Oxygen Transport Ceramic Membranes

Quarterly Report

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ABSTRACT

The present quarterly report describes some of the investigations on the structural properties of dense OTM bars provided by Praxair and studies on newer composition of Ti doped

Ti-substituted perovskites, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$, with $0 \leq x \leq 0.20$, were investigated by neutron diffraction, magnetization, electric resistivity, and magnetoresistance (MR) measurements. All samples show a rhombohedral structure (space group R3C) from 10 K to room temperature. At room temperature, the cell parameters a , c and the unit cell volume increase with increasing Ti content. However, at 10 K, the cell parameter a has a maximum value for $x=0.10$, and decreases for $x>0.10$, while the unit cell volume remains nearly constant for $x>0.10$. The average (Mn,Ti)-O bond length increases up to $x=0.15$, and the (Mn,Ti)-O-(Mn,Ti) bond angle decreases with increasing Ti content to its minimum value at $x=0.15$ at room temperature. Below the Curie temperature T_C , the resistance exhibits metallic behavior for the $x \leq 0.05$ samples. A metal (semiconductor) to insulator transition is observed for the $x \geq 0.10$ samples. A peak in resistivity appears below T_C for all samples, and shifts to a lower temperature as x increases. The substitution of Mn by Ti decreases the 2p - 3d hybridization between O and Mn ions, reduces the bandwidth W , and increases the electron-phonon coupling. Therefore, the T_C shifts to a lower temperature and the resistivity increases with increasing Ti content. A field-induced shift of the resistivity maximum occurs at $x \leq 0.10$ compounds. The maximum MR effect is about 70% for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ti}_{0.2}\text{O}_3$. The separation of T_C and the resistivity maximum temperature $T_{\rho,\text{max}}$ enhances the MR effect in these compounds due to the weak coupling between the magnetic ordering and the resistivity as compared with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

The bulk densities of the membranes were determined using the Archimedes method. The bulk density was 5.029 and 5.57 g/cc for LSFT and dual phase membranes, respectively. The microstructure of the dual phase membrane was analyzed using SEM. It is evident from the micrograph that the microstructure is composed of dual phases. The dense circular regions are enclosed by the less dense, continuous phase which accommodates most of the pores. The pores are normally aggregated and found clustered along the dense regions where as the dense regions do not have pores. Upon closer observation of the micrograph it is revealed that the dense region has a clear circular cleavage or crack as their boundary. The circular cleavage clearly encompasses a dense region and which consists of no pore or any flaw that is visible. The size distribution of the dense, discontinuous regions is varying from 5 to 20 μm with a D_{50} of 15 μm . The grain size distribution was estimated from the micrographs using image analysis and a unimodal distribution of grains was observed with an average grain size of 1.99 μm . The chemical compositions of the membranes were analyzed using EDS analysis and no other impurities were observed. The XRD analysis was carried out for the membranes and the phase purity was confirmed. The fracture toughness of LSFT membranes at room temperature has to be calculated using the Vickers indentation method.

An electrochemical cell has been designed and built for measurements of the ionic conductivity by the use of blocking electrodes. Preliminary measurements on $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-\delta}$ are reported. Modifications to the apparatus to improve the data quality have been completed. Electron microscopy studies of the origin of the slow kinetics on reduction of ferrites have been initiated. A series of isotope transients under air separation mode (small gradient) were completed on the membrane of LSCrF-2828 at 900°C. Low $p\text{O}_2$ atmospheres based on with CO - CO₂ mixtures have also been admitted to the delivery side of the LSCrF-2828 membrane to produce the gradients which exist under syngas generation conditions. The CO - CO₂ mixtures have normal isotopic ^{18}O abundances. The evolution of ^{18}O on the delivery side in these experiments after an ^{18}O pulse on the air side reveals a wealth of information about the oxygen transport processes.

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INTRODUCTION

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: 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.

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. Phase stability and stress development (University of Missouri - Rolla);
3. Mechanical property evaluation in thermal and chemical stress fields (University of Alaska Fairbanks)

Statement of Work

Task 1 Evaluate phase stability and thermal expansion of candidate perovskite membranes and develop techniques to support these materials on porous metal structures.

Task 2 Determine materials mechanical properties under conditions of high temperatures and reactive atmospheres.

Task 3 Measure kinetics of oxygen uptake and transport in ceramic membrane materials under commercially relevant conditions using isotope labeling techniques.

EXECUTIVE SUMMARY

Research on the Oxygen Transport Membranes as listed as tasks 1-3 are being performed at the various universities under the stewardship of Praxair. The quarterly technical report presents the progress of the tasks defined to understand the fundamental concepts and structural performance of the OTM material.

The magnetic and electronic transport properties of Ti-substituted $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ have been systematically investigated. All the Ti-substituted $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compositions have a rhombohedral structure, (space group R3C). The correlation between ferromagnetic TC and $T_{\rho,\text{max}}$ becomes weaker and spin glass clusters are expected in the low temperature region with increasing Ti substitution. The resistivity in the high temperature region suggests the formation of localized polarons that affect the strong correlation between local structural changes and MIT. The decrease of the bandwidth W decreases the overlap between the O-2p and Mn-3d orbitals, which in turn decreases the exchange coupling of Mn-Mn and the magnetic ordering temperature T_c as well. Our studies indicate that Ti substitution at Mn enhances the electron-phonon interaction in these compounds, which decreases the bandwidth and increases the resistivities in the entire temperature range.

Bulk densities of the LSFT and dual phase membranes were determined using Archimedes method. The bulk density was 5.029 and 5.57 g/cc for LSFT and dual phase membranes, respectively. SEM showed the presence of dense circular regions surrounded by the less dense, continuous phase which accommodates most of the pores. The size distribution of these dense regions was examined using image analysis. Most of those were of the size varying from 5 to 20 μm with a D_{50} of 15 μm . The closer observation of the micrographs revealed the presence of a circular crack that encompasses the dense region. The pores were found to be in clusters in the less dense region along the circular crack. The grain size in the dual phase microstructure was fine ($D_{50} = 1.99 \mu\text{m}$) and the distribution of grains were unimodal.

The EDX analysis was carried out to for both the membranes to study the chemical analysis. The XRD analysis for the membranes for identifying the crystal systems and for doing phase analysis was carried out and the crystal system identification has to be carried out. The fracture toughness of the membranes has to be calculated using indentation method.

