### **Oxygen Transport Ceramic Membranes**

## **Quarterly Report**

January- March 2002

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Issued: April 2002

DOE Award # DE-FC26-99FT400054

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#### Executive Summary

Conversion of natural gas to liquid fuels and chemicals is a major goal for the Nation as it enters the 21<sup>st</sup> Century. Technically robust and economically viable processes are needed to capture the value of the vast reserves of natural gas on Alaska's North Slope, and wean the Nation from dependence on foreign petroleum sources. Technologies that are emerging to fulfill this need are all based syngas as an intermediate. Syngas (a mixture of hydrogen and carbon monoxide) is a fundamental building block from which chemicals and fuels can be derived. Lower cost syngas translates directly into more cost-competitive fuels and chemicals.

The currently practiced commercial technology for making syngas is either steam methane reforming (SMR) or a two-step process involving cryogenic oxygen separation followed by natural gas partial oxidation (POX). These high-energy, capital-intensive processes do not always produce syngas at a cost that makes its derivatives competitive with current petroleum-based fuels and chemicals.

In the mid 80's BP invented a radically new technology concept that will have a major economic and energy efficiency impact on the conversion of natural gas to liquid fuels, hydrogen, and chemicals.<sup>1</sup> This technology, called Electropox, integrates oxygen separation with the oxidation and steam reforming of natural gas into a single process to produce syngas with an economic advantage of 30 to 50 percent over conventional technologies.<sup>2</sup>

The Electropox process uses novel and proprietary solid metal oxide ceramic oxygen transport membranes [OTMs], which selectively conduct both oxide ions and electrons through their lattice structure at elevated temperatures.<sup>3</sup> Under the influence of an oxygen

<sup>&</sup>lt;sup>1</sup>Mazanec, T. J.; Cable, T. L.; Frye, J. G., Jr.; US 4,793,904, 27 Dec **1988**, assigned to The Standard Oil Company (now BP America), Mazanec, T. J.; Cable, T. L.; US 4,802,958, 7 Feb **1989**, assigned to the Standard Oil Co. (now BP America), Cable, T. L.; Mazanec, T. J.; Frye, J. G., Jr.; European Patent Application 0399833, 24 May **1990**, published 28 November **1990**.

<sup>&</sup>lt;sup>2</sup>Bredesen, R.; Sogge, J.; "A Technical and Economic Assessment of Membrane Reactors for Hydrogen and Syngas Production" presented at Seminar on the Ecol. Applic. of Innovative Membrane Technology in the Chemical Industry", Cetraro, Calabria, Italy, 1-4 May **1996**.

<sup>&</sup>lt;sup>3</sup>Mazanec, T.J., *Interface*, **1996**; Mazanec, T.J., *Solid State Ionics*, 70/71, **1994** 11-19; "Electropox: BP's Novel Oxidation Technology", T.J. Mazanec, pp 212-225, in "The Role of Oxygen in Improving Chemical Processes", M. Fetizon and W.J. Thomas, eds, Royal Society of Chemistry, London, **1993**; "Electropox: BP's Novel Oxidation Technology", T.J. Mazanec, pp 85-96, in "The Activation of Dioxygen and Homogeneous Catalytic

partial pressure gradient, oxygen ions move through the dense, nonporous membrane lattice at high rates with 100 percent selectivity. Transported oxygen reacts with natural gas on the fuel side of the ceramic membrane in the presence of a catalyst to produce syngas.

In 1997 BP entered into an OTM Alliance with Praxair, Amoco, Statoil and Sasol to advance the Electropox technology in an industrially sponsored development program. These five companies have been joined by Phillips Petroleum and now are carrying out a multi-year \$40+ million program to develop and commercialize the technology. The program targets materials, manufacturing and engineering development issues and culminates in the operation of semi-works and demonstration scale prototype units.

The Electropox process represents a truly revolutionary technology for conversion of natural gas to synthesis gas not only because it combines the three separate unit operations of oxygen separation, methane oxidation and methane steam reforming into a single step, but also because it employs a chemically active ceramic material in a fundamentally new way. On numerous fronts the commercialization of Electropox demands solutions to problems that have never before been accomplished. Basic problems in materials and catalysts, membrane fabrication, model development, and reactor engineering all need solutions to achieve commercial success.

