

Oxygen Transport Ceramic Membranes

Quarterly Report

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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

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:

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)

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 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 & 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 will be submitted in the final report.

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

Prof. Sukumar Bandopadhyay and Nagendra Nagabhushana
University of Alaska Fairbanks

Effect of Temperature, Pressure and Environment

In this quarter, the perovskite tubes 20573 (a-f) were evaluated for their strength as a function of temperature and pressure in air and in N₂ environment. The average strengths (from 3 test) are plotted graphically in figure 1.

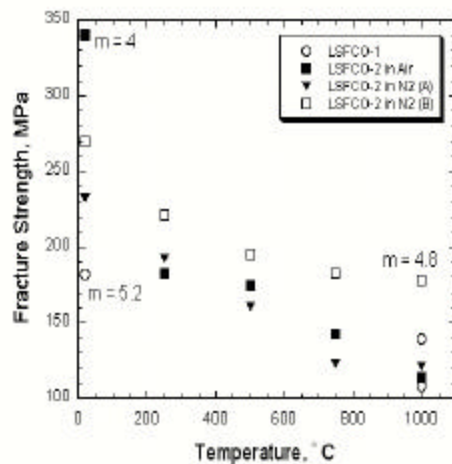
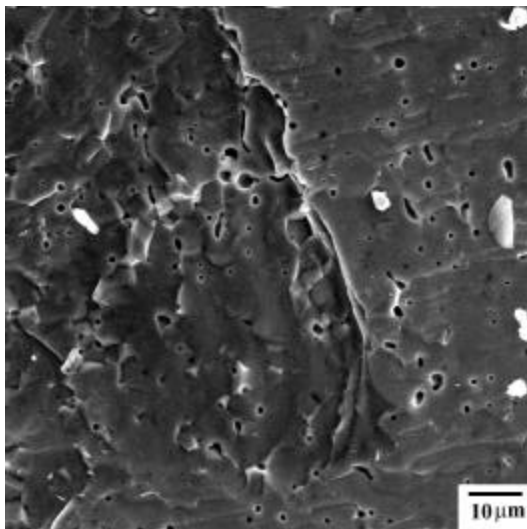
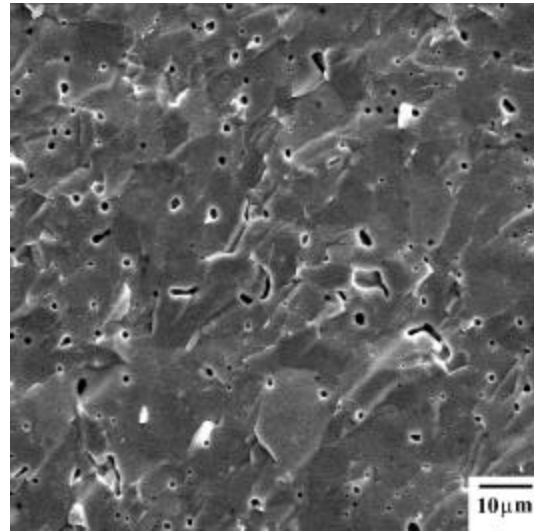


Fig. 1 Influence of temperature, pressure and environment on the fracture strength of perovskite tubes

The perovskite tubes showed a slight change in fracture strength in air and in UHP nitrogen (with or without pressure). However, the strength values were within the acceptable range in comparison with the reported strength in Weibull modulus studies (in

air). In air at 250°C, the perovskite tubes showed a big drop in strength value from ~350 MPa at RT to 180 MPa. A second drop in strength to 140 MPa occurred at 750°C and fracture at 120 MPa at 1000°C. In N₂, the strength gradually decreased till upto 750°C and evened out at 1000°C. In N₂ with a pressure of 25 PSI (0.17 MPa), the strength of the tubes were consistently higher than the corresponding strength in air or in N₂ (no pressure) at all temperatures. The degradation in strength had a similar trend to that with out pressure. For comparison, the strength values of 20572 tubes are plotted in the graph (fig 1). The tubes showed lower strength than the 20573 tubes and in introspection were higher in N₂ as compared to in air.