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. We have previously reported characterization, stoichiometry, conductivity, and dilatometry measurements for samples of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$. In this period, we have investigated the use of a transient technique to separately determine the ionic conductivity. The experimental apparatus and the preliminary results are presented. We have initiated some transmission electron microscopy experiments to study the microstructure of ferrites that show very slow kinetics in the intermediate pressure range. The data suggest non-equilibrium behavior which is associated with the formation of nano-particles of a reduced component which re-react at long times.

In the area of isotope transient studies at steady state, the current quarter has been dominated by continued analysis of the data from the isotope transients and the analysis of the profile in the quenched membrane.

**Task 1: Structure, magnetic and transport properties of Ti-substituted
La_{0.7}Sr_{0.3}MnO₃**

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The A_{1-x}A'_xMnO₃ perovskites are interesting systems because of the anomalous magnetic and transport properties exhibited by them such as colossal magnetoresistance (CMR), metal-insulator transitions, antiferromagnetic-ferromagnetic ordering, and lattice dynamics associated with the phase transitions. [1–8] Zener’s double exchange (DE) interaction between Mn³⁺ and Mn⁴⁺ ions through charge carriers in the oxygen 2*p* orbitals was introduced in order to explain the coupling of magnetic and electronic properties in these compounds. [9–12] Undoped LaMnO₃ is an *A*-type antiferromagnetic insulator. By substitution of La³⁺ with a divalent cation, LaMnO₃ can be driven into a metallic and ferromagnetic state. Both Mn³⁺ and Mn⁴⁺ ions possess a local spin (*S*=3/2) from their lower *t*_{2*g*}³ orbitals, and Mn³⁺ has an extra electron in the *e_g* orbital which is responsible for conduction. The spin of the *e_g*¹ electron in Mn³⁺ is ferromagnetically coupled to the local spin of *t*_{2*g*}³ according to Hund’s rule. Sr doping induces holes in the *e_g* band near the Fermi energy, producing mobile holes and conduction. However, recent studies have shown that DE is not sufficient to explain the complex physics in these compounds, especially as regards the lattice distortions coinciding with the emergence of CMR [13,14]. An understanding of the Sr-doped systems requires one

to consider both DE interactions in the $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ pairs and the strong electron-phonon coupling, including lattice polarons and dynamic Jahn-Teller(J-T) distortions. [15,16] The polaron effect arising from J-T distortion was introduced to explain the electronic transport mechanism in the high temperature region, $T \approx T_C$, where a strong electron-phonon interaction is required to reduce the kinetic energy of the conduction electrons. The local J-T distortion of the MnO_6 octahedron lowers the energy of the e_g^1 electron and the charge carrier can then be localized to form a lattice phonon. Therefore local lattice distortion above T_C rapidly decreases electron hopping, thus increasing the resistivity. [14] Recently, it was found that polaron hopping was also the dominant conduction mechanism below T_C . [17–20] A sharp increase of polaron density at temperatures below T_C leads to a charge carrier density collapse, which is related to the resistivity peak and the CMR of doped manganites. [21]

In order to understand the unusual magnetic and transport properties of doped perovskites $\text{A}_{1-x}\text{D}_x\text{MnO}_3$, many studies have been carried out by doping the trivalent rare earth site(A site) with divalent atoms(Ca, Sr, Ba, etc). [5,22–26] Other studies have also shown that substitution for Mn (B site) dramatically affects the magnetic and transport properties of perovskites. [27–29] The B site modification has merit in that it directly affects the Mn network by changing the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and the electron carrier density. Therefore in order to better understand the role of Mn and its local environment in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, we studied the effects of replacing some of the Mn with Ti. The structural, magnetic and electrical phase transitions and transport properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ with $0 \leq x \leq 0.20$ have been investigated by neutron diffraction, magnetization, electric resistivity, and magnetoresistance measurements and the results are presented here.

Experimental:

Samples of Ti-substituted $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$, with $0 \leq x \leq 0.2$, were prepared using the conventional solid state reaction method. Highly purified La_2O_3 , SrCO_3 , TiO_2 , MnO were mixed in stoichiometric ratios, ground, and then pelletized under 10,000 psi pressure

to a 1 cm diameter. The pelletized samples were fired at 1500°C in air for 12 hours, then reground and sintered at 1250°C for 24 hours in air. X-ray diffraction of the powders was carried out at room temperature using a SCINTAG diffractometer with $\text{Cu-K}\alpha$ radiation. X-ray diffraction data indicated all samples to be single phase. Powder neutron diffraction experiments were performed at the University of Missouri-Columbia Research Reactor(MURR) using neutrons of wavelength $\lambda=1.4875 \text{ \AA}$. The data for each sample were collected between $2\theta = 5.65 - 105.60^{\circ}$ at 300K and 10 K. Refinement of the neutron diffraction data was carried out using the FULLPROF program [30], which permits multiple phase refinements as well as magnetic structure refinements. Magnetic measurements were conducted with a SQUID magnetometer(MPMS, Quantum design). The magnetization curves with zero-field cooling(ZFC) and field cooling(FC) were measured in an applied magnetic field of 50Oe. Resistivity data were obtained using a physical properties measurement system(PPMS, Quantum design) with a standard four-point probe method.

