Ceramic Membrane Enabling Technology for Improved IGCC Efficiency

Final Report

For Reporting Period Starting September 30, 1999 thru December 31, 2004

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ABSTRACT

This final report summarizes work accomplished in the program from October 1, 1999 through December 31, 2004.

While many of the key technical objectives for this program were achieved, after a thorough economic and OTM (Oxygen Transport Membrane) reliability analysis were completed, a decision was made to terminate the project prior to construction of a second pilot reactor.

In the program, oxygen with purity greater than 99% was produced in both single tube tests and multi-tube pilot plant tests for over 1000 hours. This demonstrated the technical viability of using ceramic OTM devices for producing oxygen from a high pressure air stream. The oxygen fluxes that were achieved in single tube tests exceeded the original target flux for commercial operation. However, extended testing showed that the mean time to failure of the ceramics was insufficient to enable a commercially viable system. In addition, manufacturing and material strength constraints led to size limitations of the OTM tubes that could be tested. This has a severe impact on the cost of both the ceramic devices, but also the cost of assembling the OTM tubes in a large reactor. As such and combined with significant progress in cost reduction of large cryogenic oxygen separation devices, an economic gain that justifies continued development could not be derived.

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1.0 Executive Summary

Integrated Gasification Combined Cycle (IGCC) processes offer the advantage of improved efficiency, lower emissions and the potential for CO_2 capture. An effective gasification process is also an integral part of FutureGen. Methods to reduce the cost of the IGCC process are being sought in all areas. One potential cost reduction comes from the oxygen separation process. Currently, cryogenic oxygen is used for the process. However, an alternative separation technology offers the potential for improved efficiency and lower capital cost. The oxygen is separated using an oxygen transport membrane. In this process, air is extracted from the turbine, passed over the membrane, and returned to the cycle with only small losses. As the air passes over the membrane, a fraction of the oxygen in this stream is separate and diffuses through the membrane to be collected as pure oxygen on the other side. This oxygen is at high temperature but low pressure. The oxygen only has to be pressurized to be used in the gasification process. Furthermore, the air to be separated can be pre-heated with the turbine exhaust, resulting in integration potential greater than with conventional air separation processes, enabling improved efficiency.

This program had the objective of identifying process schemes, and OTM elements that can capitalize on the potential for improved efficiency. The program consisted of eleven tasks, ranging from identify composition of matter of the OTM device, to operation of many of the elements in a large (> 1 tpd oxygen) reactor, to the development of a a business and commercialization plan.

Some of these tasks were not accomplished due to concerns surrounding the reliability of the OTM elements coupled with a less than compelling economic driver. Progress in producing high oxygen fluxes across the OTM membranes were encouraging; however, there was a low mean time to failure of the elements under such conditions. The options for improving the mean time to failure resulted in a decrease in oxygen flux and an increase in manufacturing cost of the OTM.

Due to the combination of insufficient element reliability and lack of substantial economic gain the decision was made to terminate the program prior to the construction of a second, large pilot reactor.

2.0 Introduction

The Department of Energy's Office of Fossil Energy responded to an unsolicited proposal from Praxair, Inc. to create a program to develop ceramic membrane technology that could be integrated in a commercial IGCC process. On 9/29/99 Praxair, Inc. was awarded Cooperative Agreement number DE-FC26-99NT40437 for work entitled "Ceramic Membrane Enabling Technology for Improved IGCC efficiency"
The objective of this work 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 program is focused on addressing key issues in materials, processing, manufacturing, engineering, and system development that will make the Praxair, Inc. OTM a commercial reality for oxygen production.

The project was broken into two phases: Phase 1 was to provide the proof-of-concept of ceramic membrane oxygen generation in a small lab-scale reactor, and Phase 2 to scale up the process to a pilot reactor to the 1-10 tons per day of oxygen size.

The objectives of this project were:

Material Optimization and Characterization – Develop and optimize complete material systems for the high performance composite membranes required in both unpurged and steam purged OTM oxygen systems.

Composite OTM development – Develop the architecture and fabrication techniques necessary to construct stable, high performance thin film OTMs supported on suitable porous load bearing substrates.

Manufacturing development – Develop scalable manufacturing processes, protocols, and tools to enable low cost fabrication of large elements for commercial systems.

Process development – Define optimal cycles and module designs through a combination of validated modeling and testing at lab-scale and pilot plant operation

Economic Assessment and Commercialization Planning – Through economic process modeling, monitoring of competitive technology developments, and commercial target planning, define the initial products, performance and cost targets required to penetrate key markets.

Some of the tasks were revised in 9/30/02 in response to technology issues that will be described later in this report. The specific tasks after this revision were identified as:

In the Phase 1 program there are seven major tasks: Task 1 - Oxygen Transport Membrane (OTM) Materials Development, Task 2 – Composite OTM Element Development, Task 3 – Manufacturing Development, Task 4 – Process Development, Task 5 – Lab-scale Reactor System, Task 6 – Preliminary Business Development, and Task 7 – Phase 1 Program Management and Reporting.

