Oxygen Transport Ceramic Membranes

Quarterly Report

July- September 2002

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Issued: January 2003

DOE Award # DE-FC26-99FT400054

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ABSTRACT

In the present quarter, the possibility of using a more complex interfacial engineering approach to the development of reliable and stable oxygen transport perovskite ceramic membranes/metal seals is discussed. Experiments are presented and ceramic/metal interactions are characterized. Crack growth and fracture toughness of the membrane in the reducing conditions are also discussed. Future work regarding this approach is proposed and 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.

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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 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

¹Mazanec, 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**.

²Bredesen, 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**.

³Mazanec, 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

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ABSTRACT

The possibility of using more complex interfacial engineering approaches to the development of reliable and stable perovskite/metal seals is discussed. Experiments are presented and ceramic/metal interactions are characterized. Future work regarding this approach is proposed.

PREVIOUS WORK

In previous experiments with $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$, it has been observed that the reaction zone at the ceramic substrate was approximately 100 microns thick. The ceramics used previously had been pressureless sintered at high temperatures. In these past experiments, it was observed that the main result from the reaction between Ni-based brazing alloys and the ceramic substrate was the segregation of Fe from the ceramic lattice:

Figure 1 Perovskite/Metal Interactions $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$

In these experiments, Fe “islands” precipitated in the region close to the reaction zone and extensive segregation of Sr and La towards the interface with the metal was observed. Despite promising results, it was observed that there was a tendency for crack formation at the region close to the interface with the braze. This crack formation was attributed to the extensive decomposition undergone by the ceramic substrate when in contact with the braze.

As it became evident that the extent of the reaction needed to be limited somehow, the focus of the experimental program was switched to the creation of diffusion barriers on top of the ceramic substrate. These diffusion barriers would be able to still promote adhesion to the perovskite surface but at the same time would limit the extent of the reaction with the braze.

In order to test the concept of diffusion barriers, the depositing of Chromium through PVD means was considered. If the joint were to be held at high temperatures for long enough time, we

speculated that the Cr layer would partially reduce a localized region of the Perovskite substrate very close to the interface with the braze. The migration of oxygen from the Perovskite substrate into the Cr layer would then lead to the formation of a protective Cr_2O_3 that would function as an oxygen diffusion barrier. To test the concept, we created several joints using RF sputtering to deposit layers about 10 microns thick on the substrate layers:

**Figure 2 Perovskite/Cr/Ni-N/Inconel Joint.
SEM , secondary electron image.**

**Figure 3 Perovskite/Cr/Ni-N/Inconel Joint.
SEM , backscattered image.**

From the figures above, it can be observed that an interface was formed between the braze metal and the perovskite surface. Contrary to our expectations, though, the Cr layer sputtered on the ceramic surface was somehow dissolved by the braze and the reaction with the ceramic was rather extensive (the reaction zone was almost as wide as in the previous series of experiments). One of the possible causes for this excessive reaction is the excessive porosity of the samples used. From the analyses of the samples it was obvious that the Cr layer was not being able to prevent further penetration of the braze into the Perovskite substrate. Since the braze was able to penetrate deep into the porous network of the substrate the extent of the reaction zone was basically limited by the permeation rate across the porous media and any slowing process due to solid-state diffusion phenomena was insignificant by comparison.

NEW APPROACH:

We determined that it was necessary to find other options, probably more complex, in order to prevent this excessive reaction between the perovskite and the braze. By limiting the extent of this reaction, the mechanical integrity of the membrane would not be compromised and the reliability of the entire system would also be improved. Figure 4 presents the concept that we have been exploring so far:

Figure 4 Interfacial Modification of Perovskite Membranes

Figure 4 depicts a rather complex interfacial structure that could allow the formation of a strong, stable interface between a perovskite ceramic and a nickel-based super alloy:

Based on the recent progress done by the University of Missouri-Rolla regarding the deposition of ceramic coatings on perovskite substrates it is believed that a ceramic oxide such as ceria or zirconia-based coating could be used as an effective diffusion barrier to prevent excessive interaction between the braze and the perovskite membrane.

A stable ceramic such as ceria or zirconias have the problem that, due to their relatively low surface energy, they do not tend to be wetted by molten metals, such as Ni-based braze alloys. A further processing of such composite interfaces is thus needed to promote wetting. One option is the use of active coatings (materials with high oxygen affinity) that would promote the formation of a stable interface between the ceramic substrate and the Ni-braze:

Figure 5 Zirconia/Inconel Joint: Use of active coating and Ni-based super alloy

Figure 5 depicts a zirconia/Ni-based super alloy joint created using the process described above: A relatively thin Ti coating was deposited on top of the zirconia substrate and a Ni-based amorphous foil was placed between the coated zirconia sample and the Ni-based super alloy. The process was designed so at a relatively high temperature, the Ti coating would react with the zirconia and produce a Ti-based oxide that could in turn be wetted by the Ni-braze. Oxygen

vacancies were created within the zirconia lattice and oxygen migration was promoted due to the large oxygen potential gradient across the zirconia/Ti interface. Once the Ti-oxide layer was formed, the joint was heated up until the solidus-liquidus two-phase region of the Ni-based braze alloy was reached. The liquid wetted the Ti oxide and a stable interface between the Ti-O coating and the Ni-based was created. As can be seen from the figure above, no interfacial defects were observed at the joint.