Fracture at lower temperature in air or in N₂ did not show any dramatic changes in comparison with fracture at room temperature. However, more incidences of particle pullout were observed. Instances of material degradation were observed at 750°C, but were markedly more severe at 1000°C. Fracture and fracture morphology at 1000°C have been discussed in much detail in earlier sections.



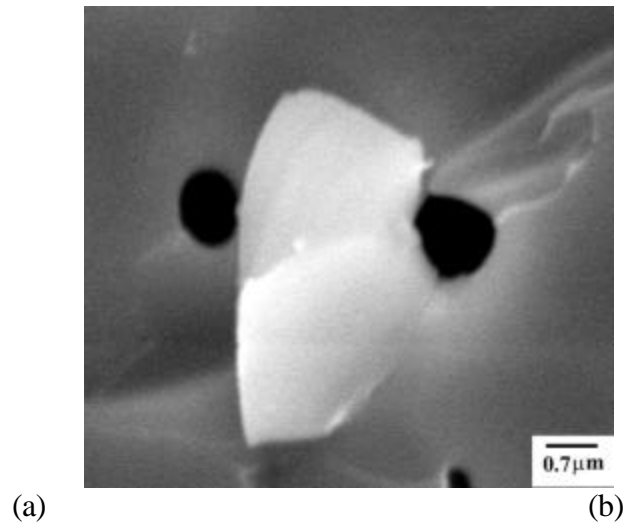


Fig 2

Typical fracture observed in membranes tubes at temperatures lower than 1000°C in air/N₂ and CO₂/CO gas mixtures. Fracture is by brittle transgranular cleavage (a and b). A higher magnified view (c) indicates formation of precipitates.

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

Composite Structures

In order to put dense films on porous support substrates it is necessary to reduce the diameters at the surfaces and to make the surfaces smoother. Studies have been initiated to achieve these goals.

The initial studies were done using colloidal ceria as the surface treatment layer.

Nanocrystalline cerium oxide powder with an initial grain size of approximately 5nm was produced using an aqueous precipitation processing route. 99.999% cerium (III) nitrate (Alfa Aesar, Inc.) was dissolved in distilled water and precipitated to cerium hydroxide particles using hydrogen peroxide and ammonium hydroxide.

Aqueous colloidal suspensions were prepared by mixing 10 weight percent of CeO₂ powder in pH 4 distilled water (balanced with HNO₃) along with 4 weight percent butoxyethanol to aid in drying and decrease the wetting angle. The butoxyethanol also partially polymerizes due to the acidic content of the solution, and as a consequence aids in increasing the solution viscosity and in the formation of a continuous film. The power was then dispersed in the solution using a high intensity ultrasonic probe for about one hour. The solution was then filtered through a 0.45µm glass fiber filter (Whatman, Inc.) in order to remove any foreign matter.

Thin films of CeO₂ were prepared by spin coating the colloidal suspension on a variety of substrates. Optical quality, both sides polished (0001) oriented sapphires substrates were used for both the optical measurements as well as the DC conductivity measurements.

Films were spun on the prepared substrates at 1500rpm for 30 seconds and subsequently dried at 70°C for about an hour. The films were then heat treated at 350°C for about an hour and cooled back to room temperature after which subsequent coatings could be deposited. Sintering of the porous films was done in a standard furnace using a ramp rate of 5°C/min to the maximum temperature, at which they were held for 2 hours.

The sintered films were characterized according to their grain size, thickness and density using X-ray diffraction, mechanical profilometry, ellipsometry, and UV-Vis spectroscopy, as shown in previous studies. The results as to the grain size, film density and thickness are shown in figures 1-6. Initially, the films have a density of approximately 50% and a grain size of 5nm after 400°C and densify to 85% with a grain size of 60nm after annealing at 1000°C. The X-ray diffraction patterns of CeO₂ samples on sapphire substrates annealed at different temperatures showed that the films are single-phase fluorite structured and show no reaction with the substrate over the investigated temperatures. Peak broadening grain size calculations (Reitfield analyses) from the diffraction patterns correlate well with those in FESEM images (figure 4).

