diameter, cm	1.87

CONCLUSION

A composite BCN membrane with a dense layer supported on a porous BCN layer was fabricated. The thickness of the dense layer, 0.2 mm was about the same as the previous supported BCN membrane. As a consequence, the hydrogen permeation flux was very similar for both supported BCN membranes.

The SEM analysis of the SCTm membrane shows that the fresh sample has much clearer grain boundary than the tested sample, indicating further sintering of the membrane during the permeation testing. The mechanical strength of the membrane could be enhanced if further densification actually occurred.

The SCTm membrane was tested in the permeation unit under continuous hydrogen feed at 1 atm and about 1010^{o}C for over 250 hours. No deterioration of hydrogen flux was observed. This long term test indicates that the perovskite membrane have good thermal stability under reducing conditions in the hydrogen atmosphere.

A conceptual design of the membrane reactor configuration for a 1000 TPD coal gasifier was completed. The design considered a tubular membrane module located within the freeboard area of a fluidized bed gasifier. The membrane ambipolar conductivity was based on the value calculated from the measured permeation data. The GTI's gasification model combined with a membrane reactor model were used to determine the dimensions of the membrane module. It appears that a membrane module can be configured within a fluidized bed gasifier without substantial increase of the gasifier dimensions.

PLAN FOR NEXT QUARTER

- Conduct testing for evaluation of perovskite stability under CO_2 environment.
- Identify options for improving the chemical stability of the perovskite membrane, such as Zr doped perovskite.
- Begin development of process options for coal to hydrogen using membrane reactor.

REFERENCES

1. G.A. Karim and M.M. Metwally "A Kinetic Investigation of the Reforming of Natural Gas for the Production of Hydrogen", Int. J. Hydrogen Energy, Vol. 5, pp 293, 1979
2. H.J.M. Bouwmeester and A.J. Burggraaf "Dense ceramic membranes for oxygen separation", in Fundamentals of Inorganic Membrane Science and Technology, Ed. By A.J. Burggraff and L. Cot, pp 435-528, 1996, Elsevier Science B.V.
3. T. Norby and Y. Larring "Mixed hydrogen ion-electronic conductors for hydrogen permeable membranes", Solid State Ionics, 136-137, pp139-148, 2000