One of the advantages of using Ni-based brazing alloys is the fact that this alloy system usually uses both Si and B as melting point depressants. This means that in theory, it is possible to create the joint at one temperature and then let Diffusional processes drive the melting point depressants out of the Ni-based interlayer and into the base materials (in this case the Ni-based super alloy). Since B is a fast diffusant and has the greatest effect regarding the depression of the liquidus surface in the Ni-B-Si system, it is expected that by heat-treating the joint at temperatures comparable to the joining temperature it is possible to achieve isothermal solidification of the interface. This implies that the actual maximum operating temperature of the joint could be actually higher than the joining temperature.

Figure 6 Ni-B-Si Ternary System: Liquidus Surface

Figure 6 illustrates the primary surface of solidification for the Ni-B-Si system. The Ni barzes being used in this project lie at the Ni-rich corner of the diagram, and from the figure it can be seen how the liquidus surface descends with a great slope as the amount of Si and B increase.

Figure 7 EDS Analysis of Zirconia/Ni Super Alloy Joint

Figure 7 shows the back-scattered image of one of the zirconia/Ni-based super alloy joints created with the technique outlined above and a table showing the atomic concentrations of different elements at different regions of the joint. Point number 1 corresponds to the Ni-based super alloy, while point number 2 corresponds to the braze. It is important to note that the initial Cr content of the braze alloy is around 7%. As can be seen, the Cr content, after creating the joint, has increased noticeably, which implies that the oxidation resistance of the braze alloy is also improved once the joint has been created. Point 6 corresponds to the Ti-O coating formed after zirconia has been partially reduced and oxygen ions have migrated towards the lowest oxygen chemical potential region (Ti). One interesting feature to note is the fact that the Ti coating was not dissolved by the braze, which means that this approach can create effective diffusion barriers that would prevent the braze alloy from further reacting with the perovskite substrate.

Figure 8 Compositional Profiles across Zirconia/Ni-braze Interface

Figure 8 illustrates the compositional profile across the Zirconia/Ni braze interface. It can be seen how Zr is being dissolved into the braze, which can be explained by a localized transformation of the zirconia lattice into zirconia + Zr metal, plus a very negative Gibbs free energy of dilution of Zr in a Ni-based liquid alloy. From the figure, the Ti peak is a clear proof of the relative stability of the Ti-O coating against further dissolution by the Ni-based braze. The Cr-profile illustrates the further Cr enrichment of the braze alloy, which in turn would have great effects on the overall oxidation resistance of the braze.

FUTURE WORK

In the future, similar joints with concentric geometries will be created and characterized. The sealing abilities of such joints will be evaluated and the long-term stability of ceramic/metal interfaces will be experimentally assessed.

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

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Introduction

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. In this quarter, the toughness of the membranes has been evaluated and the fracture morphology characterized by Scanning Electron Microscopy [SEM]. The results indicate that under similar test conditions, toughness is less sensitive to the environment as compared to strength. In addition, fracture mode transitions are observed that can be possibly linked to localized changes in stress states. The fracture transitions are also observed to be dependent on the magnitude of the residual stresses and occur at close to the surface at shallow cracks.

EXPERIMENTAL PROCEDURE

LSFCO membranes of the general composition $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$ 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 $\log_{p_{\text{O}_2}} = (-0.7)$, $\log_{p_{\text{O}_2}} = (-4)$ and $\log_{p_{\text{O}_2}} = (-12.1)$ respectively. The rings were soaked for a period of 15 mins. at the testing temperature prior to application of load. To evaluate the crack growth characteristics in the membranes, tests were done with a Vickers indent as a starter flaw. The indent formed with 9.8N load was placed on the polished outer surface (tensile mid-plane) of the ring and corresponded to a flaw size of 157 μm . To study the effect of flaw size, indents with different loads were placed in two different conditions: i) individually and ii) in a profile as shown in figure 1. The cracked specimens were then placed in the chamber and loaded to fracture at a constant crosshead speed of 0.5 mm./min. respectively.

RESULTS

The hardness of the as-received material was reported in the earlier reports as 450 VHN (4.4 GPa). Typical median cracks emanating from the indentation were recorded and the fracture toughness was calculated to be in the range of $\sim 1\text{-}1.5 \text{ MPa}\sqrt{\text{m}}$. The cracks did not show an interaction with the microstructure ruling out the possibility of any passive toughening processes. Post fracture indentation crack studies were also reported indicating a drastic drop in toughness upon exposure to reducing conditions.

Figure 1 Pre-Crack profile with Multiple Indents

In crack growth tests with an indent on the tensile mid-plane of the C-ring, failure was catastrophic and the load-displacement curves did not reveal any non-linearity. Since it was not possible to distinguish stable crack growth from the load-displacement curves, crack lengths could not be directly measured. For these samples, the critical strain energy release rate (G_c) during fracture was determined from the integrated area under the load-displacement curve and the cross sectional area of the fractured surface. With an assumed value of $E = 123$ GPa, representative of a similar composition, K_c was determined using the equation

$$K_c = \sqrt[3]{EG_c} \quad (1)$$

The values of G_c and K_c are calculated and tabulated in Table 1. The critical flaw sizes were estimated using the fracture mechanics equation:

$$K_c = Y\sigma\sqrt{c}, \quad (2)$$

Where Y is the factor related to the crack shape (assumed here as 1.4 for a surface flaw and 1.77 for a volume flaw), σ is the measured fracture strength and c is the flaw size. The flaw sizes of the order 0.9 - 4 μm were consistent with the measured flaws in the material.