Results and Discussion:

Figure 1 shows the x-ray diffraction patterns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ samples, with $x=0.03, 0.05, 0.10, 0.15$, and 0.20 , at room temperature(RT). All the samples are single phase and all peak positions can be indexed to $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{2.91}$ (JCPDS 50-0308), space group $R\bar{3}c$. In order to investigate the details of the structural distortion and the magnetic interactions in these compounds, powder neutron diffraction measurements were performed at different temperatures. Figure 2 shows the neutron diffraction patterns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.03$ and 0.15 measured at RT and 10 K. All patterns can be fitted with the $R\bar{3}c$ rhombohedral space group (No. 167) in which the atomic positions are La(Sr): 6a (0,0,1/4), Mn(Ti): 6b (0,0,0); O18e (x,0,1/4). The $P1$ space group was used to fit the magnetic structure because of its flexibility. Refined structural and magnetic parameters are listed in Tables I and II for RT and 10K, respectively. For samples with $x \geq 0.10$, there is no magnetic ordering at RT since $T_C < \text{RT}$, whereas for samples with

$x \leq 0.10$, $T_C > \text{RT}$ magnetic ordering is observed. The arrows on the neutron diffraction patterns of the $x = 0.03$ sample (Figure 2) indicate magnetic reflection peaks that are not present for the $x = 0.20$ sample at RT. The peak intensities of the magnetic reflections decrease with Ti substitution at both RT and 10 K. In addition, the refinement results confirm that the substituted Ti ions go into B sites, not into A sites, because the ionic radius of Ti^{4+} ($0.605\text{\AA}$) lies between the ionic radius of Mn^{4+} ($0.530\text{\AA}$) and Mn^{3+} ($0.645\text{\AA}$) [32]. The tolerance factor, which is the geometric measure of size mismatch of perovskites,

$$t = (r_{(La,Sr)} + r_O) / [(r_{(Mn,Ti)} + r_O)\sqrt{2}] \quad (1)$$

decreases linearly from 0.928 for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ to 0.921 for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ti}_{0.2}\text{O}_3$, which is in the stable range of the perovskite structure $0.89 < t < 1.02$. [26] Therefore, substitution of Mn by Ti does not change the crystal structure itself but changes the bond lengths and the bond angles of the MnO_6 octahedra.

The lattice parameters a, c and the unit cell volume increase with the Ti content at RT. At 10 K, the lattice parameter a shows a maximum value at $x = 0.10$ and then decreases as $x > 0.10$, and the unit cell volume increases up to $x = 0.10$ and becomes almost constant for $x > 0.10$. The refined magnetic moment value of the Mn atom decreases with increasing Ti content with a rate of $6.4\mu_B$ per Ti atom at 10 K. The values of the Mn moments indicate that Mn atoms have a high spin state, and the average valence state of the Mn varies from $3d^{3.5}$ to $3d^{2.3}$ for $x=0.03$ and $x=0.20$, which suggests that the Ti atoms are in the Ti^{4+} state.

The average (Mn,Ti)-O bond length and (Mn,Ti)-O-(Mn,Ti) bond angle extracted from the Rietveld refinement at RT and 10K are shown in Figure 4. The bond length of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ increases up to $x = 0.15$ and remains constant thereafter for $x \geq 0.15$, while the bond angle decreases and attains an anomalous minimum value for $x = 0.15$ at RT. At 10K, the bond length increases up to $x = 0.10$ and remains constant for $x > 0.10$, while the bond angle decreases with increasing x . The bond length and the bond angle are closely related to the oxygen positions. Therefore, an increasing (Mn-Ti)-O bond length and a decreasing (Mn,Ti)-O-(Mn,Ti) bond angle are strongly correlated. The changes in

bond length and bond angle of MnO_6 compensate one another to diminish the internal strain induced by Ti^{4+} . Since the exchange interaction between Mn-Mn depends on both the bond angle and the bond distance, the decrease in bond angle and the increase in bond length decrease the Mn-Mn exchange interaction which leads to a lower magnetic ordering temperature T_C (see later discussion of M-T curves).

The electronic bandwidth W has been used to discuss magnetic and transport properties of perovskites with varied A-site doping. [16,33]. The empirical formula of the bandwidth W for ABO_3 -type perovskites using the tight binding approximation [24] is

$$W \propto \frac{\cos\omega}{(d_{\text{Mn-O}})^{3.5}}, \quad (2)$$

where $\omega = \frac{1}{2}(\pi - \langle \text{Mn-O-Mn} \rangle)$ and $d_{\text{Mn-O}}$ is the Mn-O bond length. The calculated values of $\cos\omega/(d_{\text{Mn-O}})^{3.5}$ using the refinement results are shown in Figure 4c. We assumed the bandwidth W is proportional to the values of $\cos\omega/(d_{\text{Mn-O}})^{3.5}$. It is found that the bandwidth W decreases with increasing Ti content. Further, the bandwidth at RT is smaller than the bandwidth at 10K for a given Ti content. The evolution of the bandwidth follows the change in the $\langle \text{Mn-O-Mn} \rangle$ bond angle. The decrease in bandwidth reduces the overlap between the O-2p and the Mn-3d orbitals, which in turn decreases the exchange coupling of Mn^{3+} - Mn^{4+} , and the magnetic ordering temperature T_C as well. For a charge-transfer insulator, the band gap energy E_g in the insulating phase can be written as $E_g = \Delta - W$, where Δ is the charge-transfer energy and W is the O-2p-like bandwidth. In practice, Δ changes little in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system and thus the bandwidth W becomes a main factor in tuning the band gap energy. [34] For the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds, the decrease in bandwidth W increases the band gap, E_g , and leads to the metal to insulator transition for $x > 0.10$.

Figure 5 shows the magnetization versus temperature (M-T) curves measured under field-cooled (FC) and zero field-cooled (ZFC) conditions in a magnetic field of 50 Oe for the $x = 0.05, 0.10$, and 0.15 samples. A sharp paramagnetic to ferromagnetic transition is observed at a critical temperature T_C . Figure 6 shows the Curie temperatures, T_C , of

$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ for differing Ti content. The decrease in T_C is obviously related to the changes in bandwidth as seen in Fig 4c. The T_C drops at a rate of about 10K per Ti. λ -shaped magnetization curves in ZFC emerge for $x \geq 0.10$ samples. The existence of λ -shaped curves under ZFC may be evidence of the formation of ferromagnetic clusters with a spin glass state. The Ti substitution weakens the exchange interaction and breaks the Mn-O-Mn network, and creates short range ordered ferromagnetic clusters. As more Ti is substituted, more inhomogeneous clusters are formed, which leads to a broadening of the paramagnetic to ferromagnetic phase transition peak. A similar phenomenon has been observed in the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ system. [26]

Magnetization versus field (M-H) curves of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ at different temperatures are plotted in Figure 7. At 20 K, all samples reach a nearly constant value of magnetization under a field, $H = 0.6$ T. The estimated magnetic moments of the $x = 0.05$, 0.10 and 0.15 samples from magnetization data at 20 K are 3.54, 3.24, and $2.49 \mu_B$ per Mn atom, respectively. These moment values are in good agreement with the neutron diffraction refinement results (see Table II). The theoretically estimated magnetic moments of Mn from its valence state taking into account the dilution effect of Ti^{4+} , are 3.55, 3.40 and $3.35 \mu_B$ respectively. This suggests that the decrease of magnetization with increasing Ti content is not only due to the dilution of magnetic Mn^{4+} atoms but also due to the weakening of exchange coupling by the cluster formation.