In Phase 2, Task 3- Manufacturing Development will continue in order to develop OTM elements for the pilot reactors. The Phase 2 program shall therefore be in

five Tasks: Task 3 – Manufacturing Development, Task 8 – Multiple –Tube Reactor System Development, Task 9 – Business Development and Commercialization Planning, and Task 10 – Phase 2 Program Management and Reporting, and Task 11 – Element Reliability.

To achieve these objectives, a dedicated team at Praxair, Inc. was set up, and Praxair, Inc. partnered with University of Missouri, Rolla to assist in materials characterization and Foster-Wheeler to assist in engineering design and heat management.

3.0 Phase 1 Results and Discussion

3.1 Task 1: OTM Materials Development

3.1.1 Goal - Task 1

The Participant shall optimize OTM membrane and substrate materials for both the unpurged (Type 1A) and purged (Type 1B) processes of oxygen production using OTM. The Participant shall identify a Type 1A and a Type 1B material that meets key performance criteria. The materials shall be fully characterized for their physical and thermochemical properties, optimum oxygen flux, direct electronic conductivity, decomposition threshold, strength, thermal and compositional expansion, compatibility with other reactor materials, phase stability, and resistance to steam and CO_2. Advanced characterization and interaction studies shall also be completed. The Participant shall select suitable membrane and substrate materials in consultation with the DOE COR for chemical and thermochemical compatibility as well as for resistance to densification. Sealing of the substrate material shall be demonstrated. The Participant shall determine interfacial reaction products and select in consultation with the DOE COR suitable transition materials. An optimum oxygen surface exchange rate using various coatings shall be demonstrated to increase flux through the composite OTM.

3.1.2 Experimental - Task 1

The experimental facilities and methods in Task 1 were described in previous Topical Reports for Phase 1. Topical [Appendices 1,2,4].

3.1.3 Task 1 Results and Discussion

The goal of this Task was to develop superior materials for fabricating OTM elements. Two distinct types of materials were developed. One for non-purged operation (Type 1A) and one for purged (Type 1B). Substantial development was made during the program on the Type 1A materials. The initial material of choice (PSO1) showed an order/disorder transition that led to a negligible flux at temperatures below 850°C as well as a substantially non-linearity in both thermal and chemical expansion. New materials, PSO1d and PSO1x, were developed

during the program that eliminated this transition, produced even higher oxygen fluxes (above target), and in the case of PSO1x, showed a substantial improvement in resistance to CO_2 corrosion. However, when experiments were conducted under the high pressure differentials encountered in an IGCC cycle, the materials had a mean time to failure significantly below commercial use. As a result, Task 11 in Phase 2 was used to improve the element reliability.

The development of Type 1B materials was less successful. Under purge conditions that contained substantial amounts of steam, the elements failed within the first few hours of operation. Alternate materials that were expected to have the required thermodynamic stability, proved to have a low flux and other reliability problems. This, coupled with process analyses and transport models, which showed little to no benefit of a purged cycle resulted in the termination of further development of Type 1B materials.

Further details of the development of both sets of materials can be found in earlier Topical Reports [Appendices 1-12]

3.2 Task 2: Composite Element Development

3.2.1 Goal – Task 2

The Participant shall define the composite architecture and substrate material, develop an effective interface layer, fabricate a dense coating of the OTM material, and enhance surface exchange reactions. Advanced characterization of the interactions shall also be completed. Both the Type 1A and 1B composites shall be developed through closely paralleled development efforts. The Participant shall fabricate optimum OTM tubes as necessary for tube experiments to be conducted under Task 4 and Task 5.

3.2.2 Experimental – Task 2

Experimental techniques are described in Appendix I,2 and 4. However, much of the work completed in this area is proprietary and was included in EPACT data.

3.2.3 Results and Discussion – Task 2

Composite architectures for Type1A materials were developed that resulted in dense OTM coatings being deposited on porous substrate materials that were able to meet the target oxygen flux and leak rates. Multiple deposition techniques were developed with their own particular advantage. Due to the extremely high coefficient of thermal expansion of the PSO1 class of materials, the substrates chosen were comprised primarily of the same composition with the addition of second phases in order to improve robustness of the device. Tubes developed in this Task were used for testing in Tasks 4 and 5, and the technology was transferred to Task 3 for manufacturing.

No substantial work was completed on Type 1B materials due to the problems encountered in Task 1.

3.3 Task 3: Manufacturing Development (Phase I part of Task 3)

3.3.1 Goal – Task 3

The Participant shall produce as necessary all OTM tubes for single-tube (Task 4) and lab-scale (Task 5) reactor testing. This work shall include scale-up of the powder making process and scale-up of the membrane manufacturing process for both the selected Type 1A and Type 1B materials. The Participant shall demonstrate that the scaled-up membranes provide the expected performance in the reactors. Proof testing to ensure that the membrane tubes meet the criteria shall be conducted to evaluate in the minimum, the strength, stability, and microstructure of the substrate; and chemistry, flux and integrity (bonding as well as pinholes) of the coating.