Table 1: Strain energy (G_c) and fracture toughness (K_{Ic}) as a function of oxygen partial pressure.

Environment	Oxygen Partial Pressure ($\log_{PO_2}$), atm	σ_o MPa	Weibull parameter m	G_c (J/m ²)	K_{Ic} (MPa ^{1/2})
Air (RT)	-0.67	340	4	6.7	0.914
Air (1000°C)	-0.7	-	-	0.15	0.13
N ₂ (1000°C, 0.17 MPa)	-4	188	4.8	0.77	0.30
CO ₂ /CO (1000°C, 0.17 MPa)	-12.1	89	3.8	0.67	0.29

Fracture in the specimen was always observed to initiate from the indent on the tensile midplane of the C-ring. Microscopic observations revealed that under room temperature conditions and in air at 1000°C the fracture initiated from the indented flaws remained transgranular (Fig. 2).

Figure 2. *Transgranular* fracture in LSCFO membranes at room temperature. Crack originating from the indented flaw is visible in (a) and quasi-stable crack growth in (b)

However, in reducing conditions, the surfaces were a mix of intergranular and transgranular fracture modes (Fig. 3a and b). The zone affected by the introduction of a flaw (stress field of the indent) exhibited intergranular fracture, while regions away from zone showed a transgranular mode of fracture. A distinct transition from intergranular to transgranular mode could always be observed. The transition distance varied as a function of the indented load and neared the sample surface at very low loads. Line scan profiles indicated the grain boundary edges in both the reducing conditions were rich in Fe and La and the grain boundary surfaces rich with Fe and Sr. Interestingly, following a transition in the fracture mode, the elemental distribution in grains reverted to the earlier line scan profiles observed in transgranular fracture.

Figure 3: *Intergranular* fracture observed in samples tested in a) N_2 and b) CO_2/CO . The arrow indicates the crack growth direction and transition from Inter to transgranular fracture is clearly marked in (a)

Figure 4: Schematic indication of fracture mode transitions in the LSFCO membranes tested with indented surface flaws.

Effect of induced Flaws

Introduction of a indentation induced flaw into the above system lead to changes in the local stress distribution, the magnitude of which is dependent on the applied indentation load. Expectedly, crack growth for as-indented cracks are much greater than naturally occurring surface flaws (Griffith flaws), because of the additional driving force provided by the residual tensile contact stress. The observed transitions in fracture modes are similar to the fracture behavior in many polycrystalline ceramics wherein transgranular fracture at higher crack speeds is often preceded by regions of intergranular fracture due to sub-critical crack growth. The transitions are prevalent in ceramics prone to weakening of the grain boundaries due to interaction with temperature and environment. In the present case, the tensile residual stresses in the indent's stress field possibly weaken the grain boundaries (enrichment of Fe and La at the grain surfaces) and thus aiding intergranular fracture. Away from the stress field, Sr enrichment and the reported perovskite-brownmillerite transitions possibly leads to compressive stresses at the grain boundaries counteracting the tensile forces driving the crack and resulting in the more typically observed transgranular fracture. Thus upon annealing at low oxygen pressure, Sr enrichment can be assumed to strengthen the grain boundary (compressive) and weaken the grains (tensile). If this condition were true, it could also explain the higher incidence of volume-dominated failure in specimens tested in reducing conditions. Arguably, the compressive stress in the grain boundaries ahead of the natural flaws could arrest them from further growth into the grains. As shown in Fig. 4, fracture toughness (K_{IC}) measurements indicated similar degradation trends as shown by strength measurements. However, the toughness values showed lowered sensitivity as compared to strength to the reducing environment. At 1000°C, a drastic drop of toughness in air was followed by a slight recovery in N₂ and CO₂/CO. Post fracture hardness and indentation toughness previously reported indicated a hardness of 4.4 ± 0.5 GPa and toughness of 1-1.5 MPa $\sqrt{m}$ respectively. At room temperature, upon fracturing under applied load P, the samples indicated an increased hardness and lowered toughness. In samples fractured in reducing environment, any increase in hardness was concomitant with a similar decrease in toughness values (Fig. 4). In general, indentation toughness measurements served to confirm the strength and toughness degradation as a function of oxygen partial pressure.

Further Studies:

Crack growth studies to further validate the observed transitions are planned. To establish stable crack growth, any drop in load vs. displacement data will be observed at lower strain rate. In addition, test will be done at longer soaking periods to establish the effect of environment on crack propagation. Studies are planned to resolve issues such as reason for crack initiation.

Figure 5: Effect of environment on mechanical properties of LSFCO membranes

Design of 4-point flexure fixtures:

As part of the third year study, flexure tests are planned on dense bars of membranes and composite structures. For this 4-point flexure were designed to evaluate in chemical environment. The flexures are designed to test samples of ASTM standard A and Standard D.

Figure 6: Fixtures designed for 4-Point flexure testing of LSFCO bars

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**

INTRODUCTION

The perovskite-type oxides encompass a large variety of chemical compositions that contribute to their diverse and unique properties. Of them, $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ is of particular interest in the applications of gas separation membrane, mixed ionic and electronic conductors and solid oxide fuel cells because of their special structural, electric and magnetic properties. Dann et al.¹ have reported the orthorhombic phase for $0 \leq x \leq 0.2$, the rhombohedral phase for $0.4 \leq x \leq 0.7$ and the cubic phase for $0.8 \leq x \leq 1.0$. Néel temperatures of this series compounds were measured by Shimony et al.² with values from 750K to about 100K as x changes from 0 to 1 and around 300K when $x = 0.4$.