Figure 8 shows the resistivity as a function of temperature under different applied fields for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds with $x = 0.05$, 0.10, and 0.15. In the temperature range 4 - 300 K, the resistivity of the samples increases as the Ti content increases. The resistivity of $0.05 \leq x \leq 0.10$ shows a maximum value at temperature $T_{\rho,max}$ below T_C , and then decreases as the temperature decreases. Finally the resistivity increases again as T decreases further for $x \geq 0.10$. The difference between T_C and $T_{\rho,max}$ becomes larger as the Ti content increases and $T_{\rho,max}$ is lower than T_C . This behavior is quite different from that observed in the Ti-substituted $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ series which exhibit large differences between T_C and $T_{\rho,max}$ [25], and $T_{\rho,max}$ is higher than T_C . [26]. For the $x \leq 0.15$ sample, a

metal(semiconductor) to insulator transition (MIT) appears in the low temperature region. The field-induced shift of maximum resistivity to higher temperature appears for the $x \leq 0.10$ samples, and becomes negligible for $x \geq 0.15$. The suppression of the resistivity by the applied magnetic field occurs over the entire temperature range for all samples. At $T > T_C$, the suppression of the resistivity becomes weaker. According to the DE mechanism, the mobility of the charge carriers e_g electrons improves if the localized spins are polarized. The applied field aligns the canted electron spins which should reduce the scattering of itinerant electrons with spins and thus the resistivity is reduced. Therefore an applied magnetic field competes with the thermal fluctuations and maintains magnetic ordering around T_C for the $x \leq 0.10$ samples, and thus shifts the $T_{\rho,max}$ to higher temperatures.

Figure 9 shows the typical temperature dependence of the magnetoresistance [$MR = (\rho_0 - \rho_H)/\rho_0 \times 100$] of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ samples with $x = 0.05$ and 0.15 under an applied field of 1 and 3T. The MR increases with increasing Ti concentration over the entire temperature region. For example, the MR values are 30%, 55% under 3T for $x = 0.05, 0.15$, respectively. The temperature of the MR peak shifts to a lower temperature, approximately 15 K per Ti. It is known that in A-site, electron-doped $\text{A}_{1-x}\text{A}'_x\text{MnO}_3$ ($x=0.3$) compounds, the metal-insulator transition temperature T_{MI} coincides with the T_c , and the metal-insulator transition is strongly coupled with the magnetic ordering transition. Therefore, a strong variation of the electrical resistivity up to several orders of magnitude, namely the colossal magnetoresistance (CMR) effect, occurs upon application of a magnetic field near T_C . However, for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds, the T_C is different from the metal to insulator transition temperature (MIT). The application of a magnetic field has much more effect on the change of electric resistivity when compared to $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ due to the weak coupling between the MIT and the magnetic ordering. An enhancement of the MR effect is observed in these compounds, similar to that in $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ [25,26] and $\text{Pr}_{1-x}(\text{Ca,Sr})_x\text{MnO}_3$ compounds. [35]

The change of the electronic properties of Ti-substituted $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds is strongly related to the electron phonon coupling [14]. Accordingly, in the

La_{1-x}Sr_xMnO₃ system, the strong electron-phonon coupling localizes the conduction band electron as a polaron, due to the competition between the self trapping energy E_{JT} and the electron itinerant energy. The electron-phonon coupling constant $\lambda = E_{JT}/t$, where t is the electron hopping parameter, is proportional to the electronic bandwidth W . As mentioned above, the substitution of Mn by Ti decreases the overlap of the O-2*p* and Mn-3*d* orbitals due to the decrease in W , thus increasing the electron-phonon coupling. This results in a shift of T_C to lower temperatures and an increase of resistivity with increasing Ti content. As a consequence, one should consider a possible dependence of E_{JT} on Ti content. We cannot rule out the contribution from E_{JT} , even though our data indicate that all the observed T_C and resistivity changes can be explained, at least qualitatively, by the change in W . Especially, for $x \geq 0.15$, the electron-phonon coupling becomes very strong, and the insulator behavior occurs below T_C as shown in Figure 8. The changes in bandwidth W are not large enough to account for the dramatic changes in resistivity, and therefore, E_{JT} might be contributing significantly to the change of resistivity in these samples.

It has been proposed that, above T_C , charge may be localized in the form of J-T polarons. [21] At $T \geq T_C$, the resistivity of the CMR materials can be explained by the activated adiabatic polaron equation [36]

$$\rho = AT \exp(E_{hop}/kT) \quad (3)$$

where A is a constant and E_{hop} is the contribution from polaron formation and other interactions. [37] Figure 10 shows the plot of $\ln(\rho/T)$ as a function of $1/T$ for La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO₃ compounds with $x = 0.05, 0.10, 0.15$ and 0.20 in the high temperature region. Resistivity of all the samples shows a similar slope at $T \geq T_C$, which can be fitted well with the small polaron model indicating the formation of a polaron. The polaron hopping energy E_{hop} is calculated from the slopes. The calculated values of E_{hop} are 49.8, 132.0, 138.3, and 152.5 *meV* for $x = 0.05, 0.10, 0.15$, and 0.20 , respectively. The increase of E_{hop} is due to the substitution of Mn by Ti which depletes the oxygen *p* holes and leads to an increase in the polaron binding energy. This further confirms that Ti substitution at

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Tables:

Table I. Refined parameters for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compound with $R\bar{3}C$ space-group at room temperature ($T=300\text{K}$). Numbers in parentheses are statistical errors. a and c are the lattice parameters. m is magnetic moment. V is the unit cell volume. B is the isotropic temperature parameter. χ^2 is $[\text{R}_{wp}/\text{R}_{exp}]^2$ where R_{wp} is the residual error of the weighted profile.