3.3.2 Experimental – Task 3

Experimental techniques are described in [Appendices 5 and 8].

3.3.3 Results and Discussion – Task 3

Ceramic OTM elements were produced using the techniques developed in Task 2. These elements were made available for testing in Tasks 4 and 5. Ceramic elements produced at Praxair's semi-works facility in Indianapolis, IN had the same desired properties as those produced at the Praxair Technology Center in Tonawanda, NY.

No manufacturing development was undertaken on Type 1B materials.

3.4 Task 4: Process Development

3.4.1 Goal – Task 4

The Participant shall conduct laboratory testing of both OTM materials using single-tube high-pressure reactors. The Participant shall provide for the design, fabrication and safe operation of all necessary single-tube reactors. As a minimum, three process models shall be developed; a single-tube model, a multiple-tube model and a reliability model. Each model shall be validated using the results data generated through single-tube experimentation.

3.4.2 Experimental – Task 4

Experimental techniques are described in [Appendices 5 and 8].

3.4.3 Results and Discussion – Task 4

High pressure tube testing of Type 1A materials was undertaken in years 2 and 3 of phase 1. The results from these tests were used to validate the models that had been developed in year 1. The combined results of the tests and models demonstrated an optimum design for the OTM tubular elements. Oxygen flux

targets were routinely met in this task. However, the results of these tests also illustrated the severity of the process as indicated by numerous tube failures under high pressure conditions. Efforts were made to increase the mean time to failure of the tubes with considerable success.

One area of significance identified in these tests was the susceptibility to chromium poisoning. Most high temperature metals alloys that meet the structural requirements of the reactor vessel contain significant quantities of chromium. Under operation chromium vapor from these metals contaminated the surface of the OTM material, leading to substantial flux reduction over time. Solutions to reduce the chromium vapor pressure were implemented and the flux degradation was reduced.

However, at the end of Phase 1 it was evident that PSO1d and PSO1x in their current form were unable to meet the commercial target for element reliability. As a result, Tasks 1,2 and 4 were combined into a new Task – Task 11, to improve element reliability.

3.5 Task 5: Lab scale Reactor System

3.5.1 Goal – Task 5

The Participant shall provide for the design, fabrication, operation, and evaluation of the required lab-scale multi-tube reactor (O-1) to demonstrate progress towards commercialization. The O-1 reactor plant shall be in the production range of 0.2 to 0.5 tons per day of oxygen, and be fabricated from materials suitable for safe use when in contact with high-temperature pure oxygen. The initial reactor shall utilize the Type 1A tubes. The Participant shall evaluate and select in consultation with the DOE COR appropriate seal fixtures and packing materials and provide for the O-1 seal fixtures. The Participant shall develop seal fixtures suitable for use in commercial operation. The Participant shall demonstrate start-up, shutdown, and plant turndown operations of the O-1 plant. The Participant shall develop and demonstrate operation of membrane isolation systems designed to prevent contamination of the oxygen product in the event of membrane breakage. At least 50 percent of the commercial flux target shall be demonstrated.

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3.5.2 Experimental – Task 5

The reactor was constructed according to required safety regulations. Measurement techniques used were the same as the used in Task 4.

3.5.3 Results and Discussion – Task 5

A multi-tube reactor was constructed and operated using Type 1A tubes. High purity oxygen was produced from the reactor at a flux greater than 50% of the anticipated commercial target. The reactor vessel was modified with the solutions to prevent chromium contamination that enabled long term testing. A

test of more than 1000 hours was completed in Phase 1 of the program. Seal designs were developed that were used in both this Task and Task 4 for single tubes tests. The lab-scale reactor was started up and shut on many occasions. During these tests, it became apparent the materials reliability was a major concern, particularly during transient operation, but also after prolonged operation at high temperatures and pressures.

3.6 Task 6: Preliminary Business Development

3.6.1 Goal – Task 6

The Participant shall conduct a preliminary market study addressing potential products and markets, complete an economic comparison of competing processes, establish OTM target properties, and identify ancillary technologies required for successful commercialization. The Participant shall also make preliminary assessments (using process simulation) of IGCC-OTM process schemes, and shall develop and exercise economic models to determine the preliminary economic viability if integrated IGCC/OTM processes.

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3.6.2 Experimental – Task 6

Standard process, economic and marketing tools were used to complete this Task.

3.6.3 Results and Discussion – Task 6

Processes comparing a cryogenic air separation unit (ASU), and OTM based IGCC cycle and the integration of an SOFC into the OTM-IGCC cycle were compared. Details of the comparison are found in the 1st Annual Report (Appendix 4). The following table summarizes the results.

