

**CERAMIC MEMBRANE ENABLING TECHNOLOGY**  
**FOR IMPROVED IGCC EFFICIENCY**

**QUARTERLY TECHNICAL PROGRESS REPORT**

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## **TABLE OF CONTENTS**

A.	Introduction	Page 3
B.	Experimental Data	Page 3
	B.1. OTM Materials Development	Page 3
	B.2. Composite OTM Development	Page 4
	B.3. Process Development	Page 5
C.	Results and Discussions	Page 6
	C.1. OTM Materials Development	Page 6
	C.2. Composite OTM Development	Page 7
	C.3. Process Development	Page 7
D.	Conclusion	Page 7
E.	References	Page 8
F.	Appendix – Limited Rights Data	Page 9

## **A. Introduction**

The objective of this program is to conduct a technology development program to advance the state-of-the-art in ceramic Oxygen Transport Membranes (OTM) to the level required to produce step change improvements in process economics, efficiency, and environmental benefits for commercial IGCC systems and other applications. The IGCC program is focused on addressing key issues in materials, processing, manufacturing, engineering and system development that will make the OTM a commercial reality.

The objective of the OTM materials development task is to identify a suitable material that can be formed into a thin film to produce the target oxygen flux. This requires that the material have an adequate permeation rate, and thermo-mechanical and thermo-chemical properties such that the material is able to be supported on the desired substrate and sufficient mechanical strength to survive the stresses involved in operation.

The objective of the composite OTM development task is to develop the architecture and fabrication techniques necessary to construct stable, high performance, thin film OTMs supported on suitable porous, load bearing substrates.

The objective of the process development task of this program to demonstrate the program objectives on a single OTM tube under test conditions simulating those of the optimum process cycle for the power plant.

## **B. Experimental Data**

### **B.1. OTM Materials Development Experimental Data**

A candidate material had been identified before the outset of the program based on promising oxygen fluxes obtained on unsupported, relatively thick membranes. This lead candidate material, designated PSO1, had not been fully characterized. Some information regarding its crystal structure and expansion behavior is known, but a more complete understanding is required in order to determine its viability as the lead material for large-scale manufacturing and application.

In this program a more detailed characterization of PSO1 has been undertaken. Although the results show promise, alternative materials have been developed which have shown even superior properties to PSO1 in some areas. A more detailed analysis of these materials is ongoing and the search for new compositions is continuing.

Two compositions that have superior oxygen transport properties than the current lead candidate material are being more rigorously tested to determine their viability as a new lead candidate. Tests include determination of thermo-mechanical, thermo-chemical and mechanical properties. New compositions which represent different tradeoffs between thermomechanical and thermochemical properties and flux are under investigation.

#### **B.1.1. Materials Selection Criteria**

There are a number of important materials properties that a potential candidate material must possess to be considered for use in the large-scale processes. These include, oxygen flux, thermal expansion, expansion due to the chemical gradient across the membrane (chemical expansion), mechanical strength, creep resistance, chemical reactivity and corrosion resistance under

operating conditions. It is important when screening materials that a large number of compositions can be tested. Therefore a procedure has been developed, such that candidate materials must pass certain minimum criteria before further more detailed and time consuming characterization is undertaken. Thus while all candidates will be subjected to the early screening tests, only about 5-10% will be subjected to all the tests. Table 1 lists the types of tests which are used as part of material characterization.

**Table 1. Materials Characterization Tests**

<b>Experiment</b>	<b>Purpose</b>	<b>Experiment</b>	<b>Purpose</b>
O <sub>2</sub> flux on discs and tubes	Maximum potential flux, determine limiting rates	4-point tensile strength	Mechanical strength
Dilatometry	Thermal expansion	Composite mechanical strength	Element mechanical strength
TGA/DSC	Phase/thermal stability, oxygen stoichiometry	Conductivity relaxation	Diffusion and oxygen surface exchange
Creep	Operational Lifetime determination	High temperature chemical reactivity	Chemical stability
Environmental corrosion *	Corrosion resistance under operating conditions	Composite flux and stability	Target flux, life determination

**B.1.2. Experimental procedures employed and objectives**

In order to determine the lead material for large-scale development the screening tests given in Table 1 will be employed. This will involve the use of several different testing apparatus. These include a permeation test facility, a dilatometer, XRD, TGA/DSC, 4-point bend test, conductivity relaxation, and creep test facility.

**B.1.3. Development of Modified Materials**

A series of compositions based on PSO1 have been prepared and tested for flux, TEC, crystal structure and TGA/DSC. The objective is to produce a material that has oxygen fluxes comparable or better than PSO1, and possesses superior thermo-mechanical and thermo-chemical properties.

