Oxygen Transport Ceramic Membranes

Quarterly Report

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Table of Contents

ABSTRACT

In the present quarter, oxygen transport perovskite ceramic membranes are evaluated for strength and fracture in oxygen gradient conditions. Oxygen gradients are created in tubular membranes by insulating the inner surface from the reducing environment by platinum foils. Fracture in these test conditions is observed to have a gradient in *trans* and *inter*-granular fracture as opposed to pure trans-granular fracture observed in homogenous conditions. Fracture gradients are reasoned to be due to oxygen gradient set up in the membrane, variation in stoichiometry across the thickness and due to varying decomposition of the parent perovskite. The studies are useful in predicting fracture criterion in actual reactor conditions and in understanding the initial evolution of fracture processes.

DISCLAIMER

Executive Summary

Conversion of natural gas to liquid fuels and chemicals is a major goal for the Nation as it enters the 21st 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.[1] 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.[2]

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.[3] Under the influence of an oxygen partial pressure

[1]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.**

[2]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**.

[3]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 Oxidation", D.H.R. Barton, A. E. Martell, D.T. Sawyer, eds, Plenum Press, New York, **1993**; "Electrocatalytic Cells for

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)

Statement of Work

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.

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 & 2   Development 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

Introduction

In a membrane reactor, the oxygen partial pressure (chemical potential) of the gas atmospheres on the two sides of the membrane typically varies from 0.21atm on the air side to as low as 10^{-17} atm on the methane side. As shown in Fig 1, the oxygen chemical potential at any point in or on the solid under steady state operating conditions is the result of dynamic balancing of the rates of each sequential oxygen transfer process along the path. Oxygen molecules are activated at the surface of the membrane on the airside and move through the membrane via coupled transport of oxide ions and electron holes. On the low partial pressure side of the membrane, oxide ions are available for direct oxidation of methane to synthesis gas or for recombination to form oxygen molecules, which may then subsequently react with the various gas species present on the fuel side. Thus in principle, any part of the oxide membrane can experience oxygen activities which cover the entire range. The entire solid will experience the conditions of the airside if the reaction of surface oxygen at the fuel side is rate limiting. In this case, all regions of the membrane (towards the air side) can be in partial equilibrium with air. At the other extreme, if oxygen activation is rate limiting, the entire solid operates under the reducing conditions of the fuel side. If oxygen transport through the solid is rate limiting, then a gradient across the solid between the two extremes is present. In all cases, the key kinetic parameters, surface reaction rates, oxygen diffusion, and electronic conductivity depend on the oxygen activity.

In earlier reports, issues such as mechanical strength, stability and fracture behavior of the membranes upon exposure to reducing conditions have been addressed. The results indicate an inherent dependence of strength on the stability of the microstructure as a resultant of changes in oxygen content in the structure. However, in gradient conditions, the resultant oxygen gradient can create a lattice mismatch across the ceramic bulk due to oxygen enrichment (air side) or depletion (reducing side), with concurrent expansion or contraction of the lattice, respectively. Failures arising from this conditions have been reported in studies on discs exposed to gradient

conditions. In the present study, fracture evolution in LSFCO membranes has been characterized in partially gradient conditions. A partially gradient condition has been created by insulating one of the surfaces with Platinum foils and the oxygen partial pressure (P_{O_2}) varied on the reducing side. The resultant fracture morphology is characterized by Scanning Electron Microscopy [SEM] and correlated with earlier observations on phase transition, defect structure and oxygen fluxes.

EXPERIMENTAL PROCEDURE

LSFCO membranes of the general composition $La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-\delta}$ were evaluated in three different environments: air at room temperature, 0.17 MPa N_2 at 1000°C and in 0.17 MPa CO_2/CO (90/10) at 1000°C. The test conditions corresponded to oxygen partial pressure of $\log_{PO_2}$ =(-0.7), $\log_{PO_2}$ = (-4) and $\log_{PO_2}$ = (–12.1) respectively. The rings were soaked for a period of 15 mins. at the testing temperature prior to application of load. Additional tests were done on C-rings insulated by Platinum foils such that only the tensile surface were exposed to the atmosphere. After testing, the fractured surfaces were examined under a Scanning Electron Microscope (SEM) with an attached Electron Dispersive X-ray analysis (EDX) to characterize the dominating flaws and fracture mechanisms. The outer surfaces exposed to the environment were analyzed to determine phases separation if any in a Seimens D5000 θ/θ diffractometer using Cu radiation at 40kv/30 ma. The samples were tested in a parallel beam arrangement to minimize the displacement errors caused by the curved surfaces.