Composition	0.03	0.05	0.10	0.15	0.20
a ($\text{\AA}$)	5.5107(1)	5.5157(2)	5.5225(2)	5.5306(2)	5.5310(2)
c ($\text{\AA}$)	13.3654(4)	13.3699(5)	13.3845(5)	13.4032(6)	13.4124(6)
V ($\text{\AA}^3$)	351.446(17)	352.263(20)	353.508(21)	355.042(22)	355.341(23)
m (μ_B)	2.037(37)	1.042(30)	0.0	0.0	0.0
χ^2 (%)	3.29	3.61	2.81	4.64	2.98
O, 18e,x	0.5437(2)	0.5448(2)	0.5459(2)	0.5468(2)	0.5461(2)
B($\text{\AA}^2$), La(Sr),6a	0.812(36)	0.857(38)	1.004(41)	0.978(43)	1.143(40)
B($\text{\AA}^2$), Mn(Ti),6b	0.536(58)	0.551(62)	0.358(62)	0.399(67)	0.424(63)
B($\text{\AA}^2$), O,18e	1.265(30)	1.332(32)	1.503(34)	1.474(37)	1.586(35)

Table II. Refined parameters for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compound with $R\bar{3}C$ space-group at low temperature($T=10\text{K}$). Numbers in parentheses are statistical errors. a and c are the lattice parameters. m is magnetic moment. V is the unit cell volume. B is the isotropic temperature parameter. χ^2 is $[\text{R}_{wp}/\text{R}_{exp}]^2$ where R_{wp} is the residual error of the weighted profile.

Composition	0.03	0.05	0.10	0.15	0.20
a ($\text{\AA}$)	5.4940(1)	5.5038(1)	5.5116(1)	5.5089(2)	5.5053(3)
c ($\text{\AA}$)	13.3037(4)	13.3238(3)	13.3354(4)	13.3421(6)	13.3747(10)
V ($\text{\AA}^3$)	347.758(14)	349.529(13)	350.822(15)	350.657(22)	351.053(35)
m (μ_B)	3.459(35)	3.402(35)	3.453(33)	3.315(39)	2.895(48)
χ^2 (%)	3.51	2.89	2.69	3.72	4.90
O, 18e,x	0.5442(2)	0.5448(1)	0.5467(1)	0.5468(2)	0.5472(2)
B($\text{\AA}^2$), La(Sr),6a	0.224(33)	0.272(31)	0.284(32)	0.408(4)	0.276(52)
B($\text{\AA}^2$), Mn(Ti),6b	0.197(54)	0.261(52)	0.112(52)	0.226(66)	0.150(63)
B($\text{\AA}^2$), O,18e	0.552(28)	0.596(27)	0.684(27)	0.976(35)	0.940(43)

Figures

FIG. 1. X-ray diffraction patterns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x=0.0, 0.05, 0.10, 0.15, 0.20$) at room temperature.

FIG. 2. Neutron diffraction patterns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ at 10 K and RT. (The bottom curves(Yobs-Ycal) are the difference between experimental data and refinement data. The vertical bars indicate the magnetic(bottom) and Bragg(top) peak positions). Arrows indicate magnetic diffraction peaks.

FIG. 3. Lattice parameter a , c , and volume of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ at room temperature and at 10 K.

FIG. 4. Average (Mn,Ti)-O bond lengths(a), (Mn,Ti)-O-(Mn,Ti) bond angles(b) and c)electronic bandwidth parameter $\cos\omega/(d_{Mn-O})^{3.5}$ (c), of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ at room temperature and at 10 K.

FIG. 5. The magnetization versus temperature(M-T) curves of La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO₃ ($x=0.05$, 0.10 , 0.15) measured under field cooling (FC) and zero field cooling (ZFC) conditions in a magnetic field of 50 Oe .

FIG. 6. The Curie temperature (T_C), and the temperature of maximum resistivity ($T_{\rho, \max}$) of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds with $x=0.0, 0.05, 0.10, 0.15$, and 0.20 .

FIG. 7. Field dependent magnetization of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ at different temperatures.

FIG. 8. Electric resistivity ρ versus temperature for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds ($x=0.05$ (a), 0.10 (b), and 0.15 (c)) in applied magnetic field $H=0, 1, 3$, and 5 T. Arrows indicate the $T_{\rho,max}$. The inset in (c) is the plot of resistivity of $x=0.15$ compound (with log scale) in $H=0$ T.

FIG. 9. Temperature dependence of magnetoresistance of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds ($x=0.05$ (a) and 0.15 (b)) in the magnetic field of $H=1, 3\text{ T}$.

FIG. 10. $\ln(\rho/T)$ versus $1/T$ plots in the high temperature region of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds ($x=0.05, 0.10, 0.15$, and 0.20). Dot line is the fitting line .

TASK 2: Determine material mechanical properties under conditions of high temperature and reactive atmosphere

Prof. S. Bandopadhyay and Dr. T. Nithyanantham

In order to understand the mechanical properties it is essential to understand the microstructure and chemical composition of membranes. The mechanical properties of the membranes are entirely dependent on the grain size, its distribution and the kind of flaws they have. While the fracture toughness of the membrane is influenced by the microstructure of the membranes, the flexural strength is controlled by the critical flaw size. In this quarter the much of the work is devoted to the microstructural characterization of the dual phase membrane and compositional analysis.

Density measurements of LSFT and dual phase (LSFT-CGO) membranes:

The bulk densities of the membranes were determined using the Archimedes method. The membranes were cut into small pieces and the dry weights of them were measured. The sample pieces were then immersed in distilled water and boiled for 5 hrs and allowed for overnight to cool. The weight of the samples suspended in water was measured and the wet weight was also measured after the samples were cleaned with wet cloth to remove the adsorbed water from the surface. The bulk densities were calculated using the weights that were measured and the results are presented in Table III. The LSFT membrane has a bulk density of 5.029 g/cc and the dual phase membrane shows a density of 5.57 g/cc.