It is the intent of this report to summarize the studies over FY 2002 on the ferrites, with an emphasis on the compound of $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$, which is particularly interesting in the applications for use as oxygen membranes and as the cathode for intermediate temperature solid oxide fuel cells (SOFCs). Most of the studies have been focused on the SOFC applications, but the results are applicable to oxygen separation as well. Recently, $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ has been demonstrated at Pacific Northwestern National Lab as a better cathode in SOFCs at relatively low operation temperature (750°C) than $\text{La}(\text{Ni}, \text{Fe})\text{O}_3$ and $(\text{La}, \text{Sr})(\text{Ni}, \text{Fe})\text{O}_3$ ³. Initial studies on both separation membranes and SOFCs in our group on ferrite materials have shown that the structure plays an important role in electrical and catalytic properties and that the electrical, catalytic and magnetic properties have an inter-relationship that is commonly related to the electronic structure and oxygen vacancy concentration (See appendices). Therefore, it is critical to study the ferrite materials from the atomic structure point of view, for example the hybridization of transitional metal and oxygen orbitals that plays a dominant role in the properties such as the generation of oxygen vacancies, holes, and spin state of the transitional metals. This interrelationship is shown in the $(\text{La}, \text{Sr})(\text{Fe}, \text{Co})\text{O}_{3-\delta}$ system. For 20% Co compound, electrons (holes) move indirectly between Co ions via an O ion rather than directly between Co ions, i.e., the fluctuation of the charges of O ions as well as Co ion causes electrons (holes) to move with a complicated interaction between the generated holes and electrons⁴. The effects of Fe doping in $\text{La}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$ ⁵ showed that no apparent structure change was introduced by Fe doping up to $x = 0.3$, but the Curie temperature T_c , magnetization M and electrical resistivity are lowered by Fe substitution. A smaller localization length and a more severe disorder in the lattice due to Fe doping were observed. Previous research showed that two transitional metals, Fe and Co, at B site of ABO_3 allowed a better performance compared to only Co or Fe located at B site. For example, cobaltites exhibit a significant weight loss when the annealing temperature is higher 1000°C (in some case 800°C) and a higher resistivity and oxygen diffusivity were observed in ferrites.

Experimental

The Pechini method ^{6, 7} was used to synthesize nanocrystalline particles, in this process a polymeric solution was formed due to a chelating reaction between cations and chelants. The polymeric solutions were also used as the thin film sources, which were used to fabricate thin films by spin coating and thermal processing. Electrical conductivity was measured by the four-probe method at the temperature from 150 – 1000°C in a wide range of oxygen activities (10^{-25} to 1). Thermogravimetric analysis was conducted at 1000 and 1200°C in O₂, air and Ar. Mössbauer spectroscopy and neutron diffraction were performed at room temperature on the sintered and quenched specimens. During the quenching experiments, the specimens were first heated at 1000°C with a flowing gas atmosphere of N₂, air, or CO/CO₂ mixtures for 24 hours, and then quenched to room temperature. For Neutron Diffraction (ND) studies, samples were contained in 3 mm V metal cells and data were collected at 1.4785 Å over a range of 5°-105° (2θ). Rietveld refinement was carried out using the FULLPROF code, in which the magnetic ordering was taken into account because of the sensitivity of neutron diffraction to the magnetic ordering of the Fe atoms.

RESULTS

Figure 1 shows powder Neutron Diffraction Patterns of La_{0.60}Sr_{0.40}FeO_{3-δ} quenched at various gas environments. The powder Neutron Diffraction results showed that all specimens were single phase with an exception of the sample quenched with 90%CO/10%CO₂, in which peak broadening and asymmetry took place that indicated a decomposition of the sample. Four models were used to fit the data for each sample and all results seemed reasonable. However, there did exist different preferred models for the reduced samples than for the air- and N₂-quenched samples and the neutron diffraction patterns for the samples quenched from the reducing atmosphere are significantly different with those quenched from air or N₂. The diffraction peak splitting for the reduced samples is dramatically reduced compared to the N₂- and air- treated samples. The first diffraction peak (~ 19°) is much stronger in the reduced samples than in the air- or N₂- quenched samples. This peak proves to be purely magnetic and the change reflects a large increase in magnetic moment for the reduced samples vis-à-vis the air- and N₂- quenched samples.

Figure 1. Powder Neutron Diffraction patterns of $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ quenched at various gas environments.