RESULTS

Unique strength values for the material in the insulated specimen geometry could not be determined due to significant contribution from the Platinum foils. At room temperature, the strength values were consistently higher by approximately 50% and similar values were observed at elevated temperatures. Fracture analysis as shown in Fig. 5 indicated a gradient morphology with three distinct fracture regions. In N_2 (Fig. 2 a), a region (~ 25μm) very close to the surface exhibits entirely transgranular fracture and is followed by a region (~250μm) with a mix of transgranular and intergranular fracture. The interior of the membrane is entirely transgranular cleavage and extends up to ~ 600μm. This region is again followed by a mix of inter- and trans-granular fracture leading to complete transgranular failure at the inner wall surface. In CO_2/CO (Fig. 2b), similar features are observed. The first region extends to only ~ 100μm and is followed by a mid region with a mix of inter- and trans- granular fracture extending over larger distance (~ 750 μm). Transgranular fracture dominates in the beginning of the region leading to a more pronounced intergranular fracture. This conditions leads to the third region (~150 μm) with a small region of transgranular fracture at the surface. A higher magnification study of the comparative effect of environment on the fracture morphology in the three region is shown in figure 3.

Regime I: In N_2, the initial region of transgranular mode is characterized by enrichment of Sr at the grain boundaries. With appearance of grains fracture in intergranular mode (Fig. 3a), a concurrent change in elemental distribution is observed. In CO_2/CO, significant precipitation of second phase is observed in grains fracture in a transgranular mode (Fig. 3b). The overall structure appeared to be very similar to that observed in earlier studies in the environment and as

8

shown in earlier reports. The precipitates are relatively coarse with a size distribution varying from 0.25-1.5µm. The precipitation is high at near the surface (fully transgranular fracture mode) and reduces away from the surface. Single grains fractured in a intergranular mode in N_2 (Fig. 4a) indicated a clear breakdown in structure. On the other hand, grains fractured intergranularly in CO_2/CO (Fig. 4b) showed clean surfaces and edges. Formations of precipitates on the surfaces were clearly in evidence.

Regime II: In N_2, characteristic transgranular fracture of the perovskite grains was observed (Fig. 3c). The grain indicated beginning of formation of banded structure. However, the conspicuous thickening of the grain boundaries as seen in earlier studies on fracture was absent. In CO_2/CO, grains fractured in a transgranular mode indicated precipitation of a second phase at the grain boundaries (Fig. 3d)

Regime III: In N_2, although the fracture was a mix of trans- and inter-granular fracture was characteristically different from region I. The grains appear to have broken down aided by formations of very coarse precipitates (Fig. 3e). Overall, the structure appeared to similar to that of fracture in air with the coarse particles corresponding to the brittle $(La,Sr)Fe_{12}O_{12}$ phase. In CO_2/CO, the region is dominated by intergranular fracture (Fig. 3f). Second phase precipitation is markedly reduced in grains failed in both intra- and trans granular fracture modes

DISCUSSIONS

Earlier reports on the mechanical properties of tubular LSFCO perovskite membranes have reported on the characterization of failure mechanisms and fracture morphology as a function of environment and temperature. At 1000°C, strength degradation is severe in air followed by CO_2/CO and N_2 environment respectively. The strength degradation is accompanied by decomposition of the parent perovskite. The decomposition products are formed as precipitates either at the grain boundaries and/or inside the grains aiding in fracture of the grain and the membranes. Fracture is observed to be transgranular and argued to be assisted by transformation to the Brownmillerite or Laves phases depending on the test temperature. In the evaluation of fracture in the partially gradient conditions, two important issues are of merit and will be further addressed: i) Stresses in the membrane arising due to tubular geometry and oxygen transport; and, ii) Stresses arising due to differential decomposition of the parent perovskite structures. In the evolution of fracture morphology in the partially gradient conditions, the two factors are observed to be synergistic with a fair degree of complexity. The contributions from the two factors are discussed in subsequent sections.

Stresses arising due to Specimen geometry and Oxygen transport:
Perovskite are characterized by vacancy mechanism of oxide ionic transport. Assuming that at a given gradient of oxygen chemical potential, the phase composition of the oxide is constant, the partial conductivities under isothermal conditions can be expressed as

$$\sigma_o = K_o \times c_o \times [V_O] \times N \qquad\qquad 1$$

$$\sigma_e = K_e \times h \times \frac{N}{3} \qquad\qquad 2$$

where $[V_O]$ and c_o stand for the fraction of vacant and occupied sites in the oxide ion sub lattice; N is the concentration of oxide ion sites; h x $(N/3)$ is the concentration of holes (h is a relative concentration of holes); K_o and K_e are constant. In accordance with the equation for oxygen entering and leaving the crystal lattice