Several compositions showed a different crystal structure from PSO1. From the flux, TEC and DSC data, two compositions, designated PSO1d and PSO2d seem to be promising candidates. The average TEC of both these materials over the 25-950°C range is somewhat higher than PSO1. Additional optimization work is continuing.

**B.2. Composite OTM Development Experimental Data**

**B.2.1. Dense OTM Films**

Producing high quality dense OTM films on porous supports is the primary goal of this task. Improved processing protocols have enabled production of high quality films on porous supports that consequently have very low leak rates. OTM films have been prepared on porous discs and

tubes via processes developed in prior work and in other programs. Defects in the dense film of a composite OTM membrane are undesirable. Optimization of technologies to reduce film defects further is in progress. Analysis via SEM indicates the OTM films look uniform and dense with good bonding with the porous substrates.

## **B.2.2. High Temperature Permeation Tests of Composite OTM Discs**

### **B.2.2.1. Composite discs**

Dense OTM films were deposited on porous substrates of the same material to avoid chemical and mechanical incompatibility between the OTM film and substrate material. For the fabrication of composite disc, a porous substrate disc with porosity of 34% was prepared. Using optimal parameters, a dense PSO1 film was deposited on the disc. High temperature permeation tests were performed using a mixture of O<sub>2</sub> and N<sub>2</sub> as a feed gas and He as a purge gas. Oxygen flux of ~50% of the commercial target was achieved at 900° C and was stable for >500 hrs. This composite disc remained intact and showed a good bonding between the film and the substrate after testing.

### **B.2.2.2. Flux improvement by the reduced resistance of porous support**

Six porous substrate discs with the porosity from 34 to 50% were prepared using various combinations of powder and pore former and dense PSO1 films applied. High temperature permeation tests were conducted at 900° C using a mixture of O<sub>2</sub> and N<sub>2</sub> as a feed gas and He as a purge gas. The flux increases slightly with porosity of the substrate. This is likely due to the reduced resistance of the porous support.

## **B.2.3. Composite OTM Tubes Fabrication**

Expansion mismatch can occur when applying a coating to a porous ceramic tubular substrate. Due to the brittle nature and low shock resistance of ceramic materials, this can lead to failure during fabrication. In order to overcome substrate failure and to obtain a dense and crack-free film, special tube fixtures were designed which held porous PSO1 tubes in preferred configurations. Film coating techniques were optimized and dense and uniform PSO1 films were successfully applied on porous tubular substrates with no damage to the substrates.

## **B.3. Process Development Experimental Data**

The membrane tester is placed in a three-zone furnace. The oxygen transport membrane is sealed to the seal holders with a gold butt seal. The seal is established at about 1000° C. The membrane separator is typically operated above atmospheric pressure in order to direct some sample of the purge gas to the gas chromatograph (Hewlett Packard). The gas chromatograph is used to detect any nitrogen in the purge gas. Any nitrogen in the helium purge would indicate a leak arising from seal failure or pinholes in the membrane. The computed oxygen flux is corrected for that kind of leakage.

The following equation is used to compute the oxygen flux (N<sub>O<sub>2</sub></sub>) through the OTM tube from the measured flow rate and oxygen and nitrogen content of the purge gas:

$$N_{O_2} = x_{O_2} F_{He} \frac{273.15}{T} \frac{P}{1.01325 \times 10^5} \frac{P - P_{H_2O}}{P} \left( 1 - \frac{x_{N_2}}{x_{O_2}} \left( \frac{x_{O_2, feed}}{1 - x_{O_2, feed}} \right) \right) \quad \text{Equation [1]}$$

Where:

- $N_{O_2}$  = Average oxygen flux [sccm/cm<sup>2</sup>]  
 $x_{O_2}$  = Oxygen mole fraction in the helium purge gas as measured by the oxygen analyzer [-]  
 $x_{N_2}$  = Nitrogen mole fraction in the helium purge gas as measured by gas chromatography [-]  
 $F_{He}$  = Volumetric flow rate of the purge gas as measured by the bubble flow meter [cm<sup>3</sup>/min]  
 $P$  = Atmospheric pressure during the time of measurement [Pa]  
 $T$  = Temperature of the bubble flow meter during the time of measurement [K]  
 $P_{H_2O}$  = Vapor pressure of water in the bubble flow meter [Pa]  
 $x_{O_2, feed}$  = Oxygen mole fraction in feed gas [-]

The last term provides a correction for any leak of feed gas through seals or pinholes to the permeate side of the membrane. The term in the middle corrects the measured flow towards standard temperature and pressure (1 atm and 0° C), including a correction for the water vapor partial pressure in the bubble flow meter. The oxygen flux is being reported as standard cubic centimeter per minute per square centimeter (sccm/cm<sup>2</sup>).