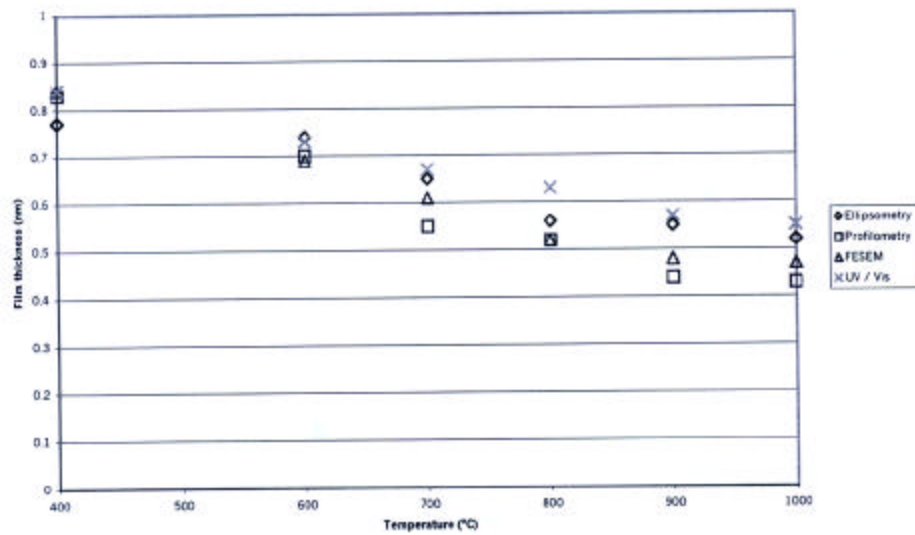


Figure 1. Variation in the film thickness of porous CeO₂ thin films as a function of annealing temperature as measured with different techniques.

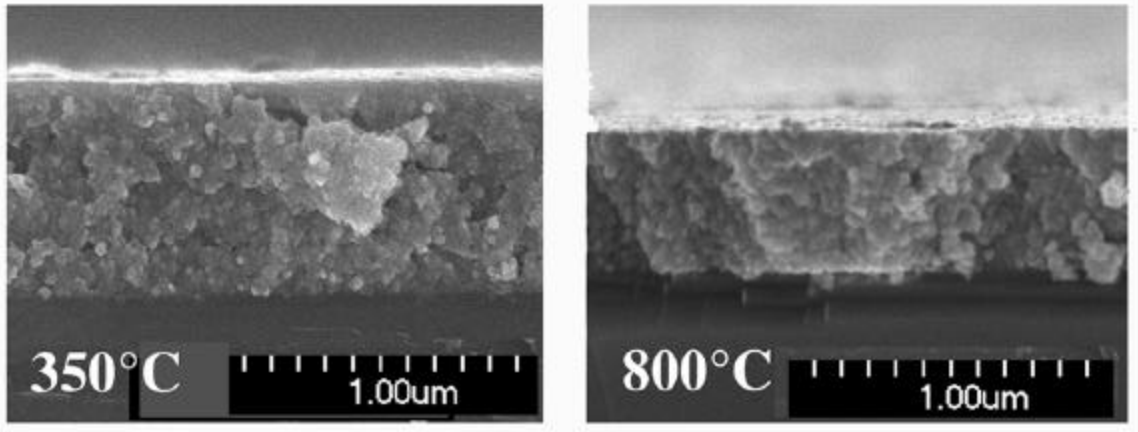


Figure 2. SEM cross-sections of CeO₂ coatings on the sapphire substrate. A, B – after sintering at 400°C and 800°C correspondingly.