Table III. Density of the membranes

	Bulk Density (g/cc)	App. Specific Gravity	Volume of the impervious material (cc)	Mean Bulk Density (g/cc)
LSFT	4.9305	4.98982	0.2161	5.029
	4.99433	5.03557	0.4723	
	5.16073	5.19103	0.6643	
LSFT-CGO	5.4	5.76667	0.081	5.57
	5.62998	5.94777	0.2374	
	5.67944	5.98951	0.3242	

Microstructure analysis of dual phase membranes:

The microstructure of the dual phase membrane was analyzed using SEM. The dual phase membrane samples were cut and ground down to 600 grade SiC paper. Further polishing of the samples did not improve polishing of the surface rather it spoiled the surface and affected the polishing. The polished samples were thermally etched at 1300°C for 1hr and were subjected to gold coating before the SEM analysis. The SEM micrographs of dual phase membrane are shown in Figure 11. It is evident from the micrograph that the microstructure is composed of dual phases. The dense circular regions are enclosed by the less dense, continuous phase which accommodates most of the pores. The pores are normally aggregated and found clustered along the dense regions where as the dense regions do not have pores.

Figure 11. SEM micrographs of dual phase membrane. The dense spherical regions (which are dark in color in Fig 1.a) are enclosed by the less dense, continuous phase which accommodates the pores. The closer observation (Figure 1 b) shows that the dense regions have a clear circular boundary or crack. The white arrow marks are used to point the circular cleavage.

The size distribution of the dense, circular region in the microstructure can be examined using image analysis. The dense regions are clearly distinguishable from the surrounding porous, continuous phase. Hence the dense regions in micrographs are

layered with a color marker which was later used to analyze the size distribution of the dense regions in the microstructures. The total area of the dense region was also calculated and found to be 26% of the microstructure.

Figure 12 (a) shows the size distribution of the dense, discontinuous regions. Most of those are of the size varying from 5 to 20 μm with a D_{50} of 15 μm . Another important thing that one can observe from the micrographs is that the discontinuous regions are mostly near circular in shape. This shape factor of this region can be used to understand the nature of the regions and would allow to postulate the formation of those regions.

Figure 12. Size distribution of the discontinuous phase in the dual phase membrane microstructure.

Upon closer observation of the micrograph it is revealed that the dense region has a clear circular cleavage or crack as their boundary. The white arrow marks that are shown in Figure 11 (b) are used to point the circular cleavage. This unique microstructure is better revealed in the higher magnification which is shown in Figure 13(a). The circular cleavage clearly encompasses a dense region and which consists of no pore or any flaw that is visible. The white arrow marks show the cleavage which is transgranular in nature. This crack clearly separates the less dense regions which accommodate pores and continuous from the dense region. The Figure 13 (b) shows the micrograph of the

dense region in which the grains are well fused and contains no pores. The spherical nature of the dense region in a three dimensional network is associated with the segregation of pores along the boundaries which resulted the porous continuous phase to encompass the dense region. The segregation of the pores may have caused due to the pore formers which were added during the processing or as a result of the sintering process. The formation of the cleavage around the dense region can be explained by the differential shrinkage of the pore free regions during sintering of the membranes. The highly dense region shrinks more than the rest of the surrounding phase with a different sintering rate which eventually leads to the formation of the cleavages or cracks.

Figure 13. (a) The circular crack or cleavage at higher magnification. The crack is transgranular and encompasses a dense region; (b) Micrograph of the dense region.

Figure 14. Microstructures of the dual phase membrane. The Figure (a) shows the presence of pores which are clustered together. The closer observation of the microstructure shown in Figure (b) reveals that the grain growth is controlled in the porous region.

The microstructure of the dual phase membrane is shown in Figure 14. The microstructure clearly shows that the pores are clustered together. The grain growth in the non-porous region is favored by the increased diffusion channels which are formed by the better packing during compaction or particle rearrangement during initial stage of sintering. The pores hinder the grain growth and result fine grains in the porous region.

Apart from the pores and circular cracks in the microstructure, the next significant flaw that was observed was the craters that were formed mostly due to the burnout of the organic additives like binder that were added during the processing of the membranes. One of such craters is shown in the Figure 15. It is observed that the size of the craters varies between 10 to 30 μm which are bigger than the grain boundaries or pores. The craters can reduce the flexural strength of the membranes to a greater extent. These craters can be avoided by refining the processing methods and identifying suitable organic additives.

Figure 15. A crater is shown in the micrograph which might have formed during removal of organic additives during the sintering.

The grain size distribution was estimated using image analysis and is shown in Figure 16. An unimodal distribution of grains is shown in the Figure 16(a) with an average grain size of $1.99\ \mu\text{m}$. The finer grains which are less than $1\ \mu\text{m}$ are mainly observed in the porous region caused by the hindered diffusion process.

Figure 16. Grain size distribution in the dual phase microstructure.

Energy Dispersive X-ray analysis (EDXA):

The presence of impurities in the chemical composition of the membranes can affect the structural and mechanical properties the materials significantly. Hence EDX analysis was also carried out on the LSFT and dual phase membrane samples to do the elemental analysis. Figure 17 shows the EDX spectrum of the LSFT membrane.

Figure 17 EDX analysis spectrum of LSFT membrane

The elements identified from the analysis are Sr, La, Fe, Ti, and Au. The presence of Au is only due to the gold coating applied to the sample prior to SEM analysis. No other impurities were detected.

Figure 18. EDX analysis spectrum of dual phase membrane

The dual phase membrane was also subjected to the EDX analysis and the elements identified were Sr, La, Fe, Ti, Ce, Gd and Au. No other major impurity was observed from the analysis. The EDX analysis was also carried out independently in the circular, dense region and the continuous porous region to verify any possible element segregation or evaporation during this phase formation. The EDX patterns taken from the dense regions as well as from the porous regions were identical and all the relevant elements were found to be there in both the patterns. This analysis showed that there was

no such segregation or evaporation of elements which could be detected by this EDX analysis.

X-ray diffraction analysis of the membranes:

The x-ray diffraction analyses were carried out for the LSFT and dual phase membranes for identifying the crystal systems and for doing phase analysis. The membranes were crushed into fine powders and analyses were done at a very slow scan rate.

Figure 19. XRD powder patterns of LSFT and dual phase membrane.

Figure 19 shows the XRD pattern of the LSFT and dual phase membranes. The analysis could not be completed due to the lack of interface with the data base. The data interface problem is expected to be resolved soon and further analysis would be undertaken in the next quarters.