IGCC Key Process Parameters and Cost/Performance				
CASE	**Standard Cryogenic Case**	**Base Case Adv. Cryo**	**OTM**	**SOFC / OTM**
Gas Clean-up	Mdea	Mdea	Rectisol	Rectisol
Oxygen (100%,TPD)	2403	2405	2411	3419
Oxygen purity, %	95	95	>99%	>99%
Coal (TPD)	3150	3153	3192	4516
Gas Turbine (MWe)	273	272.2	272.8	272.7
Steam Turbine (MWe)	188.3	186.6	193.9	223.4
SOFC (MWe)	—	—	—	257.8
Misc. Power (MWe)	54.3	43.2	40.0	50.9
Net Power (MWe)	407.1	415.6	426.7	703
Efficiency: % HHV	45.4	46.3	46.9	54.6
ASU cost, relative	142	100	85	114
IGCC cost, $MM	$597	$559	$552	$966
Capital cost, $/kW	$1467	$1344	$1294	$1374
SOFC costs, $/kW				$600,$1000
COE in current $, mils/kWh	53.4	49.7	48.1	46.5, 52.5

The reduction in the cost of the ASU provided enough confidence to continue with the project. The cost reduction assumed an OTM performance target of >4 $scc.cm^{-2}sec^{-1}/\$/cm^2$. Further analysis required more detailed reactor design and manufacturing cost development that occurred in Phase 2 of the project.

3.7 Task 7: Phase 1 Program Management

3.7.1 Goal – Task 7

The Participant shall provide for project management and reporting activities. An Industrial Advisory Panel shall also be established by the Participant with DOE participation to solicit comments and guidance on the technical, economic, and market acceptability of the IGCC technologies developed in the program and to assist in establishing design parameters for process development.

A cooperative determination for continuation into Phase 2 program shall be made jointly by DOE and the Participant with 30 days of submission of the Task 5 Topical Report detailing the results and conclusions from all tests conducted and of the Task 6 studies and analyses. Should the Phase 2 program not be initiated, the Task 5 and Task 6 reports shall serve as the final technical report for DOE purposes.

3.7.2 Results and Discussion – Task 7

Execution of the deliverables of Phase 1 was made in a timely manner. The project was executed within budget. Topical Reports were provided as necessary. Cooperative determination to continue the project in Phase 2 was made. The Tasks of Phase 2 were modified from the original cooperative agreement to encompass the additional work required around element reliability. In addition, it was determined that the O-1 reactor would not be used for Type 1B testing in Phase 2 as originally planned, but would be used to continue testing of Type 1A elements. Construction of the O-2 reactor would not commence until element reliability had been sufficiently proved.

4.0 Phase 2 Results and Discussion

4.1 Task 11: OTM Element Reliability

4.1.1 Goal - Task 11

The Participant shall develop a combination of materials, processing techniques, element architectures, and operating conditions to meet longevity and reliability targets at the performance required for economic success.

4.1.2 Experimental - Task 11

The experimental facilities and methods in Task 11 were described in previous Topical Reports for Phase 2. Topical [Appendices 13-16].

4.1.3 Results and Discussion – Task 11

The mean time to failure of the ceramic elements that had been developed in Tasks 1 and 2, manufactured in Task 3 and tested in Task 4 was less than one month at the end of phase 1 of the program. Failure was defined as the oxygen purity decreasing below 90%.

A combination of materials compositional changes, manufacturing processes, architectural changes, and process control measures were deployed with an end result of increasing the time to failure to greater than 9 months. However, an offset of this ten fold increase in reliability was a reduction in oxygen flux to around 40% of the Phase 1 results, and increase in tube cost (around 100%) of the projected Phase 1 cost. Another important area that was identified was that long ceramic tubes were unsuitable for a reactor design in which a large pressure differential was required due to the potential for buckling.

In summary, it was determined that a substantial improvement in element reliability was still required, and the new performance indicators reduced the economic value of the OTM integration to below the projected developments that had been achieved by cryogenic distillation processes. A mean time to failure of greater than 30 years is required to have an OTM ASU life of 10 years, from which the economics were derived. The OTM cost performance of these membranes was less than 0.75 $scc.cm^{-2}sec^{-1}/\$/cm^2$.

Given the dramatic improvements that were required to meet the commercial targets, more radical approaches to modifying the element architecture that significantly increased the surface area per unit of ceramic were also examined from both an element reliability and a manufacturing and assembly cost stand point. It was evident that the performance target could be improved by increasing the surface area per volume of ceramic (whether using finned tubes or stacked plate assemblies). However, the cost performance of these designs was still in the range of 1.5 $scc.cm^{-2}sec^{-1}/\$/cm^2$, far below the commercial targets. The complexity of the OTM elements may also lead to a lower manufacturing yield and increase in potential for stress concentration factors that can result in reduced element reliability.