$$\frac{1}{2}O_2 + V_{\ddot{o}} \Leftrightarrow O^x + 2\dot{h} \qquad\qquad 3$$
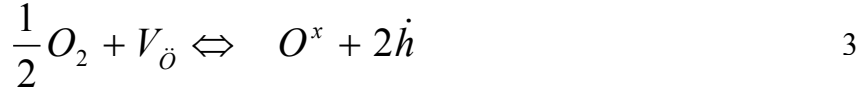
with h$^\bullet$ being an electron hole), the concentration of oxide ions and vacancies in terms of point defects model are related by the expression

$$K_p = \frac{\sqrt{p} \times [V_O]}{c_o \times h^2} \qquad\qquad 4$$

$$K_g = \frac{h}{3} + 2[V_O] \qquad\qquad 5$$

$$[V_O] + c_o = 1 \qquad\qquad 6$$

Where K_p and K_g are constants; p is the partial pressure of oxygen. In accordance with eqn (1), the density of the molecular oxygen flow passing through a ceramic material under the action of the chemical potential difference can be expressed as follows

$$J = K_m \int_{c_1}^{c_2} \frac{\sigma_o \times \sigma_h}{\sigma_o + \sigma_h} \times \frac{d(\ln p)}{dc_o} dc_o \qquad\qquad 7$$

Where $K_m = (RT)/(16F^2d)$, c_1 and c_2 are the values of c_o in the surface layers of the membrane

To date, published models have assumed constant properties (for example, a simple first order rate constant for oxygen surface activation and a single value of the diffusion coefficient). Clearly, if the surface and bulk transport rates have a strong dependence on the oxygen activity, these models will contain significant errors and will not provide reliable predictions especially when the P_{O_2} gradient is large as is the case for syngas generation. The distribution of the P_{O_2} gradient depends on the relative rates of the surface and bulk processes and consequently kinetic data for the whole range of partial pressures is relevant. In case B, the left hand surface is neither

at the oxygen potential of the bulk or of the gas phase and the surface exchange kinetics may exhibit different values from either. To model this results for $La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-x}$ Initial values of D_{chem} and k_{chem} of 4.1 x 10^{-6} cm^2/s and 6.8 x 10^{-4}cm/s were obtained from earlier reports. Work is currently in progress to evaluate the amplification of stress due to transport of oxygen vacancies along the thickness of the membrane.

Stresses due to decomposition of the parent perovskite
The perovskite structure, with the general formula ABO_3, is a simple cubic system having one formula unit per unit cell. The B cation is octahedrally coordinated to six oxygen ions, and these octahedra are corner-shared. The A cation occupies the space between eight octahedra and has twelve nearest-neighbor oxygen ions. Thus, there are many possible distortions of the perovskite structure depending on the relative sizes of the A and B cations. Replacement of the A cation with cations of lower charge (A') begins to distort the perovskite crystal structure through the introduction of oxygen vacancies into the lattice. Likewise, replacing the B cation with B' affects the crystal structure. The resulting material is an intergrowth of perovskite and a material termed brownmillerite $(AA'BB'O_5)$ in which (due to oxygen vacancies) some of the B cations are tetrahedrally bound to oxygen rather than octahedrally. The transformation of the crystal structure from the cubic perovskite structure to the orthorhombic perovskite-brownmillerite intergrowth results in a change of structural dimensions. Changes in temperature results in additional mechanical stresses since the cubic perovskite structure undergoes uniform isometric changes in all dimensions, whereas the brownmillerite pseudomorph undergoes anisotropic changes due to its orthorhombic crystal habit.