Fracture toughness studies:

The fracture toughness of LSFT membranes at room temperature has to be calculated using the Vickers indentation method. The indentations were given with a load

of 1 Kg for the duration of 10 sec on polished samples. At first, the crack length measurements were made using the optical microscope. Since the measurements were not accurate enough to calculate the fracture toughness, SEM was used for measuring the crack lengths. The SEM micrograph of an indentation and a part of the crack is shown in Figure 20.

Figure 20. Crack length measurements in LSFT using SEM

(a) indentation (b) a part of the crack that was generated during indentation

Fracture toughness will be calculated using the crack length measurements from the SEM micrographs.

Plans for the next quarter:

1. *X-ray diffraction analysis will be done for the LSFT and dual phase membranes.*
2. *The thermal analysis will be carried out for the both the membranes at different environment.*
3. *Fracture toughness of both the membranes will be calculated using indentation method.*
4. *Thermomechanical studies will be continued.*

Task 3: Measurement of Surface Activation/Reaction Rates in Ion Transport Membranes using Isotope Tracer and Transient Kinetic Techniques

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EXPERIMENTAL

Most of the work at UH this quarter has been directed towards electrochemical polarization experiments on $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-\delta}$ and further analysis of the non-equilibrium data.

The electrochemical cell for polarization measurements is shown schematically in Figure 21a. The sample disc (0.05-inch thickness) is located between two YSZ electrodes (1/2-inch diameter, 0.04-inch thickness). The outside surface of two YSZ discs were connected to Pt wires (0.004-inch diameter) using Pt meshes (150 × 150 mesh, 0.002-inch wire diameter, Unique Wire Weaving Co., Inc) and Pt paste (Engelhard 6926). In order to avoid any side reaction between the sample and YSZ, the inside surface of the YSZ was covered with Pt paste. The YSZ discs covered with Pt were annealed at 1300 °C for 30 min. Thin porous platinum layers were formed on the YSZ and the porosity was determined to be ~ 29% by scanning electron microscopy (JEOL JSM-6330F) as shown in Fig. 1(b). The sample was sealed with Pyrex glass to prevent oxygen ingress from air. The voltages across the cylindrical sample and two YSZ disks was monitored by 2000-20 multimeter (Keithley). Data acquisition was controlled by the Lab View program.

Fig. 21. (a) The symmetric electrochemical cell for polarization measurement and (b) scanning electron micrograph of YSZ covered with Pt after annealed at 1300 °C for 30 min.

The other experimental techniques used to generate the results reported here have been described in previous quarterly reports.

RESULTS AND DISCUSSION

University of Houston

In the previous reports, we have studied the electrical conductivity properties, the oxygen non-stoichiometry behavior, and the thermal/chemical expansion effects of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-\delta}$ (LSFTO285545). We also investigated the thermoelectric power by using a gas tight electrochemical cell in order to understand the mobilities. The oxygen ion conductivities obtained from AC 4-probe conductivity experiments need to be confirmed or compared to those determined by a different experimental technique such as the ion blocking electrode method.

According to E. Bucher *et al.*, the polarization and the depolarization process can be defined as follows:

$$U_p(t) = -\frac{jL}{\sigma_i} + \frac{jLt_e}{\sigma_i} \left(\frac{8}{\pi^2} \exp\left(-t/\tau\right) \right) \quad (1)$$

and

$$U_d(t) = -\frac{jLt_e}{\sigma_i} \left(\frac{8}{\pi^2} \exp\left(-t/\tau\right) \right) \quad (2)$$

These equations are based on two assumptions which are that the electronic transport number t_e of the mixed oxide is close to unity and that the kinetics of the mixed conducting interlayers can be neglected due to their small thickness compared to the relaxation process in the bulk sample.

$\ln|U(t) - U(t = \infty)|$ vs. t -plots yield linear relations in t for time $t \geq \tau/2$

$$\ln|U(t) - U(t = \infty)| = -\frac{t}{\tau} + \ln\left(\frac{8}{\pi^2} \frac{t_e jL}{\sigma_i}\right) \quad (3)$$

The slop k of and the intercept A on the y-axis are given by

$$k = -\frac{1}{\tau} = -\frac{\pi \tilde{D}}{L^2} \quad (4)$$

$$A = \ln\left(\frac{8}{\pi^2} \frac{t_e jL}{\sigma_i}\right) \quad (5)$$

where j is the total current density, L is the length of the sample, and τ is the relaxation time of the sample defined as

$$\tau = \frac{L^2}{\pi^2 \tilde{D}} \quad (6)$$

The data in figure 22a show a typical depolarization curve for LSFTO after the sample has reached steady state with an applied current of 0.1 mA at 850 °C after the current is stopped. The voltage decay is monitored as a function of time. In order to analyze the relaxation, the measured voltage at time t minus the final voltage is plotted in log form. The results can then be analyzed using equations 4 and 5. The chemical diffusion coefficient and the ionic conductivity are from the preliminary results $\tilde{D}$: 1.7×10^{-6} cm²/s and σ_i : 4.88×10^{-4} S/cm. It became apparent in the preliminary measurements that the long time data needs to be measured more precisely in order to define the slope of the curve. The present results appear to be too low. The apparatus is being modified to

incorporate a nanovoltmeter. Unfortunately this modification has required some Lab View reprogramming. This has been completed and further results will be reported in the next quarter.

Figure 22. A depolarization curve of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Fe}_{0.45}\text{O}_{3-\delta}$ at 850 °C in air (a) Voltage response of cell during the depolarization process (b) logarithmic plot of (a)

Non-equilibrium behavior

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. We have previously reported characterization, stoichiometry, conductivity, and dilatometry measurements for samples of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$. In this report, we have started to investigate the non equilibrium behavior observed in conductivity and thermal expansion previously reported. Similar, extremely slow equilibrium kinetics were also observed in the Seebeck coefficient measurements reported in the last quarter. These effects in conductivity and thermal expansion are illustrated in Figures 23 and 24.

Figure 23. Conductivity measurements for LSFTO showing the non-equilibrium behavior in the intermediate pressure range.

An understanding of this behavior is needed to predict membrane performance on pO_2 cycling. To address the question, we have initiated a study of quenched samples by

high resolution transmission electron microscopy. Samples of LSTO in the form of dense ceramic disks were quenched from different pO_2 values that span the range of behavior from 900 °C. The samples have been cut and polished and TEM specimens prepared by ion milling. Preliminary results indicate significant differences in microstructure for the samples quenched from the different partial pressures. Detailed analysis is in progress and the results will be reported in the next quarter.