Based in part on this analysis, and an expected time to commercialize after significant further materials, architecture and manufacturing development, Praxair, Inc. determined that the project was no longer commercially attractive and requested a mutual termination of the project with DOE.

4.2 Task 3: OTM Manufacturing Development (Phase II part of Task 3)

4.2.1 Goal - Task 3

The Participant shall demonstrate that the scaled-up membranes provide the expected performance in the reactors. Proof testing to ensure that the membrane tubes meet the criteria shall be conducted to evaluate in the minimum, the strength, stability, and microstructure of the substrate; and chemistry, flux and integrity (bonding as well as pinholes) of the coating.

4.2.2 Experimental - Task 3

The experimental facilities and methods in Task 3 were described previously.

4.2.3. Results and Discussion – Task 3

It had been determined that a simple tube geometry was limited in length due to reliability constraints. Thus OTM tubes in the 12 – 24" range were produced for testing in phase 2 (compared to 3 – 6' in phase 1). These tubes were successfully tested in single tube reactors and in the O1 reactor.

Detailed manufacturing cost models were generated for tubes of this geometry. The results of these cost models were incorporated into the commercialization plan. It was evident that tubes of this size would be unable to meet the cost targets. Therefore, efforts to make elements that had an extended surface area were made. These elements ranged from 1 sq. ft. to 5 sq. ft. Cost models for such elements were developed and incorporated into the commercialization plan. Elements of these complex high surface area geometries were not tested in the program due to poor results in manufacture and the decision that the cost and reliability targets resulted in a decision to terminate the program.

4.3 Task 8: Multiple-tube Reactor Systems Development

4.3.1 Goal - Task 8

Task 8.1, Multi-Tube Reactor Provision, Testing and Evaluation

The Participant shall provide for the design, fabrication, operation, and evaluation of the required multi-tube pilot reactor (O-2) to demonstrate progress toward commercialization. The O-2 plant shall have a range of ~2 TPD oxygen production. The initial reactor shall utilize the Type 1A tubes. All large OTM tubes shall be provided as required for testing during Phase 2. The Participant shall evaluate and select in consultation with the DOE COR appropriate seal fixtures and packing materials and provide for the O-2 seal fixtures. The Participant shall demonstrate start-up, shutdown, and plant turndown operations of the O-2 plant. At least 75 percent of the commercial flux target shall be demonstrated.

Task 8.2, Commercial System Design

The Participant shall prepare a conceptual design for a commercial-scale, multi-tube module for oxygen production for inclusion in an IGCC system and conduct process trade-off, economic, and optimization studies. The Participant shall design a suitable heat exchanger for a commercial OTM system integrated with an IGCC demonstration plant. The Participant shall develop a sound design basis for the successful application of hot gas expanders for recovering waste gas energy from oxygen membrane systems. Following acceptable results, the Participant shall prepare a detailed design of a commercial module to enable preparation of bid packages and cost estimates.

4.3.2 Experimental - Task 8

Standard design and process analyses tools were used in this Task.

4.3.3 Results and Discussion – Task 8

Task 8.1
Praxair, Inc. and DOE determined that construction of O-2 should not commence until sufficient reliability data was obtained to justify the expense. The reliability data generated in Phase 2 resulted in the decision not construct the reactor, but rather to terminate the program.

Task 8.2
Work was undertaken to design heat exchangers and hot gas expanders as necessary given the design of the reactor. A commercial design was developed by Foster-Wheeler. Details of the design are proprietary. The results of the design showed the unfavorable cost outcome of the OTM integration process, and thus a bid process was not commenced.

4.4 Task 9: Business and Commercialization Planning

4.4.1 Goal - Task 9

Task 9.1 Business Analyses

The Participant shall complete a market study that addresses the potential markets, the economics of competing processes, the OTM target properties required, and identify ancillary technologies required for successful commercialization. An IGCC-OTM economic and technical assessment shall be completed which results in the selection of the best process scheme. The Participant shall also conduct a final economic evaluation using the preliminary Task 6 economic evaluation and developed economic models. The final evaluation shall thoroughly describe the current economic viability and advantages of integrated IGCC/OTM/SOFC processes.

Task 9.2, Commercialization Planning

The Participant shall identify the initial products and markets for commercialization. A commercial development strategy shall be prepared by the Participant which plans for a host site for an initial commercial plant project, confirms the interface with IGCC and strategy for IGCC commercialization, identifies potential commercial partners and qualifications, and provides a manufacturing plan.

4.4.2 Experimental - Task 9

Standard process analyses tools were used in this Task.

4.4.3 Results and Discussion – Task 9

Task 9.1.
OTM target properties were identified. A detailed analysis of optimum cryogenic integration schemes was produced and new cost performance targets were set. A comparative analysis with a state of the art cryogenic ASU integrated with the IGCC was completed and provided in the table below.