Further study was then performed on the electrical conductivity of $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ at the low $p\text{O}_2$, in which oxygen vacancy concentrations were increased. Figure 3 shows the plot of $\log(\sigma)$ vs. $\log(p\text{O}_2)$ at 1000°C with a control over the oxygen activity being made by using a mixture of CO/CO_2 , from which the $p\text{O}_2$ can be determined thermodynamically. In Figure 3, a transition from p-type to n-type of conductor is obvious at relative low $p\text{O}_2$, at which the majority carriers changed from the holes to electrons because of the valence state decreases in Fe due to the further loss of oxygen. The oxygen vacancies are generated at high temperature due to loss of oxygen, which results in a higher oxygen vacancy concentration and a lower hole concentration. In addition to the conductivity, oxygen vacancy concentration also plays a key role in the function of cathodes, in particular in the catalytic properties. Determination of the oxygen vacancy level has been performed by thermogravimetric analysis (TGA) and neutron diffraction. TGA simply measures the weight changes with the variable being time, gas environment and temperatures. Neutron diffraction was performed on the samples which were quenched at 1000°C from different oxygen activities. A large decrease in $3-\delta$ was observed when the gas was changed from 90%CO to 99%CO. XRD results showed that $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_3$ decomposed in the 99% CO atmosphere. The consistence results between TGA and neutron diffraction

confirmed that the quenching experiment could be used to study the ferrites under reducing conditions.

Figure 2. $\log(\sigma)$ and $3-\delta$ as a function of $\log(pO_2)$ for $La_{0.60}Sr_{0.40}FeO_{3-\delta}$.

Further study was then performed on the electrical conductivity of $La_{0.60}Sr_{0.40}FeO_3$ at the low pO_2 , in which oxygen vacancy concentrations were increased. Figure 2 shows the plot of $\log(\sigma)$ vs. $\log(pO_2)$ at 1000°C with a control over the oxygen activity being made by using a mixture of CO/CO_2 , from which the pO_2 can be determined thermodynamically. In addition to the conductivity, oxygen vacancy concentration also plays a key role in the function of cathodes, in particular in the catalytic properties. Determination of the oxygen vacancy level has been performed by thermogravimetric analysis (TGA) and neutron diffraction. TGA simply measures the weight changes with the variable being time, gas environment and temperatures. Neutron diffraction was performed on the samples, which were quenched at 1000°C from different oxygen activities. A large decrease in $3-\delta$ was observed when the gas was changed from 90%CO to 99%CO. XRD results showed that $La_{0.60}Sr_{0.40}FeO_{3-\delta}$ decomposed in the 99% CO atmosphere. The consistence results between TGA and neutron diffraction confirmed that the quenching experiment could be used to study the ferrites under reducing conditions. Figure 3 shows a relative high oxygen vacancy level in ferrites over a wide oxygen activity, whereas, LSM only exhibits sufficient oxygen vacancy concentration in the lower oxygen activity region

Figure 3: Oxygen content ($3-\delta$) vs. $\log(pO_2)$ for $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ ⁸ at 1000°C.

Figure 4 shows Néel Temperature and Fe-O-Fe angles as a function of pO_2 , at which the specimen was quenched. The bonding angles of Fe-O-Fe were increased with decreasing oxygen partial pressures. Because the bonding lengths were nearly constant, the increasing of the bonding angle increases the overlap between Fe and O atomic states that results in an increase in the superexchange interaction between Fe and Fe. The Fe-Fe super-exchange interaction is highly dependent on the Fe-O-Fe bond angle and the superexchange through the oxygen atoms that is more effective when the Fe-O-Fe paths are close to linear^{9, 10}. It is also found that the increase in the superexchange interaction results in an increase in Néel temperature, as shown in Figure 3. The Fe moments for the three reduced samples refine between 3.72 and 3.82 μ_B while the moments for the other two samples are much smaller (1.4 μ_B and 1.2 μ_B for the air- and N₂-quenched samples, respectively).

Figure 4. Néel temperature and Fe – O – Fe angle of the specimens quenched at various oxygen partial pressures (pO_2).

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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

Conductivity and Thermodynamic Studies

We have continued to investigate the thermodynamic properties (stability and phase separation behavior) and total conductivity of prototype membrane materials. The data are needed together with the kinetic information to develop a complete model for the membrane transport.

In previous studies, we have shown that iron based perovskite oxides show evidence for phase separation at intermediate partial pressures of oxygen, $-11 < \log pO_2 < -5$. In the previous measurements, data were acquired using a computer algorithm to determine when the system reached equilibrium. It is known from studies of other systems that phase separation between perovskite and brownmillerite phases can be quite slow. Consequently, we have gone back to test that we reach equilibrium by manually acquiring data both from high to low and from low to high partial pressures. We have also switched to the simplest of the ferrites $SrFeO_{3-x}$ in order to confirm the experimental methods used and to extend the range of the published data into the region of interest in an ion-transport membrane reactor application.

The pO_2 dependence of the oxygen non-stoichiometry (x) for the perovskite $SrFeO_{3-x}$ was determined from coulometric titration measurements of the type described in previous reports. A typical example of experimental data in the form of a plot of $\log pO_2$ vs. non-

Figure 1. Coulometric titration data for the pO_2 dependence of the oxygen non-stoichiometry of $SrFeO_{3-x}$ at 1000 °C, raw data (left), after leakage correction (right).

stoichiometry is given in Fig. 1. The data are reproducible, irrespective of the direction of measurement, but in the lower pO_2 region, a small gap exists between the data measured in the two directions because of oxygen leakage through the zirconia disc, which becomes increasingly significant as the temperature increases and the pO_2 decreases. The experimental data were corrected for leakage taking into account the equilibrium time at each step and the pO_2 inside the

cell. After correction, the data measured on increasing and decreasing pO_2 agree over the entire pO_2 range, as shown in Fig. 1b. Similar results were observed at the other temperatures.