Replacement of La^{+3} on the A sites by divalent ions such as strontium (Sr^{+2}) results in materials with increased oxygen permeability. Increase in strontium content, however, has detrimental structural effects upon the crystal lattice. The thermal expansion increases with increasing strontium contents, which is consistent with the theory of cubic perovskite to orthorhombic brownmillerite transformation. The B site cations (Cr, Fe) in these substituted perovskites frequently exhibit unusually high oxidation states, which have been stabilized by the unique crystal structure. Therefore, chromium can exist as Cr^{+3}, Cr^{+4}, and Cr^{+6}, iron as Fe^{+3} and Fe^{+4}. Since, a trivalent ion is required for charge satisfaction in $LaMO_3$, reduction to a lower oxidation state will result in a brownmillerite structure, and hence oxide conduction. As the atomic number increases, the stability of the trivalent state decreases. Therefore, the trivalent oxidation states of Cr and Fe can be considered fairly stable. The crystal structures of many of the solid solutions of $(LaA')(B'B'')O_3$ compounds indicate phase transformations from cubic to orthorhombic/tetragonal/rhombohedral as the crystal lattice is subjected to temperature profiles. Likewise, a large number of CTE have been determined for these systems. Slight changes in crystal structure can thus introduce point defects into the material matrix and. mismatches in CTE could further aid in failure. These effects on the evolution of fracture gradients are being investigated.
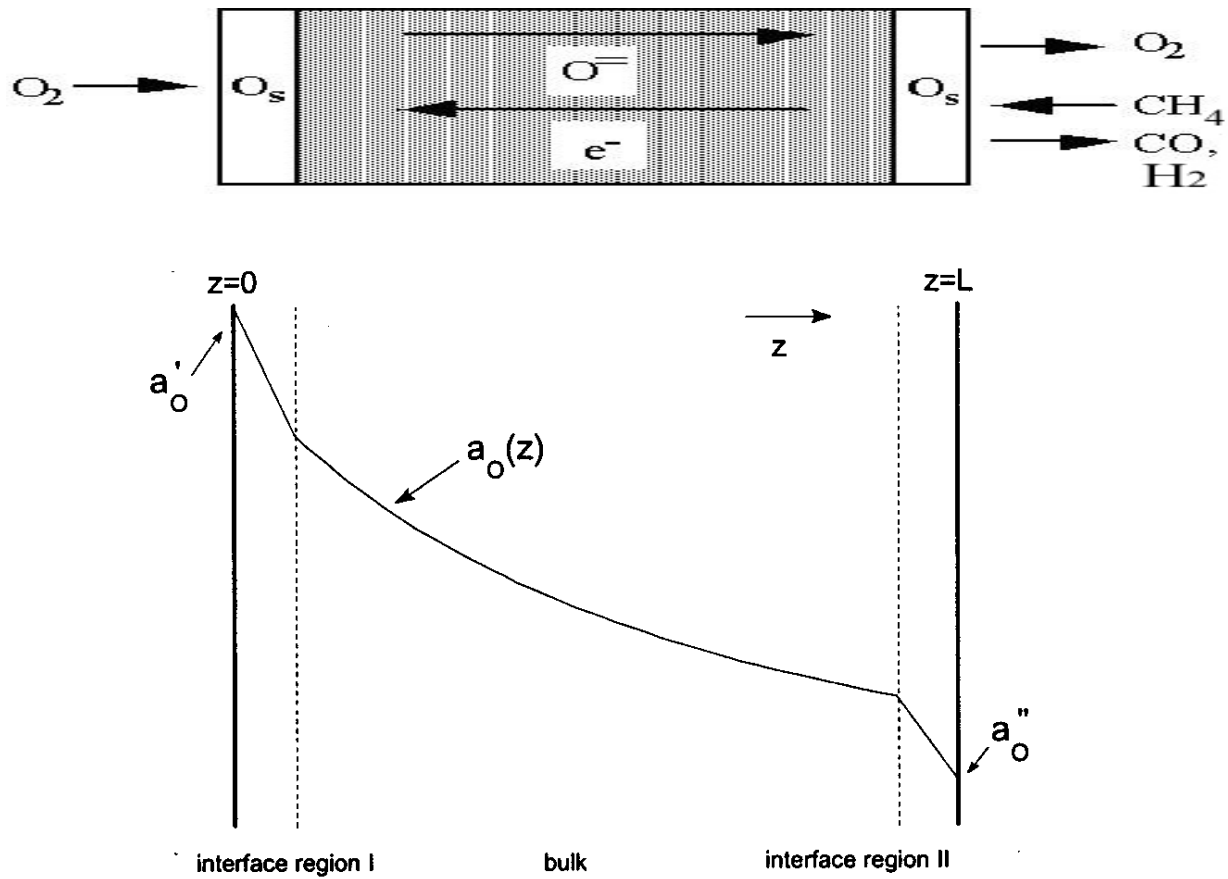
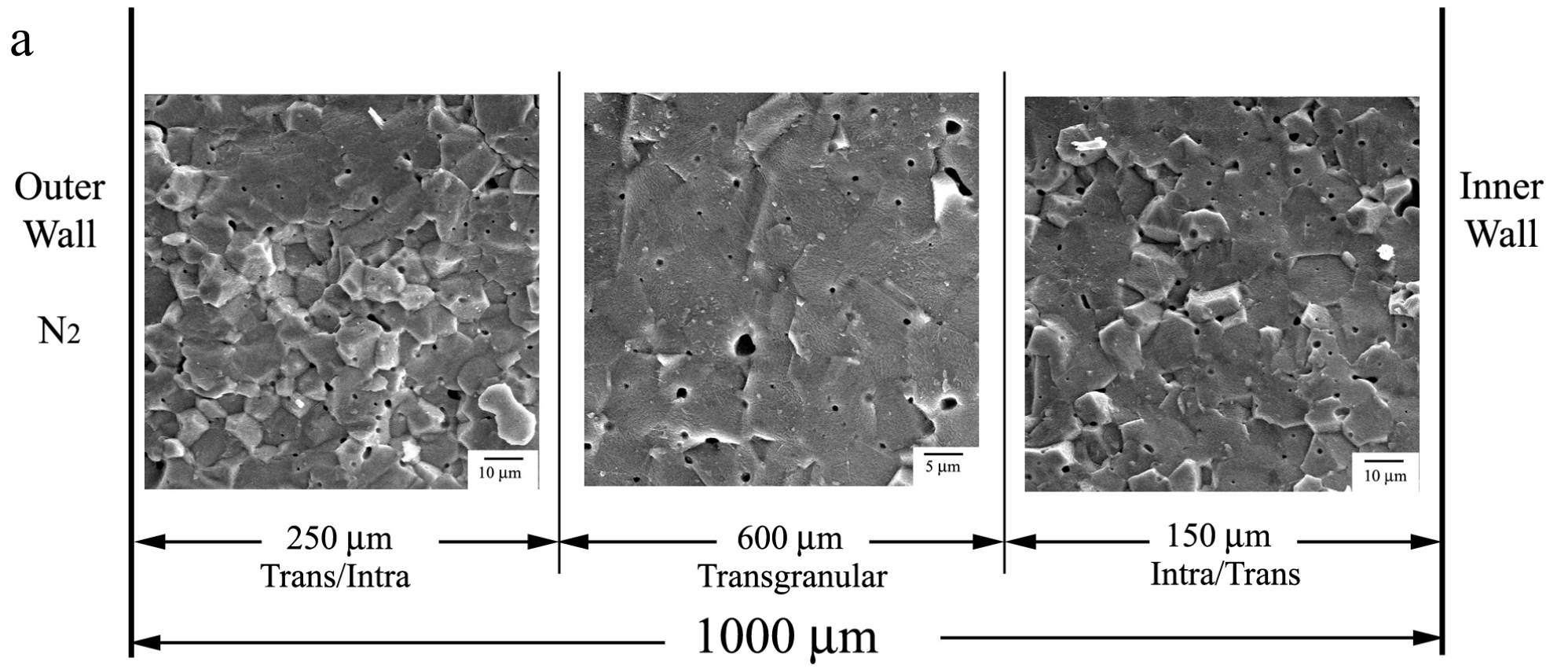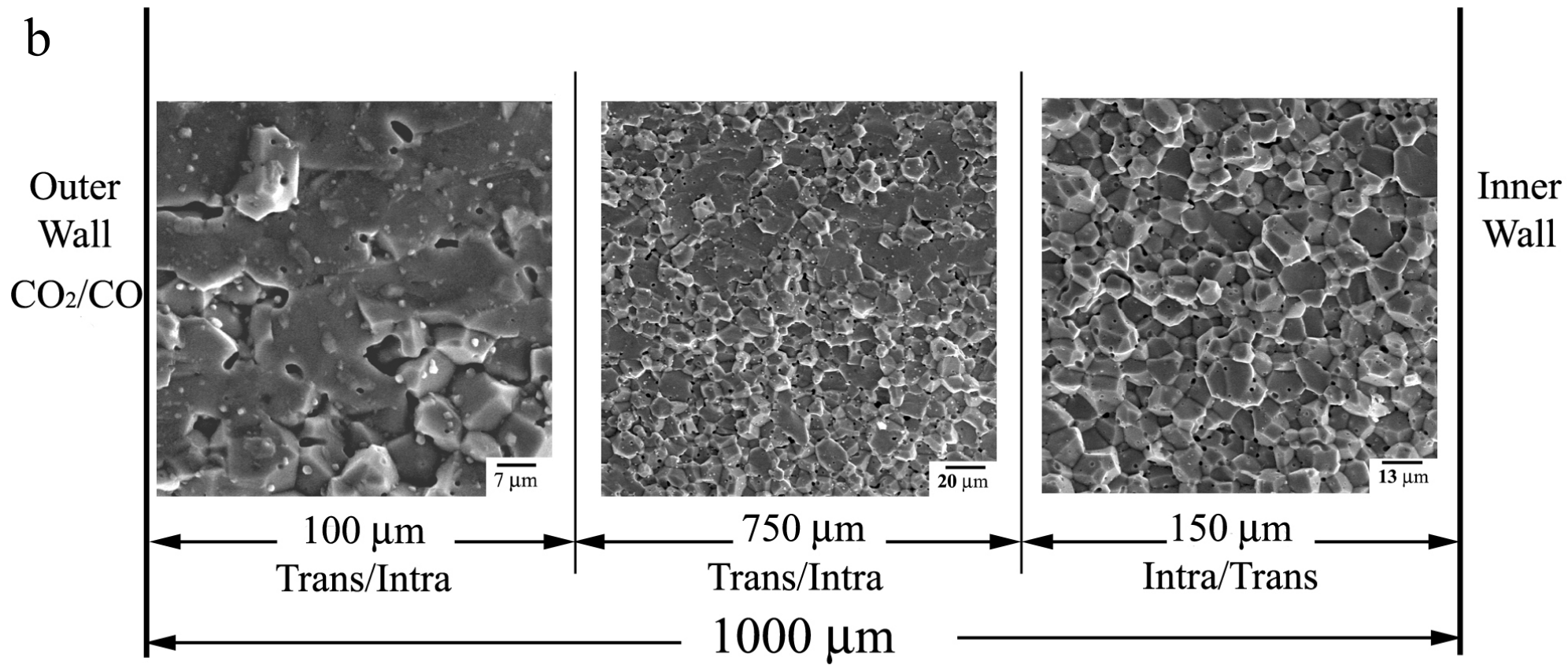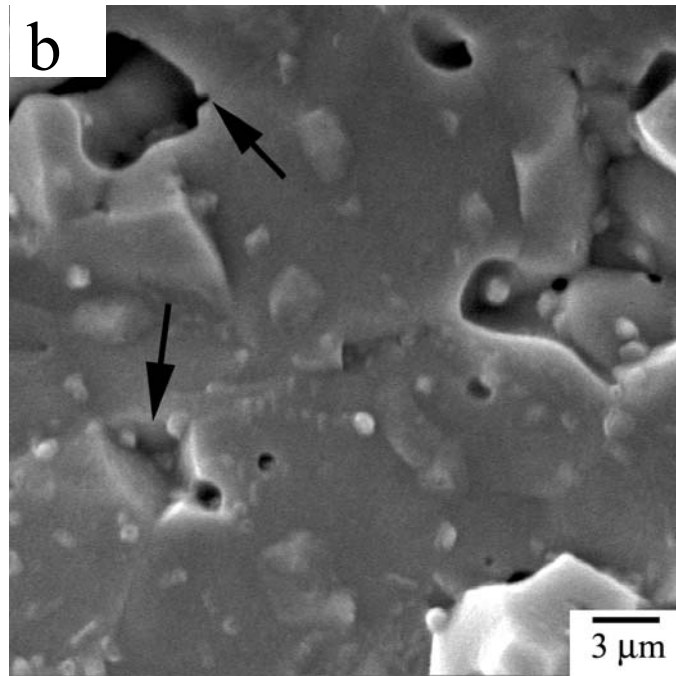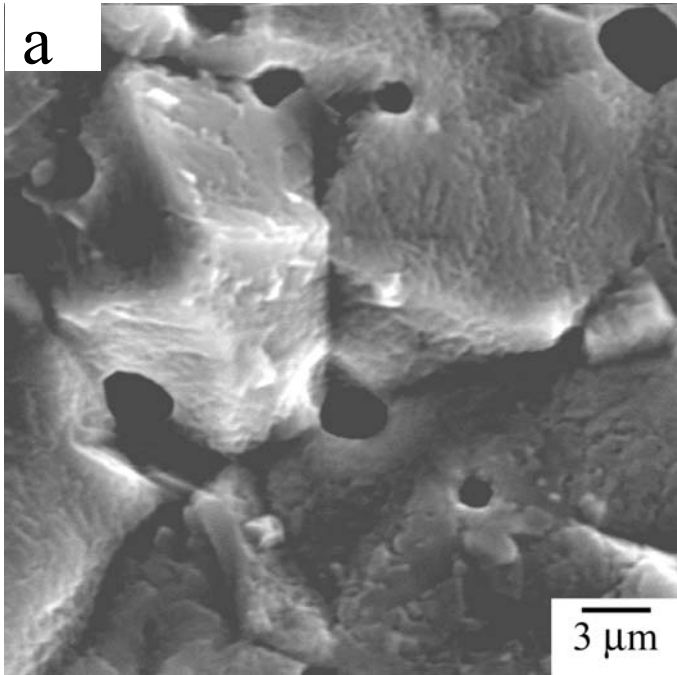Fig. 1:   A schematic diagram of a membrane reactor.