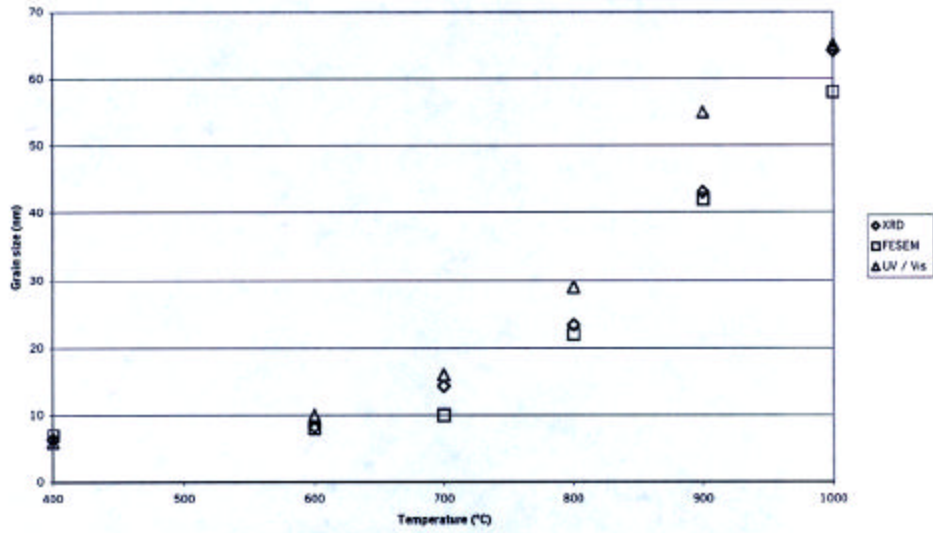


Figure 3. Variation in the grains size of porous CeO₂ thin films as a function of annealing temperature as measured with different techniques.

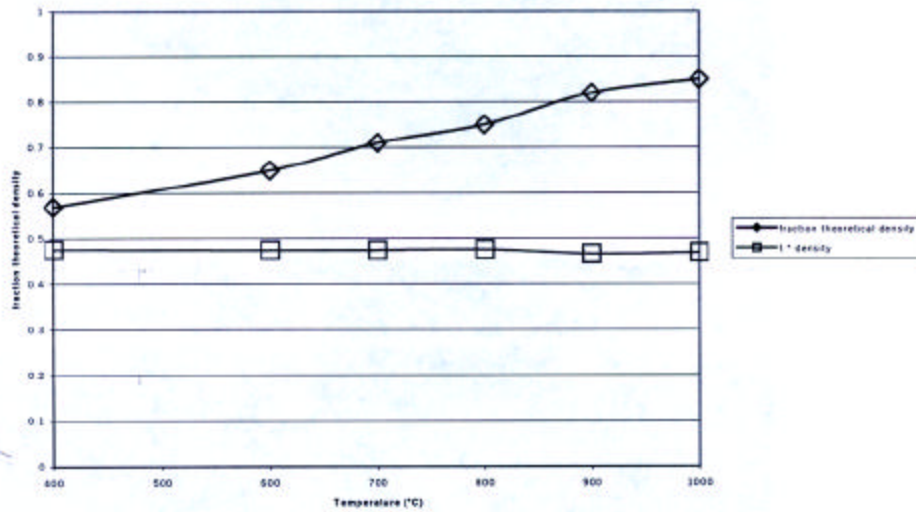


Figure 4. Variation in the density of porous CeO₂ thin films measured with UV/Vis spectrophotometry as a function of annealing temperature.