The flux measurements were performed at four temperatures (1050, 1000, 950 and 900° C) on several composite PSO1 tubes where the porous tubular supports have porosity 33-49%, with varying oxygen partial pressure in the feed gas. In order to develop and verify an oxygen transport model the oxygen flux was also measured as a function of the helium purge flow rate and the air feed flow rate at 1000° C.

## C. Results and Discussion

### C.1. OTM Materials Development Results and Discussion

There appears to be a significant improvement over PSO1 in oxygen flux, thermo-mechanical and thermo-chemical properties in several new compositions. From the results it appears that PSO1d and PSO2d are the most promising candidates. However, there has not been any investigation into the mechanical properties of these compositions to compare with PSO1. Nor have any creep measurements been made.

Based on the results thus far two parallel modes of development of new materials will continue. Firstly, mechanical testing of PSO1d and the production of composites of PSO1d will be undertaken. From this a complete comparison with PSO1 can be made and the lead candidate selected. Secondly, new compositions are being produced and tested which develop the doping system used in PSO1d further. This will determine if the material can be further improved in terms of flux and thermo-chemical and thermo-mechanical behavior. In conjunction to this work, the creep and the mechanical testing of PSO1 will continue.

## **C.2. Composite OTM Development Results and Discussion**

A porous substrate disc with porosity of 34% was prepared. Using optimal parameters, a dense PSO1 film was deposited on the disc. High temperature permeation tests were performed simulating 4 bar feed and He as a purge gas. At 900°C, oxygen flux of ~50% of the commercial target was achieved and was stable for >500 hrs. This composite disc remained intact and showed good bonding between film and the substrate after testing.

Substrates of varying porosity were coated and high temperature permeation results were obtained. The flux increases slightly with porosity of the substrate. This is believed to be due to the reduced resistance of the porous support.

## **C.3. Process Development Results and Discussion**

Oxygen permeation tests were conducted on composite OTM tubes with the oxygen partial pressure in the feed gas varied to simulate 2-4 bar operation. The program oxygen flux target was achieved in January 2000 with a composite OTM tube that had 29% porosity. This result was obtained at 1050°C, with a feed gas simulating 4 bar operation and a helium purge gas.

The flow rate dependence of the oxygen flux is typically measured at the end of the measurement cycle. The model parameters were obtained by fitting the model to the temperature and oxygen partial pressure dependence of the oxygen flux, which results from data obtained at the beginning of the test period. Hence variations in oxygen flux with time could result in the model over-or under-predicting observed data.

The model describes the trend of decreasing oxygen flux with decreasing He flow rate well. The decrease in oxygen flux results from a decrease in driving force when the oxygen percentage in the Helium increases by decreasing the He flow rate.

The molecular diffusion coefficient of oxygen in the gas can be varied by modifying composition. For example, an increase of carbon dioxide in the purge gas results in a significant decrease in the molecular diffusion coefficient of oxygen in that purge gas without affecting the oxygen concentration. The modeling results indicate that the model is predicting a stronger decrease in oxygen flux than experimentally observed. This may indicate that the resistance of the porous support to oxygen transport is somewhat lower than predicted in the model. An alternative hypothesis is that the presence of carbon dioxide is affecting the flux through the membrane itself. This could increase the oxygen flux beyond the value as calculated by the model.

## **D. Conclusion**

Good progress has been made towards achieving the DOE-IGCC program objectives. Two promising candidates for OTM materials have been identified and extensive characterization will continue. New compositions are being produced and tested which will determine if the material can be further improved in terms of flux, thermo-mechanical and thermo-chemical properties.

Process protocols for the composite OTM development of high quality films on porous supports continues to be optimized. Dense and uniform PSO1 films were successfully applied on porous disc and tubular substrates with good bonding between the films and substrates, and no damage to the substrates or films.

Process development work is on schedule. The program oxygen flux target was achieved in January 2000 with a composite OTM tube that had 29% porosity. Optimization of membrane reactor design and experimental conditions will continue.

## **References**

- [1] Handbook of Chemistry and Physics, 71<sup>st</sup> edition, 1990-1991, Editor-in-Chief: David R. Lide, CRC Press, Boca Raton, Ann Arbor, Boston.