Fig 5a:

b

Outer
Wall

CO_2/CO

Inner
Wall

|←——— 100 µm ———→|←——— 750 µm ———→|←——— 150 µm ———→|
Trans/Intra   Trans/Intra   Intra/Trans
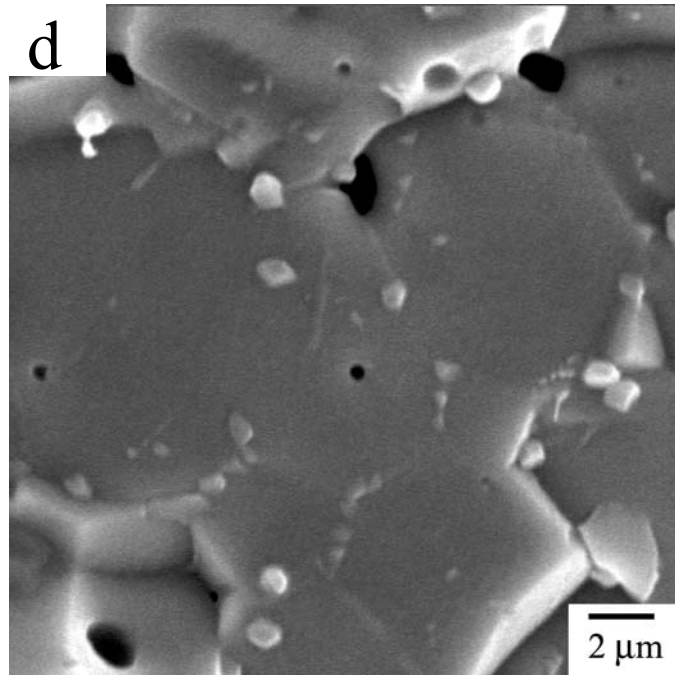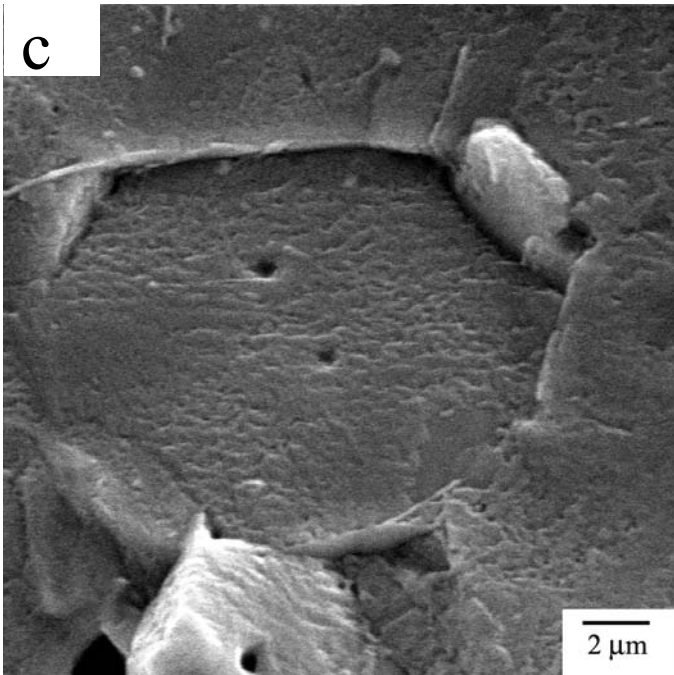
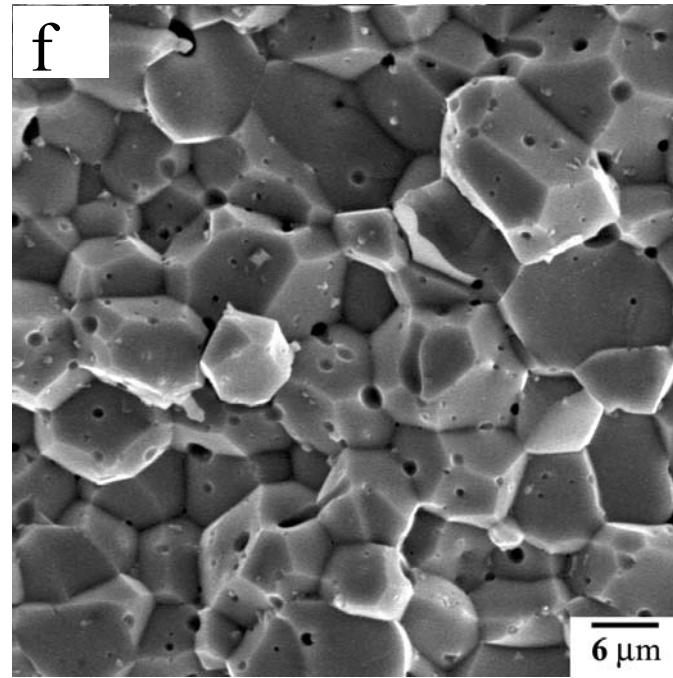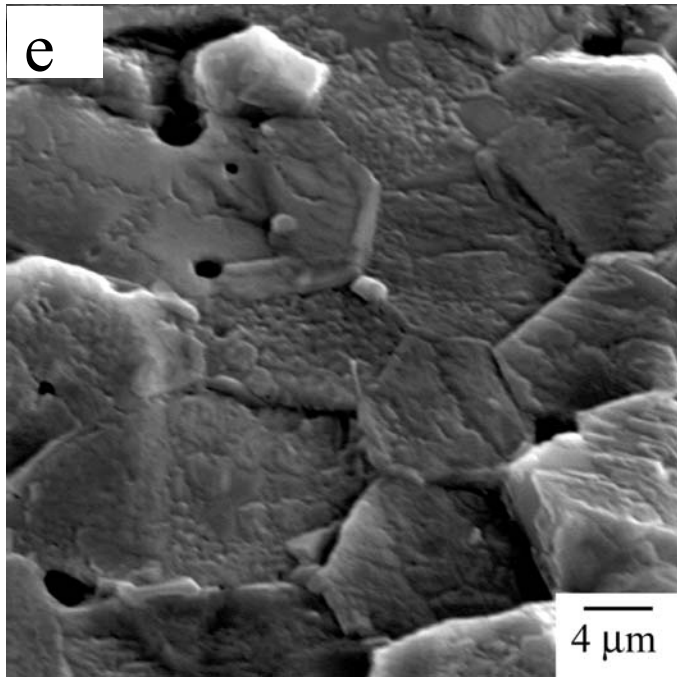|←——————————————— 1000 µm ———————————————→|