	Cryo O_2	OTM Tube	Δ, %
IGCC Net MWe	446.5	461.7	+3.4
IGCC Capital Cost, $MM	410.7	479	+16.6
Net Efficiency (%, HHV)	41.82	41.65	-0.4
Oxygen Plant Cost, $/metric TPD	26031	46039	+76.9
Oxygen Plant Power, kWh/ton O2	424.2	384.3	-9.4
IGCC Specific Capital Cost, $/kW	920	1038	+12.8
Cost of Electricity, c/kWh	4.54	4.87	+7.4

A second analysis that used the preliminary cost model developed for extended surface area elements and corresponding reactor design was also completed. This showed a more favorable outcome, although still not compelling. The results are shown below. These results were based on cost models for manufacturing an element that had a surface area of 5 sq ft. This in itself would provide significant manufacturing demands and corresponding reliability concerns.

	Cryo O2	OTM Plate	Δ, %
IGCC Net MWe	446.5	461.7	+3.4
IGCC Capital Cost, $MM	410.7	424.1	+3.7
Net Efficiency (%, HHV)	41.82	41.65	-0.4
Oxygen Plant Cost, $/metric TPD	26031	27752	+9.2
Oxygen Plant Power, kWh/ton O2	424.2	384.3	-9.4
IGCC Specific Capital Cost, $/kW	920	919	+0.3
Cost of Electricity, c/kWh	4.54	4.55	+0.2

It is important to note that the costs associated with cryogenic oxygen supply have decreased compared to the analysis that was completed early in phase 1 of the program. Thus the OTM targets had to become more aggressive to remain competitive.

An evaluation that included an SOFC was not completed.

Task 9.2
This Task was not completed due to the decision to terminate the program.

4.5 Task 10: Phase 2 Program Management

4.5.1 Goal - Task 10

The Participant shall provide for project management and reporting activities. The Industrial Advisory Panel shall be continued from Phase 1 by the Participant with DOE participation to solicit comments and guidance on the technical, economic, market acceptability of the IGCC technologies developed in the program and to assist in establishing design parameters for multi-tube reactor plants process development.

4.5.2 Results and Discussion – Task 10

Praxair, Inc. worked with DOE to restructure Phase 2 of the program to address primary concerns of reliability. Topical Reports were produced as required. The project spend was adjusted due to the decision to construct the pilot reactor. Praxair provided technical and economic details around the decision whether to pursue the project.

5.0 Conclusions

OTM technology is able to potentially improve the efficiency of an IGCC plant compared to a cryogenic ASU. Multiple process schemes where developed to provide the optimum configuration of the OTM reactor within the IGCC process. However, there are severe hurdles that require to be overcome before a commercial OTM IGCC can be realized.

The most severe hurdle to be overcome is to improve element reliability. A typical IGCC process would require of the order of 100,000 tubes and could tolerate very few failures. Substantial development work is required to attain a reliable element that justifies significant capital expenditure that accompanies pilot plant development.

Other hurdles that need to be overcome are the cost performance of the membranes. One, or both, of element cost and element performance need to be improved in order to make the case for the introduction of a new technology viable for such a large and expensive process such as IGCC.

Praxair, Inc. has made the decision that these hurdles are too great to justify continued expenditure from both Praxair, Inc. as well the U.S. Department of Energy.

6.0 References

The following appendices are previous quarterly reports for this project.

Appendix I

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period Start Date October 1999
Reporting Period End Date December 1999

Principal Investigator: Ravi Prasad
DOE Program Manager: Dan Cicero

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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter October – December 1999 in the following task areas:

Task 1 Oxygen Transport Membrane (OTM) Materials Development

Task 2 Composite OTM Development

Task 4 Process Development

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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

Efforts are underway to find material compositions which are superior to the current lead candidate PSO1. Discs and tubes of new compositions have been tested for oxygen flux. Several compositions have shown improved oxygen transport properties over PSO1 at temperatures lower than 850°C. Oxygen flux tests using a He purge gas on a 1mm disc of a new composition at 800°C resulted in significantly higher fluxes.

B.2. Composite OTM Development Experimental Data

High quality dense OTM films on porous supports is the primary goal of this task. Defects in the dense film of a composite OTM membrane diminish performance due to a decrease in selectivity. Because of this, we are establishing test procedures to quantify the extent of defects in the film of the composite OTM.

B.2.2. Flux Measurements on Composite OTM Discs

A composite OTM comprised of a PSO1 film deposited on a porous PSO1 disc was prepared and tested using He purge gas for oxygen permeation. At 900°C an oxygen flux of ~50 % of target flux was obtained. The disc was tested for >360 hours with no decline in flux. This is a very encouraging result as it shows the stability of the membrane.

It is important to have high strength of the porous support to enable robust elements to be successfully developed. Therefore, several improved substrates are being investigated. A composite OTM comprised of a PSO1 film deposited on a new porous substrate yielded O_2 flux comparable to the composite PSO1 on porous PSO1 disc at 900°C, but the new support is

expected to be significantly stronger. The long-term stability of this composite disc is being studied.