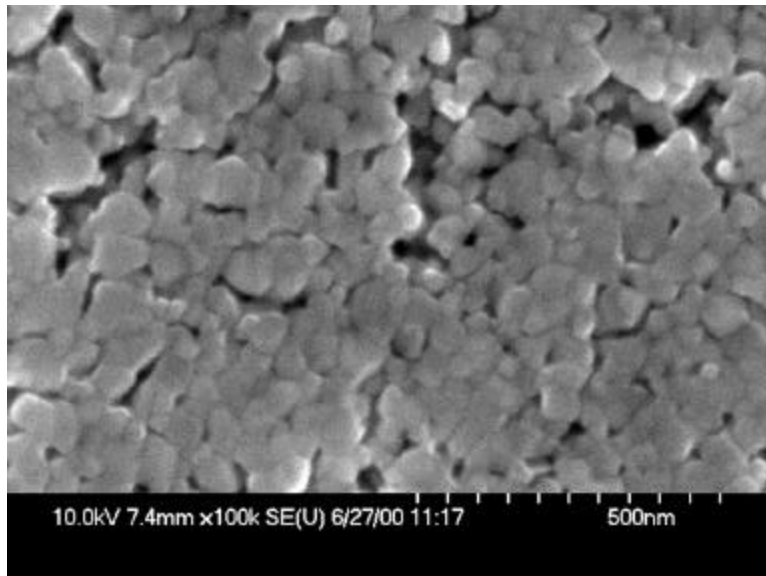


Figure 5. Surface of Ceria film on sapphire which was sintered at 1000°C.

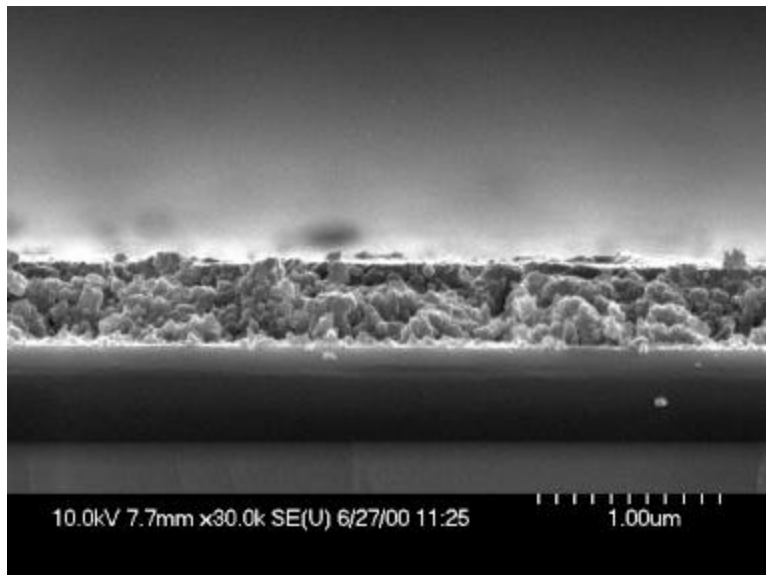


Figure 6. Cross-section of Ceria film on sapphire sintered at 1000°C.

After the initial experiments of depositing ceria onto sapphire had established the deposition process, experiments were started in which the colloidal ceria was deposited onto a porous (La,Sr)MnO₃ (LSM) substrate. Figures 7 and 8 show some of the deposition. Figure 9 shows that a dense zirconia film can be formed on the ceria coating.

The important lessons that have been learned are:

- 1) To be able to form a dense film from polymer precursor solutions on porous substrate, the surface must not have pores that are larger than about $0.2\mu\text{m}$.
- 2) Colloidal ceria can form a smooth surface on a very porous ($>10\mu\text{m}$ diameter pores) surface onto which polymer precursor techniques can be used to produce dense ($<1\mu\text{m}$ thick) films.
- 3) The thickness of ceria film must be in the order of the roughness of the underlying substrate before dense films can be formed.

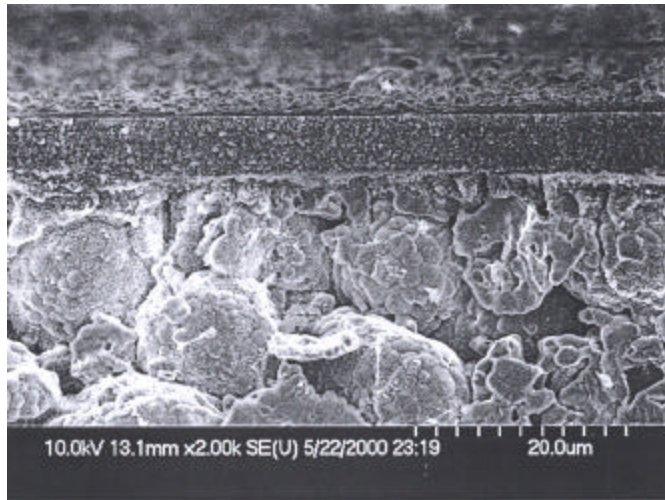


Figure 7. Colloidal CeO_2 porous (60% th. Density) thin film on porous LSM substrate. Composite was sintered at 1000°C .