Fig. 5b:

Fig. 6:	Higher magnification viewgraphs of gradient fracture in reducing conditions. (a), (c) and (e) are in Nitrogen and (b), (d) and (f) are in 90%CO_2/CO atmosphere.
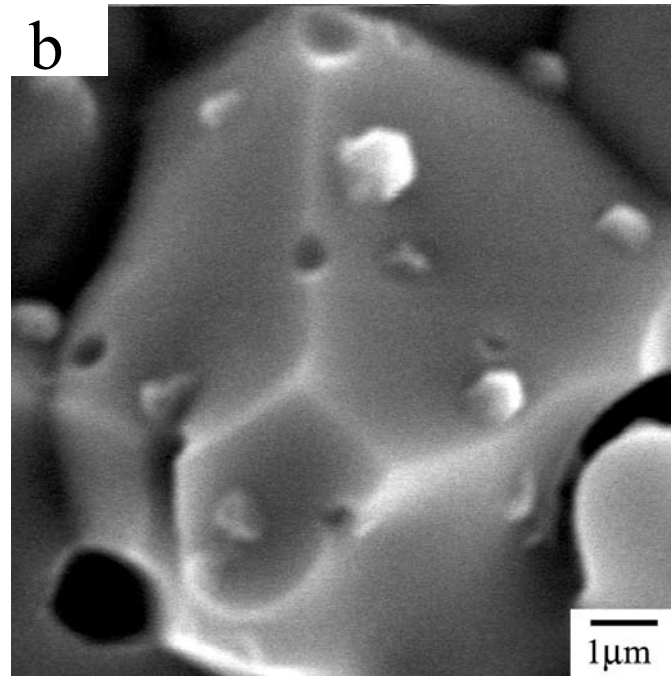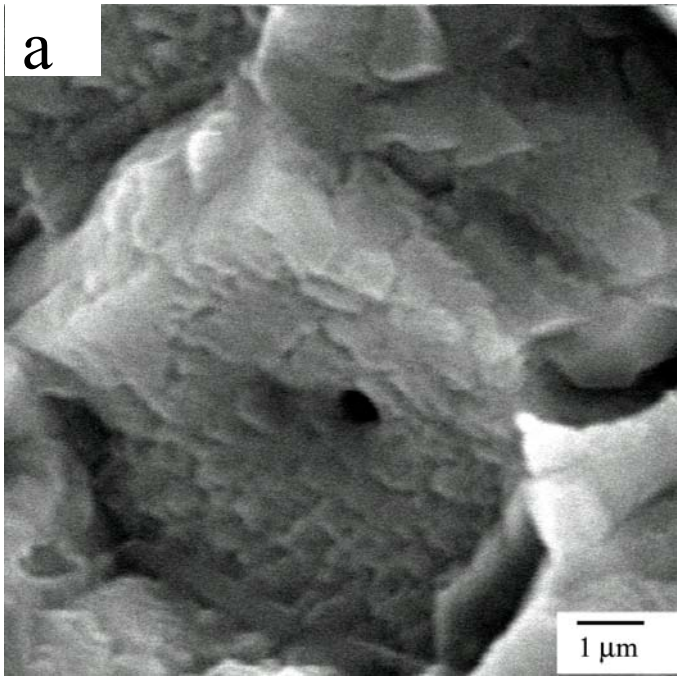
Fig. 7: Intergranular fracture observed in a) Nitrogen and (b) 90%CO_2/CO environment. In Nitrogen, the grains are broken down while in CO_2/CO fine precipitates of SrO are formed on the surfaces of the grain.

Task 4:   Preparation and Characterization of Dense Ceramic oxygen Permeable Membranes

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

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 5:   Assessment of Microstructure of the Membrane Materials to Evaluate the Effects of vacancy-Impurity Association, defect Clusters, and Vacancy Dopant Association on the Membrane Performance and Stability

Professor Nigel Browning, University of Illinois Chicago Circle

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 5:   Measurement of Surface Activation/Reaction rates in Ion Transport Membranes using Isotope Tracer and Transient Kinetic 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