CERAMIC MEMBRANE ENABLING TECHNOLOGY
FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

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Principal Investigator: Ravi Prasad
DOE Program Manager: Dan Cicero

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Submitted by:

Praxair, Inc.
175 East Park Drive
Tonawanda, NY 14151

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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 $\sim 2/3$ 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 O₂ and N₂ 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 O₂ and N₂ 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 O₂ and N₂ 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 O₂ and N₂ 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 O₂ and N₂ 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 $\sim \frac{2}{3}$ 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