At temperatures ≥ 900 °C, the stoichiometry over the whole range of pO_2 was determined but at lower temperatures, only the higher partial pressures ($pO_2 > 10^{-6}$ atm) are obtained reliably. At temperatures ≤ 850 °C, the separation into two phases, perovskite and brownmillerite, is apparent in the isotherms. For example, in the 800 °C data discontinuities are observed and significant differences in the results are obtained depending on whether pO_2 is increasing or decreasing. Equilibrium is very difficult to achieve in this region and allowing longer equilibration times compromises the precision of the stoichiometry measurements because of the larger corrections that are necessary. Consequently, only the high-pressure data are reliable where the equilibration times are much faster.

Figure 5. The effect of the low temperature phase separation on the 800 °C isotherm.

Plans for next quarter.

We will extend the studies described above to include measurements of the conductivity data for $SrFeO_{3-x}$. Recently Kozhevnikov *et al.* (1) measured the electrical conductivity and the Seebeck coefficient of $SrFeO_{3-x}$ in the temperature range $700 \geq T \geq 950$ °C and at $0.3 \geq pO_2 \geq 10^{-18}$ atm. The results that they obtained were surprising and not consistent with the data that we have obtained previously for $La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-x}$. The same group have also measure several gallium substituted compositions and obtained similar results. We plan to repeat these measurements using our own cell design and establish the true conductivity behavior. In this quarter, we will also synthesize additional tubular ceramics for use in the membrane reactor at UT.

University of Toronto

Isotope Transient Studies of Oxygen Permeation Through a Dense $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Membrane

Summary:

Isotope transients ($^{16}\text{O}_2$ - $^{18}\text{O}_2$) have been performed on a tubular (6mm O.D., 1 mm wall thickness) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF-6428) oxygen perm-selective membrane operating at steady state at temperatures between 1023K and 1123K. An $^{18}\text{O}_2$ isotope pulse was applied to the “air” (20% O_2 :Ar) side of the membrane while maintaining a constant $p\text{O}_2$. The isotopic composition of the oxygen permeate was analyzed on the delivery side, swept with helium, to reveal the residence time distribution of oxygen in the membrane under steady state transport. The resulting isotope transient allows the unambiguous separation of surface and bulk resistances to oxygen permeation under steady state conditions, a separation not possible by permeation measurements alone. The resulting transients show that both surface exchange and bulk transport resistances contribute significantly to this membrane performance. A dispersion flow model was fit to the data to provide values of the forward and reverse surface exchange rate coefficients as well as the oxygen diffusion coefficients. Oxygen flux increased substantially with the flow rate of sweeping gas, slightly with the flow rate of air.

Isotope exchange - depth profiling (IEDP) has been extensively used to study the oxygen activation and diffusion in oxides in the absence of a chemical gradient. Surface exchange coefficient, k^* , and tracer diffusion coefficient, D^* , could be extracted from the isotope distribution profile. Therefore, this technique provides an accurate and relatively simple way to get valuable parameters for MIEC materials. Since these parameters are measured under gradientless conditions for oxygen and net oxygen flux is zero, the behaviors of the membrane with oxygen chemical gradient may be different from those that are calculated from k^* and D^* .

Dynamic isotope tracing techniques, which are extensively used in catalysis research, involve placing isotopic labels on reacting atoms. Monitoring these labeled atoms as they become incorporated into reaction intermediates and eventually into reaction products will yield information on the steady state operation of the membrane under a gradient and will allow surface and bulk resistances to be separated. An experiment is typically performed by establishing two identical reactant streams (one is fed to the reactor and the other is vented), except that the isotopic labels of one or more of the constituents are different. The transient is initiated by switching feeds while maintaining steady state reactions and monitoring the change in the isotopic composition of products.

In order to eliminate the edge effect of disk-shaped sample [Allan J. Jacobson, SSI 1997, Nanping Xu, JMS 2000], a tubular membrane was used to carry out the isotope transient experiments. The transient results combined with the simultaneous measurements of oxygen flux under various conditions, will help to elucidate the mechanism of oxygen exchange and diffusion occurred in the oxygen transport through the membrane with perovskite structure. In the isotope transient measurement, a pulse of $^{18}\text{O}_2/\text{Ar}$ with same O_2 partial pressure, was introduced to the air side of the sample while maintaining the steady state conditions (Oxygen gradient keeps constant). The ^{18}O diffuses into the sample as a result of both the existing ^{18}O chemical gradient and oxygen gradient across the membrane. The isotopic ratio $^{18}\text{O}/^{16}\text{O}$ in the permeated O_2 (sweeping side) was monitored in a time-resolved manner. By fitting the obtained isotopic composition in the permeated oxygen with mathematic models, the oxygen exchange coefficient k and oxygen bulk diffusion coefficient D can be obtained simultaneously.

This study is the first use of isotope transient on MIECs to investigate the oxygen transport parameters across the membrane.

Experimental

The tubular sample of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ was approximately 6.2 mm outer diameter, 1.0 mm thickness, and 8.8 mm length. The both sides of the tube were ground with a 800 Grits silicon carbide paper to a desired flat and smooth surface. Prior to installing into the reactor, the sample was rinsed and ultrasonically cleansed with distilled water and then acetone to remove any residue and contaminant.

Experimental setup Figure 1 illustrates the configuration of the internals of the reactor. To minimize the undesired wall reactions, all parts which may contact gas mixture inside and outside of the perovskite membrane in the hot zone of the reactor are made of quartz except the gold seal. The temperature of furnace was controlled by a Omega Type I/32 PID temperature controller with an accuracy of ± 0.5 °C. Before and after each measurement, the temperature of the sample was measured by a K-type thermocouple as illustrated in Figure 1.