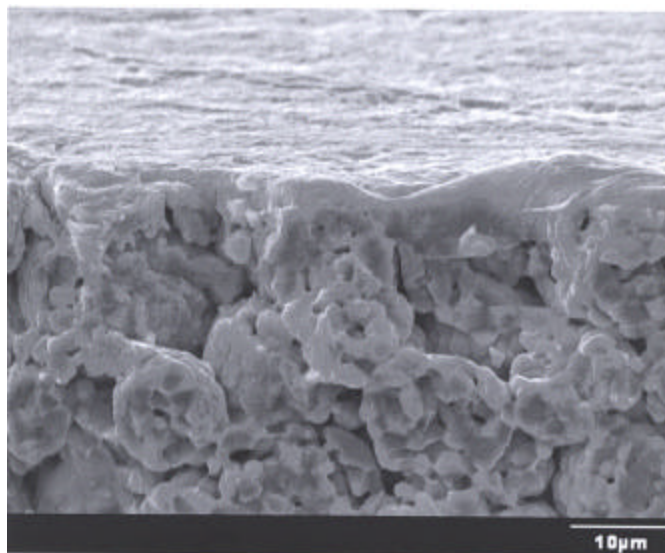


Figure 8. Colloidal ceria planarizing layer. Cross section, high resolution. Sintering temperature of composite = 1000°C.

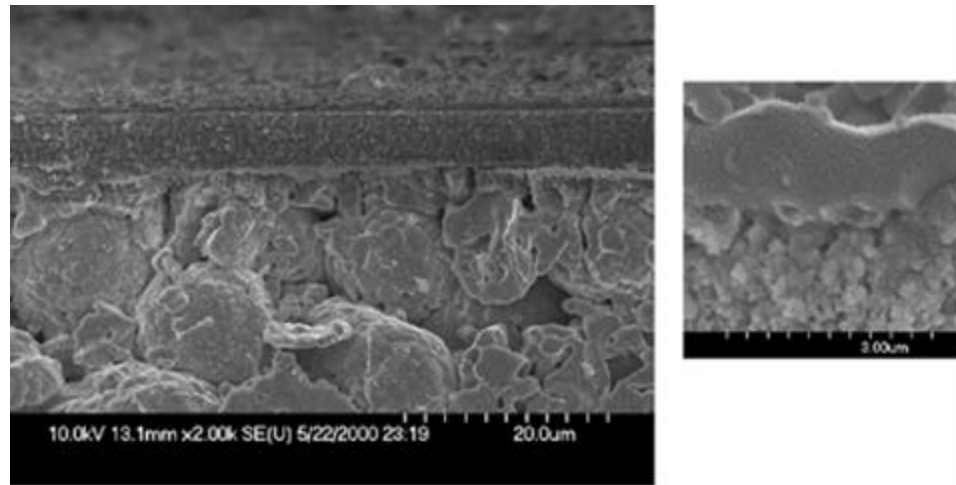


Figure 9. Field-emission SEM micrograph of a YSZ/Colloidal CeO₂/spray-pyrolized LSM composite. CeO₂ = 5μm, YSZ = 0.5μm. Composite sintered at 800°C.