Six important issues have been selected as needing understanding on a fundamental level at which the applied Alliance program cannot achieve the breadth and depth of understanding needed for rapid advancement. These issues include

- 1. Oxygen diffusion kinetics (University of Houston)
- 2. Grain structure and atomic segregation (University of Illinois Chicago)
- 3. Phase stability and stress development (University of Missouri Rolla)
- 4. Mechanical property evaluation in thermal and chemical stress fields (University of Alaska Fairbanks)
- 5. Graded ceramic/metal seals (Massachusetts Institute of Technology)

Oxidation", D.H.R. Barton, A. E. Martell, D.T. Sawyer, eds, Plenum Press, New York, **1993**; "Electrocatalytic Cells for Chemical Reaction", T.J. Mazanec, T.L. Cable, J.G. Frye, Jr.; Prep Petrol Div ACS, San Fran, **1992** *37*, 135-146; T.J. Mazanec, T.L. Cable, J.G. Frye, Jr.; Solid State Ionics, **1992**, 53-56, 111-118.

#### Statement of Work

Task 1	Design, fabricate and evaluate ceramic to metal seals based on graded ceramic powder / metal braze joints.
Task 2	Evaluate the effect of defect configuration on ceramic membrane conductivity and long term chemical and structural stability.
Task 3	Determine materials mechanical properties under conditions of high temperatures and reactive atmospheres.
Task 4	Evaluate phase stability and thermal expansion of candidate perovskite membranes and develop techniques to support these materials on porous metal structures.
Task 5	Assess the microstructure of membrane materials to evaluate the effects of vacancy-impurity association, defect clusters, and vacancy-dopant association on the membrane performance and stability.
Task 6	Measure kinetics of oxygen uptake and transport in ceramic membrane materials under commercially relevant conditions using isotope labeling techniques.

#### Task 1 & 2Development of Ceramic Membrane/Metal Joints

#### Prof. Thomas W. Eagar, Dr Harold R Larson, Mr Raymundo Arroyave and Ms Jocelyn L. Wiese

All the tasks of the project has been completed in the previous quarter. A comprehensive summary of the accomplished tasks has been submitted in the final report.

## **TASK 3:** Determine material mechanical properties under conditions of high temperature and reactive atmosphere

#### Prof. Sukumar Bandopadhyay and Dr. Nagendra Nagabhushana University of Alaska Fairbanks

In the present quarter, the hardness and fracture toughness of the materials were evaluated as a function of reducing conditions. In addition, initial experiments were attempted to create a gradient conditions across the wall of the membrane tube. The results and fracture mechanism are analyzed.

#### Hardness and Indentation Fracture toughness of membranes

The fractured samples tested in four different conditions: Air at RT and 1000°C, N<sub>2</sub> at 1000°C and 90%CO<sub>2</sub>/10%CO at 1000°C, were mounted and polished to 0.25µm finish. The Vickers hardness (*H*) and the fracture toughness ( $K_c$ ) were measured by applying varying loads (.98 N – 9.8 N) for 15 s. The diameters and crack lengths of twenty indents in each materials were evaluated using the formula:

$$K_{c} = 0.032 H a^{\frac{1}{2}} \left(\frac{E}{H}\right)^{\frac{1}{2}} \left(\frac{l+a}{a}\right)^{\frac{-3}{2}}$$

Where 2a is the indent diameter and l is the crack length measured from the indent tip to the crack tip

A typical micrograph of the indent with lateral cracks extending from the tips of the indent is shown in figure 1. The measured hardness and fracture toughness are tabulated in Table 1.



Figure 1: Vickers indent in the material for fracture toughness studies. The arrows mark the crack extending from the indent tip and used for computing fracture toughness.

Table 1:	Hardness and	Fracture toug	hness as a t	function of	f reducing	conditions

Test conditions	Hardness	Toughness (K <sub>c</sub> )	Normalized
	UI a	IVIF a VIII	Toughiness
As received	4.34±0.18	1.2 ±0.3	1
Air, RT	5.52±0.15	0.9±0.3	0.75
Air , 1000°C	5.43±0.22	0.1±0.015	0.08
N <sub>2</sub> at1.7 MPa and	4.02±0.10	0.14±0.01	0.11
1000°C			
CO <sub>2</sub> /CO at1.7 MPa	4.24±0.13	0.12±0.012	0.1
and 1000°C			

The hardness of the perovskite membrane in the as received condition was  $4.34\pm0.18$  GPa. Well-formed lateral crack extended from the tips of the indent al loads of 4.8 N. At higher loads 9.8 N a transition to a damage mode was observed. The fracture toughness was measured as  $1.2 \pm 0.3$  MPa $\sqrt{m}$ . The membrane after testing and fractured showed an increase in hardness to 5.52 GPa and a marginal decrease in fracture toughness was also observed.