Figure 1:
Experimental
apparatus for
isotope transients

Figure 2. Experimental setup for isotope transient experiments

Oxygen permeation measurements. The sample was heated at a ramping rate of ca. 2 °C/min to 750 C. The flow rates of air and the sweeping gas He were basically 20 ml/min in our experiments. As illustrated in Figure 1, another He flow (He in 2) was introduced to purge the dead volume between the reactor wall and outer quartz tube, and the flow rate is fixed at 5.0 ml/min. The composition of sweeping gas was analyzed by a SRI 8610C Gas Chromatograph with a 5A molecular-sieve column. A Helium Ionization Detector (HID) was used to measure the oxygen and nitrogen content since HID is with a high sensitivity.

Oxygen isotope transient experiments. The synthesized air, $\text{O}_2:\text{N}_2 = 20:80$, was provided by Praxair Products Inc.. The ^{18}O -containing gas, $^{18}\text{O}_2:\text{Ar} = 20:80$, was supplied by Icon Isotopes. The ^{18}O isotope purity is 97%. The sample was equilibrated at the experimental conditions for at least 24 h in the natural abundance isotope version of the gas mixture. Following this

equilibration the gas mixture O₂/N₂ in the air side of the membrane was switched to the ¹⁸O containing mixture (¹⁸O₂/Ar) and maintained for 15 min or 60 min. The flow rates of ¹⁸O₂/Ar were 1-3 ml/min for the duration of isotope pulse to avoid depletion of the isotope oxygen, which depend on the experimental temperature and oxygen flux. A “pulse” of ¹⁸O was then obtained in the oxygen-rich side. At the end of the pulse, the gas mixture was switched back to O₂/N₂ and kept the same experimental conditions as before for 4-6 days. The sweeping gas was analyzed with an on-line UTI Model 100C Quadrupole Mass Spectrometer (MS) through the experiment. The oxygen fluxes were obtained simultaneously by an on-line GC analysis. Such experiments were carried out at various temperatures.

Results

Oxygen fluxes under various conditions. Figures 2-3 present the oxygen fluxes of the membrane at 800 °C under various oxygen partial pressures in oxygen-rich side, gas flow rates in both sides of the membrane. The following equation, which was reported by Xu and Thomson [*CES* 54(1999) 3839-3850], is fit to the results.

$$J_{O_2} = \frac{\frac{k_r}{k_f} \left(\frac{1}{P''_{O_2}{}^{0.5}} - \frac{1}{P'_{O_2}{}^{0.5}} \right)}{\frac{1}{k_f P'_{O_2}{}^{0.5}} + \frac{2L}{D_v} + \frac{1}{k_f P''_{O_2}{}^{0.5}}} \quad (1)$$

Where D_v is the diffusion coefficient of oxygen vacancies. k_r and k_f are the forward and reverse reaction rate constants for surface exchange reaction. P'_{O_2} and P''_{O_2} are respectively the oxygen partial pressure in the oxygen-rich and oxygen-lean side. L is the thickness of the membrane.

Figure 2: Oxygen flux as a function of partial pressure of O₂ on the air side of an La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} membrane. The solid line is a fit to equation (1).

Figure 3 reveals a strong dependence of oxygen permeation on the oxygen partial pressure in oxygen-rich side. The oxygen flux increased to 0.072 ml/min.cm² from 0.039 ml/min.cm² while P'_{O_2} changed from 9.5 mbar to 1000 mbar. It should be noted that the oxygen partial pressure in the oxygen-lean side, P''_{O_2} , changed from 0.6 mbar to 5.0 mbar while P'_{O_2} changed from 9.5 mbar to 1000 mbar. Eq. (1) indicated that the oxygen flux decreases with decreasing P'_{O_2} and/or increasing P''_{O_2} , which was partly confirmed by Lane and Xu et al [*SSI 121 (1999) 201-208*; *JMS 166 (2000) 51-61*]. As for our results in Figure 2, it is hard to see since both oxygen partial pressures in both sides increased simultaneously. We can simply change Eq. (1) to the following form:

$$J_{O_2} = \frac{k_r \left[\left(\frac{P'_{O_2}}{P''_{O_2}} \right)^{0.5} - 1 \right]}{1 + \left(\frac{P'_{O_2}}{P''_{O_2}} \right)^{0.5} + 2L \cdot \frac{k_f}{D_v} \cdot P'^{0.5}_{O_2}} \quad (2)$$

From Eq. (2), we can account for the increase of oxygen flux with P'_{O_2} even P''_{O_2} increased simultaneously. Eq. (2) indicates apparently that the effect on J_{O_2} is negative if P'_{O_2} and P''_{O_2} increase by the same factor. In our case, P''_{O_2} increased by a factor of 8 (from 0.6 mbar to 5.0 mbar). However, P'_{O_2} increased by a factor of 1050 much more than the changes in P''_{O_2} .