Conclusions

- 1) La_{1-x}Sr_xFeO_{3-δ} can be prepared single phase at least to x=0.67
- 2) Neutron diffraction patterns of (La_{0.60}Sr_{0.40})_{0.99}FeO_{3-δ} powder show:
 - single phase rhombohedral structure (in air at 1000°C, log P_{O₂} = -0.7) and under 10% CO/90% CO₂ (log P_{O₂} = -12.1) and 50% CO/50% CO₂ (log P_{O₂} = -14.1).
 - decomposition starts under 90% CO/10% CO₂ at 1000°C (log P_{O₂} = -16.1).
- 3) Colloidal ceria can be used to act as a interface between large pore size substrates (>10μm) and dense films.

Future Work

- Further thermal expansion study of (La_{0.60}Sr_{0.40})_{0.99}FeO_{3-δ} disk.
- Neutron diffraction and modeling study of phase stability, oxygen defect.
- Scheduled study of La_{0.60}Sr_{0.40}Fe_{0.85}Ga_{0.15}O₃ in task 4.
- Preparing samples to be sent to UIC.
- Expand the preparation of dense films on porous substrate studies.
- Mössbauer studies.

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

DOE Progress report October 2001 University of Toronto

Our work during the past quarter has focussed on the commissioning of the membrane reactor transient experiments. The analysis of the final series of gradientless IEDP materials is still on hold pending further surface characterization and SIMS analysis.

Membrane reactor experiments:

- (1) The flow system and furnace used for the gradientless infusion experiments has been reconfigured for the membrane reactor.
- (2) The membrane reactor has been assembled with a quartz tube in the place of the perovskite materials to prove the gas handling system and test for leaks with the gold seals. A bellows arrangement provides a constant pressure on the seals during heating and cooling cycles. Preliminary tests have used the MS system to check for changes in the composition on one side of the membrane system after composition changes on the other. We have shown the system to be leakfree ($<0.1 \text{ cm}^3 \text{ min}^{-1}$) at temperatures up to 800°C . Leaks appear on cooling below 250°C .
- (3) The MS is currently being reconfigured to achieve sharper response times by closer coupling to the membrane furnace.

Gradientless infusion experiments on $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$ disks.

We have used the delay caused by the recommissioning of the SIMS analysis in Houston to study further the surface modifications to the disk samples of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$ that were infused during before the previous quarterly report. An interesting phenomenon is the surface enrichment in Sr in the presence of the CO_2/CO mixtures. This appears to be true for all such samples examined to date and is distinct from the surface compositions of the materials exposed to O_2 atmospheres. In some cases, a crystalline phase, presumably of SrCO_3 is visible in SEM micrographs. Such apparent fluxional changes can explain some of the variability in surface activation rates seen in our previous IEDP studies and reported in Boston in February.

The MS data from the infusions have also been analysed and show similar behaviour to the previous results, with the CO_2 showing the complete isotopic scrambling associated with surface exchange mechanism. The CO component also reveals the rate of the much slower redox process of surface exchange. Such redox reactions are significant to membrane function.

Plans for next quarter.

Transient investigation of operating membranes. After the MS response is judged adequate and leaks tested with a combination of GC and MS diagnostics to be acceptable

(our target is < 0.001 , we will replace the quartz tube with a perovskite tube. We have both $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-x}$ materials available. The cobaltite will allow calibration with the previous successful studies at Houston and will probably be used first. Experiments on this material will be limited to oxygen containing atmospheres only and transients will be investigated at conditions studied in the previous work by Abeles and Jacobson. These will likely consume a month of experimental time, after which the $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$ material will be placed in the reactor. Dr. Lenjie Hu, who joined the group in August will be responsible for these studies, with the assistance of Nader Bayani.