B.3. Process Development Experimental Data

Permeation tests were run on a composite tube at 1050°C, 1000°C and 900°C. The maximum measured fluxes under ideal conditions are approaching 100% of our target flux.

C. Results and Discussion

PSO1 is the current lead candidate for the OTM, however, new material compositions with superior characteristics to those of PSO1 are being investigated. Discs and tubes of alternative compositions to PSO1 have been prepared. Significantly higher oxygen fluxes have been measured at 800°C on a 1mm disc of a new composition.

High quality, defect-free dense films are desirable in a composite OTM. Room temperature leak tests provide an efficient method for OTM quality control of supported membranes without the added complexity of a high temperature seal that is required in oxygen permeation tests.

A composite OTM comprised of a PSO1 film deposited on a porous PSO1 disc was prepared and tested using He purge gas for oxygen permeation. At 900°C an oxygen flux of ~50 % of target flux was obtained. The disc was tested for >360 hours with no decline in flux. This is a very encouraging result as it shows the stability of the membrane. Porous substrate strength and long-term stability of the composite OTM will continue to be investigated.

High temperature permeation tests were conducted on a composite OTM tube at 900°C, 1000°C and 1050°C. Oxygen fluxes approached 100% of the commercial target flux.

D. Conclusion

The DOE-IGCC program has commenced and material, composite and process development is in full swing. New material compositions with superior characteristics to those of PSO1 are being investigated, and several show promise. Optimization of high quality films on porous supports continues. Oxygen fluxes measured on composite tubes are approaching 100% of our target flux.

References

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

Appendix II

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period Start Date January 2000
Reporting Period End Date March 2000

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Date Report was Issued: April 2000

DOE AWARD NO. DE-FC26-99FT40437

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter January – March 2000 in the following task areas:

Task 1 Oxygen Transport Membrane (OTM) Materials Development

Task 2 Composite OTM Development

Task 4 Process Development

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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 posses 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

Experiment	Purpose	Experiment	Purpose
O_2 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 looks 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_2 and N_2 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_2 and N_2 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_{O2}) through the OTM tube from the measured flow rate and oxygen and nitrogen content of the purge gas:

$$N_{O_2} = x_{O_2} F_{He} \frac{273.15}{T} \frac{P}{1.01325x10^5} \frac{P - P_{H_2O}}{P} \left(1 - \frac{x_{N_2}}{x_{O_2}} \left(\frac{x_{O_2,feed}}{1 - x_{O_2,feed}}\right)\right) \qquad \text{Equation [1]}$$

Where:

N_{O2}	=	Average oxygen flux [sccm/cm^2]
x_{O2}	=	Oxygen mole fraction in the helium purge gas as measured by the oxygen analyzer [-]
x_{N2}	=	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^3/min]
P	=	Atmospheric pressure during the time of measurement [Pa]
T	=	Temperature of the bubble flow meter during the time of measurement [K]
P_{H2O}	=	Vapor pressure of water in the bubble flow meter [Pa]
$x_{O2,feed}$	=	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^2).

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 results 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, 71st edition, 1990-1991, Editor-in-Chief: David R. Lide, CRC Press, Boca Raton, Ann Arbor, Boston.

Appendix III

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period Start Date April 2000
Reporting Period End Date June 2000

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Date Report was Issued: July 2000

DOE AWARD NO. DE-FC26-99FT40437

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter April – June 2000 in the following task areas:

Task 1 Oxygen Transport Membrane (OTM) Materials Development

Task 2 Composite OTM Development

Task 4 Process Development

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A. Executive Summary

Work performed during this quarter in the oxygen transport membrane (OTM) materials development program (Task 1) involved studying the chemical stability of PSO1 in non-atmospheric gas mixtures. Development and characterization of a new composition, PSO1d has also continued. Composite PSO1d elements have demonstrated fluxes exceeding the commercial target using bench scale units. This combined with other physical properties position PSO1d well to become the new lead candidate material. Potential substrate compositions that exhibit low adverse reactivity with film materials were identified.

Progress continued in composite OTM development (Task 2) fabrication techniques. High quality PSO1 OTM films were prepared on porous supports to study the effect of film thickness and substrate porosity. Improvement of PSO1 film properties while keeping substrate porosity constant resulted in oxygen flux data >60% of the commercial target at 900°C with composite OTM discs.

High temperature permeation tests continued at atmospheric pressure on PSO1 composite elements in the process development program (Task 4) with oxygen flux values very close to the target flux. The model of the oxygen transfer across a composite OTM element was further refined. Results show that the commercial target flux can be achieved at temperatures as low as 800°C and at pressure ratios of ~ $^2/_3$ of commercial operation using optimized membranes.