Figure 3: Effect of He flow on oxygen permeation rate through $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membrane

Figure 3 indicates oxygen flux increased remarkably when sweeping gas, He, flowed faster. The feed side of the tubular membrane was maintained at a constant oxygen partial pressure of 201 mbar. The faster flow rate of He leads to a lower oxygen partial pressure in the sweeping side. P''_{O_2} decreased to 0.8 mbar from 5.6 mbar when the flow rate of He increased from 5 ml/min to 80 ml/min. Eq. (1) predicts J_{O_2} would be bigger when P''_{O_2} is smaller. This behavior has been reported by other research groups for the same material [Xu, Kilner, Xu Nanping].

Isotope transient profile. Figure 4 presents the ^{18}O fraction of permeated oxygen in the oxygen-lean side after introducing a pulse (60 min) of 20% $^{18}\text{O}_2$ (97% isotopic purity at atom) at 800 °C as a function of time. Mass 34 ($^{18}\text{O}^{16}\text{O}$) and mass 32 ($^{16}\text{O}_2$) can be monitored by MS, and thus isotopic composition can be calculated.

This is the first application of isotope transients to oxygen membrane performance. Preliminary modelling with a constant properties 1-D dispersed flow model is capable of fitting this profile. The modelling effort explains the yield of labelled oxygen that appears on the delivery side of the membrane (1/3 of the oxygen infusion during the pulse). Preliminary fits are obtained with surface and bulk transport coefficients similar to those measured by previous IEDP studies.

Plans:

We will perform transients at a variety of conditions on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ before switching to $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. This latter material is capable of isotope transients under syngas generation conditions with large oxygen activity gradients.

Figure 4:
Isotope
transient on
operating
membrane

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Program/Project Title Oxygen Transport Ceramic Membranes

Identification Number	Description	Planned Completion Date	Actual Completion Date	Comments
Task 1	Development of Ceramic Membrane/Metal joints			Massachusetts Institute of Technology
Task 1.1	Perovskite/Metal Interactions	03/03		25% complete
Task 1.2	Mechanical Properties of Concentric Perovskite/Metal Seals	09/03		
Task 2	Membrane mechanical Properties at high temperatures and reactive atmosphere			University of Alaska, Fairbanks
Task 2.1	High temperature crack growth studies.	02/03		30% complete.
Task 2.2	Crack growth and Strength degradation studies	05/03		10% complete.
Task 2.3	Strength of OTM-Porous substrate composite structures	09/03		
Task 3	Preparation and characterization of Dense Ceramic oxygen Permeable Membranes			University of Missouri - Rolla
Task 3.1	Preparation of LSF specimens and ceramic substrates	03/03		20 % complete
Task 3.2	Interaction studies between membranes and substrates	09/03		10 % complete
Task 4	Grain Structure and atomic segregation			University of Illinois at Chicago

Task 4.1	Grain Structure and atomic segregation in fractured samples	03/03		25% complete, sample received from UAF
Task 4.2	In –situ testing and analysis of valence states and oxygen	09/03		
Task 5	Oxygen Diffusion Kinetics			University of Houston/ University of Toronto
Task 5.1	Gradientless isotope profiling experiments on perovskite oxides	03/03		25% complete
Task 5.2	Conductivity relaxation studies under reducing conditions and measurement of the ionic conductivity of LSF _{0.8} CO _{0.2} as a function of vacancy concentration	09/03		25 % complete

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1. Program/Project Identification No. DE-FC26-99FT40054	2. Program/Project Title Oxygen Transport Ceramic Membranes	3. Reporting Period 07/01/02 through 07/30/02
4. Name and Address Dr. S. Bandhopadhyay, Dr. Nagendra Nagabhushana School of Mineral Engineering, Duckering 355, PO Box 755960 Fairbanks, AK 99775-5960		5. Program/Project Start Date 04/13/99
		6. Completion Date 06/13/03
7. Approach Changes ☒ None		
8. Performance Variances, Accomplishments, or Problems ☒ None		
9. Open Items ☒ None		
10. Status Assessment and Forecast ☒ No Deviation from Plan is Expected		
11. Description of Attachments ☒ None		
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2. Program/Project Identification No. DE-FC26-99FT40054	2. Program/Project Title Oxygen Transport Ceramic Membranes	3. Reporting Period 08/01/02 through 08/31/02
4. Name and Address Dr. S. Bandhopadhyay, Dr. Nagendra Nagabhushana School of Mineral Engineering, Duckering 355, PO Box 755960 Fairbanks, AK 99775-5960		5. Program/Project Start Date 04/13/99
		6. Completion Date 06/13/03
7. Approach Changes ☒ None		
8. Performance Variances, Accomplishments, or Problems ☒ None		
9. Open Items ☒ None		
10. Status Assessment and Forecast ☒ No Deviation from Plan is Expected		
11. Description of Attachments ☒ None		
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3. Program/Project Identification No. DE-FC26-99FT40054	2. Program/Project Title Oxygen Transport Ceramic Membranes	3. Reporting Period 09/01/02 through 09/30/02
4. Name and Address Dr. S. Bandhopadhyay, Dr. Nagendra Nagabhushana School of Mineral Engineering, Duckering 355, PO Box 755960 Fairbanks, AK 99775-5960		5. Program/Project Start Date 04/13/99
		6. Completion Date 06/13/03
7. Approach Changes ☒ None		
8. Performance Variances, Accomplishments, or Problems ☒ None		
9. Open Items ☒ None		
10. Status Assessment and Forecast ☒ No Deviation from Plan is Expected		
11. Description of Attachments ☒ None		
12. Signature of Recipient and Date	13. Signature of U.S. Department of Energy (DOE) Reviewing Representative and Date	