Figure 24 Thermal expansion and stoichiometry behavior for LSFTO showing the non equilibrium behavior in thermal expansion compared with the long time equilibrium stoichiometry data.

Plans for next quarter

In the next quarter we will complete analysis of the TEM results and continue analysis of the relaxation data for $La_{0.2}Sr_{0.8}Fe_{0.55}Ti_{0.65}O_{3-x}$.

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Isotope Transient Studies at Steady State

As set forth in previous reports, the various surface and bulk transport parameters can be separately determined on an operating membrane by the application of an isotopic transient (a pulse of $^{18}O_2$ in our case) on one side of an operating membrane and the

subsequent time dependence of ^{18}O evolution from both sides of the membrane. Both the forward and reverse surface rates can be directly measured. In flux measurements, only the net rates are available.

Summary of progress:

Quenched profile:

The oxygen – 18 SIMS map reported in the last quarterly report of the cross section of the membrane quenched from operating conditions is shown in Figure 25.

Figure 25: Quenched isotope (O-18) distribution in the LSCrF 2828 membrane. The quench was performed at 900°C under high oxygen gradient conditions.

The schematic shows how the quenched membrane was cut for profile measurement. The cracks seen in the figure developed during the quench, and did not exist during the isotope transient. This is clear from the absence of isotopic anomalies near the cracks as have been seen in some IEDP experiments previously. An axial profile is also shown in the upper left part of the figure.

The profile from the lower left (radial cut) isotope map is shown in Figure 26.

Figure 26: O-18 isotope profile for LSCrF 2828 membrane quenched during an isotope transient under high gradient conditions.

The shape of this profile is asymmetric to a degree which we cannot fit with a constant diffusivity across the membrane. The shape is consistent with a higher diffusivity near the delivery side, but complications in modeling the back-exchange of O-18 with the CO₂ were identified. Further work on the modeling has continued during this quarter but is not yet complete. The next quarter will be used to complete the analysis and provide a quantitative interpretation of the data.

Plans for the next quarter:

Analysis of data: Particular attention in the modelling will be paid to any resolution of the variation in D_O across the membrane in the quenched experiment.

Experimental work and improvements: The use of GCMS will be introduced to allow us to measure small quantities of ¹⁸O in CO without the interfering signal of fragmented CO₂ which arises in the online MS analysis.

Publications and Presentation:

J. Yoo, A. Verma, S. Wang, A. J. Jacobson, "Oxygen transport kinetics in SrFeO_{3-x}, La_{0.5}Sr_{0.5}FeO_{3-x}, and La_{0.2}Sr_{0.8}Cr_{0.2}Fe_{0.8}O_{3-x} measured by electrical conductivity relaxation". Journal of the Electrochemical Society (2005), 152(3), A497-A505.

N. Bayani, C.A. Mims, A.J. Jacobson, and P.A.W. van der Heide, "Modes of surface exchange in La_{0.2}Sr_{0.8}Cr_{0.2}Fe_{0.8}O_{3-d}" Solid State Ionics (2005) 176(3-4) 319-323.

C. Y. Park and A. J. Jacobson, "Electrical Conductivity and Oxygen Non-stoichiometry of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-\delta}$ ", Journal of the Electrochemical Society (2005) in press.

C. Y. Park and A. J. Jacobson, "Thermal and chemical expansion properties of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ " Solid State Ionics submitted.

Three abstracts have been submitted to the International Solid State Ionics conference to be held in Baden-Baden Germany July 2005.

Conclusions:

The magnetic and electronic transport properties of Ti-substituted $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ have been systematically investigated. All the Ti-substituted $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compositions have a rhombohedral structure, (space group $R\bar{3}C$). The correlation between ferromagnetic T_C and $T_{\rho,max}$ becomes weaker and spin glass clusters are expected in the low temperature region with increasing Ti substitution. The resistivity in the high temperature region suggests the formation of localized polarons that affect the strong correlation between local structural changes and MIT. The decrease of the bandwidth W decreases the overlap between the O-2p and Mn-3d orbitals, which in turn decreases the exchange coupling of Mn-Mn and the magnetic ordering temperature T_c as well. Our studies indicate that Ti substitution at Mn enhances the electron-phonon interaction in these compounds, which decreases the bandwidth and increases the resistivities in the entire temperature range.

Bulk densities of the LSFT and dual phase membranes were determined using Archimedes method. SEM showed the presence of dense circular regions surrounded by the less dense, continuous phase which accommodates most of the pores. The size distribution of these dense regions was examined using image analysis. The closer observation of the micrographs revealed the presence of a circular crack that encompasses the dense region. The pores were found to be in clusters in the less dense region along the circular crack. The grain size in the dual phase microstructure was fine ($D_{50} = 1.99 \mu\text{m}$) and the distribution of grains were unimodal.

The EDX analysis was carried out to for both the membranes to study the chemical analysis. The XRD analysis for the membranes for identifying the crystal systems and for doing phase analysis was carried out and the crystal system identification has to be carried out. The fracture toughness of the membranes has to be calculated using indentation method.

The thermodynamic properties (stability and phase-separation behavior) and total conductivity of prototype membrane materials are being investigated. The data are needed together with the kinetic information to develop a complete model for the membrane transport. The characterization, stoichiometry, conductivity, and dilatometry measurements for samples of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ were previously reported. In this period, the use of a transient technique to separately determine the ionic conductivity was investigated. The experimental apparatus and the preliminary results are presented. Some transmission electron microscopy experiments to study the microstructure of ferrites that show very slow kinetics in the intermediate pressure range were also initiated. The data suggest non-equilibrium behavior which is associated with the formation of nanoparticles of a reduced component which re-react at long times. In the area of isotope transient studies at steady state, the current quarter has been dominated by continued analysis of the data from the isotope transients and the analysis of the profile in the quenched membrane.

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BIBLIOGRAPHY

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LIST OF ACRONYMS AND ABBREVIATIONS

YSZ	Yttria stabilized zirconia
XRD	X-ray diffraction
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-\delta}$	LSFTO
IEDP	Isotope exchange and depth profiling
SIMS	Secondary Ion Mass Spectroscopy