B. Experimental Data

B.1. OTM Materials Development Experimental Data

Characterization of OTM and substrate materials has been undertaken using many different experimental procedures. These include permeation, crystallographic, thermomechanical, thermochemical and electrochemical measurements.

The permeation test facility was described in the DOE IGCC second quarterly report [1]. This facility has been modified to enable the use of alternative gas mixtures in the purge gas stream. An additional test facility has also been designed for flux testing. This equipment will be used in the IGCC program.

TGA/DTA, XRD and oxygen flux studies of PSO1 in selected non-atmospheric gas compositions were used to investigate potential instability in some environments, which can result in a decrease in the oxygen flux.

Work was performed to assess the compatibility of PSO1 with other substrate materials. Materials characterization was conducted utilizing XRD, mechanical testing and oxygen permeation testing.

B.2. Composite OTM Development Experimental Data

PSO1 substrate discs with a constant porosity of 41-42% were prepared. Using a method developed in prior work, dense PSO1 films were deposited on the porous discs. High temperature permeation tests were performed using a mixture of O_2 and N_2 as a feed gas and He as a purge gas. The oxygen flux was increased through use of different processing parameters.

Four porous PSO1 disc and element supports of varying porosity were prepared and dense PSO1 films applied. High temperature permeation tests were conducted in the disc and single element permeation reactors using a mixture of O_2 and N_2 as a feed gas and He as a purge gas.

B.3. Process Development Experimental Data

Composite OTM elements comprised of dense PSO1 films deposited on porous PSO1 substrates were prepared using parameters and methods developed in prior work. These composite elements were tested for high temperature permeation utilizing the test facility and method previously described in the DOE IGCC second quarterly report [1]. Variations in fabrication parameters resulted in small variations in the oxygen flux.

C. Results and Discussion

C.1. OTM Materials Development Results and Discussion

The stability of PSO1 in selected non-atmospheric gas compositions was studied using thermochemical, electrochemical and crystallographic tests to determine the impact of any structural changes on the oxygen flux.

Flux measurements were performed on PSO1 at 900°C, ambient pressure, using air as a feed stream and different gases as a purge stream. The results show a decrease in the oxygen flux when the sample is exposed to atmospheres containing significant amounts of certain gases. Thermochemical studies also indicated an adverse reaction at high concentrations of certain gases. However, PSO1 and its derivatives are stable in air environments at higher temperatures.

PSO1 has been intimately mixed with an alternative substrate composition. Oxygen flux, mechanical strength, and XRD tests were performed on samples comprising a mixture of PSO1 and the alternative substrate. XRD of sintered elements showed that some chemical interaction between the alternative substrate and PSO1 had taken place. No subsequent development of a reaction phase was observed by XRD after being held at 1000°C for an extended time. Oxygen permeation measurements were performed on the two phase materials. No flux degradation was observed during a 100 hour test at 900°C. This indicates that no deleterious phases are produced.

C.2. Composite OTM Development Results and Discussion

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 this study, PSO1 substrate discs with a constant porosity of 41-42% were prepared. Using parameters and a method developed in prior work, dense PSO1 films were deposited on the discs while incrementally varying a parameter. High temperature permeation tests were performed using a mixture of O_2 and N_2 as a feed gas and He as a purge gas. Oxygen flux of >60% of the commercial target was achieved at 900°C at one extreme of the optimal parameter.

The effect of substrate porosity on oxygen flux was further evaluated in detail on composite discs. Four porous PSO1 discs were prepared and dense PSO1 films applied. The porous support for the composite discs had porosities of 28-50%. High temperature permeation tests were conducted in disc flux testers using a mixture of O_2 and N_2 as a feed gas and He as a purge gas. For the composite discs the oxygen flux at 900°C increases linearly with increasing porosity of the substrate, to a maximum oxygen flux of >60% of target.

C.3. Process Development Results and Discussion

Oxygen permeation tests were conducted on PSO1 composite OTM elements fabricated with variations in processing and design parameters. The samples were tested using a mixture of O_2 and N_2 as a feed gas and He as a purge gas at temperatures up to 1050°C. Oxygen fluxes in the range of 91-98% of the target oxygen flux were routinely obtained.

The modeling of the oxygen transfer through a composite OTM element was further refined and used to analyze optimal composition architecture. The model shows that it is possible to achieve the target oxygen flux at 800°C, even with an oxygen partial pressure ratio across the membrane of only ~ $^2/_3$ of the commercial operation.

D. Conclusion

- PSO1d appears to be an attractive material to replace PSO1 as the lead candidate.
- The commercial oxygen flux target has been obtained using a composite element of PSO1d
- The oxygen transport model shows that it is possible to achieve the target oxygen flux at 800°C

E. References

1. Prasad, Ravi, "Ceramic Membrane Enabling Technology for Improved IGCC Efficiency" Quarterly Technical Progress Report for DOE Contract DE-FC26-99FT40437, April 2000