Sample tested in Air at 1000°C indicated a similar change in hardness  $(5.43\pm0.22$  GPa) in comparison with as –received samples although, increase variations were noticed in the measured values. However, the fracture toughness showed a drastic drop to nearly 8% of it room temperature value. The cracks emanating from the indent tip were larger and were

observed to be predominant at lower loads of 1.96 N. Upon exposure to more reducing conditions ( $N_2$  and  $CO_2/CO$  at1.7 MPa and 1000°C), a decrease in hardness was observed. The hardness and variation was relatively lower in samples tested in  $N_2$  in comparison to  $CO_2/CO$ . The measured fracture toughness was however higher in  $N_2$  although was drastically reduced form it initial value at room temperature.

The changes in hardness and fracture toughness are probably due to the decomposition of the parent perovskite phase as discussed in the previous reports. The decomposition products and the changes in fracture mechanisms upon exposure to varied reducing conditions have been discussed extensively in earlier reports and are though to be the reason behind the different hardness and toughness degradation observed in the membranes.

#### Fracture Gradients in membrane tubes

In the earlier reports, strength of the membranes has been evaluated in a C-ring geometry as a function of temperature and reducing environment. However, in actual applications the tubes are expected to be in a gradient condition with differing oxygen partial pressures across the thickness of the tube.

The C-ring specimen was tightly enclosed in a platinum foil such that only the tensile portion was exposed to the environment. The sample (as shown in Fig 2) was prepared at room conditions and loaded to fracture in  $N_2$  at 1000°C and 0.17 MPa. In contrast to the always observed multiple fractures in  $N_2$  environment, the sample fractured into two pieces. Microscopic observation in a SEM revealed gradient fracture in the membrane

In the outer surface that is pure tensile, a mixture of predominantly intergranular fracture was observed (Fig 3a). Higher magnification fractograph (Fig 3b) indicated breakdown of the grain and thickening of grain boundaries. In the mid section that is partly tensile and compressive, the fracture was entirely transgranular with isolated pockets of intergranular fracture (Fig 4a). A higher magnified view (Fig 4b) shows typical feature of the fracture as reported in earlier work with the N<sub>2</sub> environment. However, the relief between grain boundaries was not very prominent as observed in regular specimens fractured in N<sub>2</sub>. Fracture at very close to the inner surface were observed to be a mix of inter and trans granular fracture (Fig 5a). In this case, the transgranular predominated over intergranular fracture and possible is due to the influence of compressive stresses as reported for the specimen geometry.

The fracture morphology and mechanism have been attributed to the non-equilibrium segregation of elements upon exposure to reducing conditions. A detailed study will be done to characterize the microscopic segregation of elements resulting in gradient fracture.



Figure 2: Cross section of a C-ring specimen enclosed in Pt foil to create a gradient condition.



Figure 3 Mix of *Inter-* and *trans-* granular fracture observed in the outer tensile region. Breakdown on an individual grain into smaller grains evident in (b)



Figure 4 *Trans-* granular fracture observed in mid section of the tube. The typical accentuated relief as observed in membranes fracture in N<sub>2</sub> are beginning to form (b)



Figure 5 Mix of *trans* and *inter* – granular fracture at the inner surface of the ring.

# Task 4:Preparation and Characterization of Dense Ceramic oxygenPermeable Membranes

#### **By: Professor Harlan Anderson, University of Missouri-Rolla** Dr. Wayne Huebner, Dr. Xiao-Dong Zhou

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# Task 5:Measurement of Surface Activation/Reaction rates in IonTransport Membranes using Isotope Tracer and Transient Kinetic<br/>Techniques.

#### Prof. Alan Jacobson, University of Houston/University of Toronto

All the tasks of the project has been completed in the previous quarter. A comprehensive summary of the accomplished tasks has been submitted in the final report