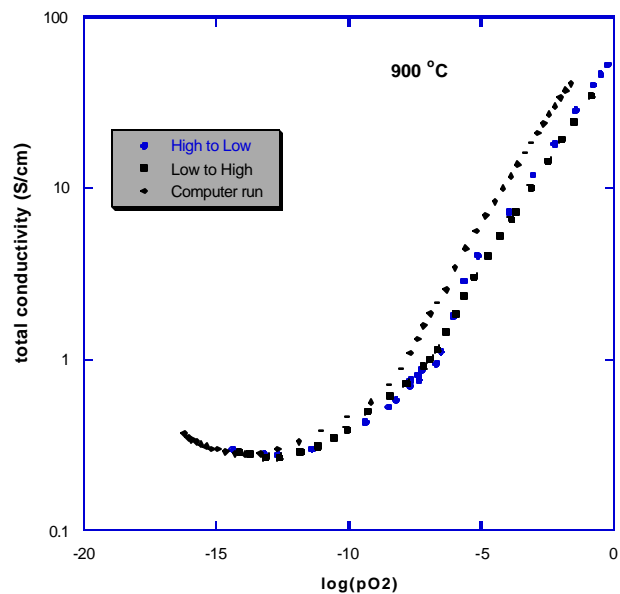
Gradientless IEDP experiments: We will measure the isotope profiles during the next quarter on the last batch of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$ disks, complete the modelling of these experiments (profile + MS data). Mr. Bayani will be in charge of the wrap up of this study.

DOE Progress Report University of Houston October 2001

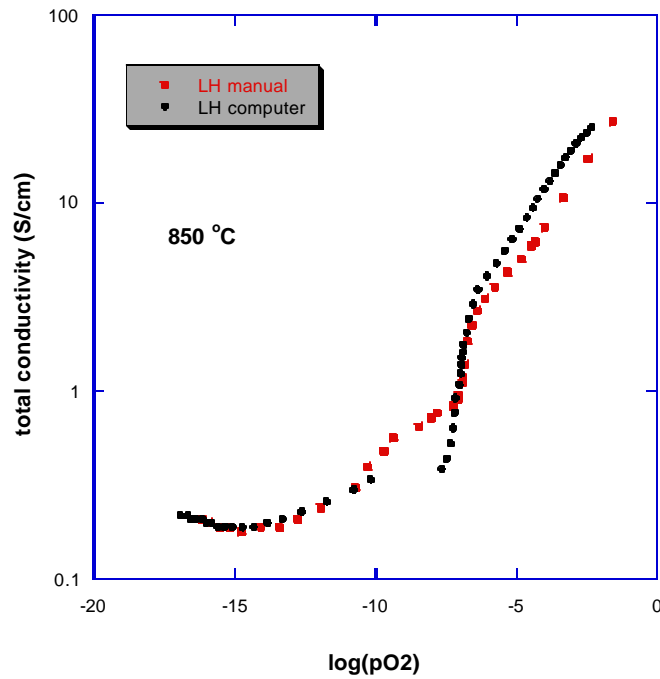
Conductivity and Thermodynamic Studies

We have continued to investigate the thermodynamic properties (stability and phase separation behavior) and total conductivity of two prototype systems, $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_{3-x}$. 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 both systems show evidence for phase separation at intermediate partial pressures of oxygen, $-11 < \log p\text{O}_2 < -5$. 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.



The figure shows results for La_{0.5}Sr_{0.5}Fe_{0.8}Ga_{0.2}O_{3-x} at 900 °C, which is just above the order disorder transition. As can be seen the data taken manually from high to low pressure and in the reverse direction are in excellent agreement and that apart from a small offset have the same pO₂ dependence. Below the miscibility gap the situation is more complex. The second figure shows two sets of data take at 650 °C both from low pressure to high pressure. The data at high and low pressure are in good agreement but show significant differences in the intermediate region where the phase separation occurs. We have now completed the evaluation of the La_{0.5}Sr_{0.5}Fe_{0.8}Ga_{0.2}O_{3-x} system is now complete.



Plans for next quarter.

We will extend the studies described above to include the $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-x}$. The other parameter that is needed for a complete model is the transference number for ions as a function of the oxygen partial pressure. To determine this, we have designed a cell that uses YSZ ironically blocking electrodes in the following configuration Pt/YSZ/LSCFO/YSZ/Pt. A third electrode located in contact with the LSCFO enables the stoichiometry of the sample to be altered by bolometric titration. We have obtained the first results using this cell and will complete the measurements in this quarter. In this quarter, we will also synthesize additional tubular ceramics for use in the membrane reactor at UT