In Situ Studies on the Catalytic and Electronic Properties of Multi-Dimensional Cathode

Phase I Final Report

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Abstract

The overall objective of this program was to provide the fundamental background to enable SECA Industrial Team Members to select and develop oxide cathodes for the operation of solid oxide fuel cells in the intermediate temperature (500-700°C). A number of experimental techniques were used to address the specific obstacles within the program. The work expanded our existing experimental techniques to the use of in situ diffraction and spectroscopic techniques that are sensitive to the oxygen and iron structural and chemical environment. Such measurements were coupled with the evaluation and determination of the catalytic properties of potential cathode oxides.

The scope of the work was to prepare carefully controlled cathode samples of various compositions and microstructure and perform fundamental measurements of their physical properties. The measurement of physical properties of the cathode materials systems were used to correlate those properties to the overall effectiveness of the material as a constituent of an SOFC cell. The measurements techniques of neutron scattering and Mössbauer are relatively unique capabilities which have significance to the LSCF cathode system. The unique ability to make thin film samples can provide special samples for surface science efforts to understand cathodic catalytic activity.

The data obtained from neutron diffraction, Mössbauer Spectroscopy, electrical measurements and modeling show that the oxygen vacancy content at 500°C in air for La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$FeO$_3$ and La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$-$\delta$ are 0, 1% and 5% respectively. This is a significant finding that should relate to performance as a cathode, and gives criteria for the selection of new cathode materials.
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Executive Summary

The overall objective of this program has been to provide the fundamental background to enable SECA Industrial Team Members to select and develop oxide cathodes for the operation of solid oxide fuel cells in the intermediate temperature (500-700°C). A number of experimental techniques have been used to address the specific obstacles within the program. The work expands our existing experimental techniques to the use of in situ diffraction and spectroscopic techniques that are sensitive to the oxygen and iron structural and chemical environment.

The technical issues that were addressed are related to gaining an understanding as to what properties a cathode must possess to successfully operate at T<750°C. In particular, we have focused on answering the question of why Co and/or Fe or Cu containing compositions perform better than (La,Sr)MnO3?

This was accomplished by preparing films, powders and sintered specimens of selected perovskite compositions by previously developed processing techniques. The compositions studied are: (La,Sr)MnO3 and (La,Sr)(Fe,Co)O3. The electrical conductivity, defect structure and cation valence of these perovskites were studied by electrical conductivity, thermopower, x-ray diffraction, neutron diffraction and Mössbauer Spectroscopy techniques. The early results show that the primary differences in these oxides are the levels of oxygen vacancy concentrations at a given temperature and oxygen activity.

This manifests itself in the minimum temperature at which significant oxygen vacancy concentrations can be present under oxidizing conditions. This minimum has some acceptor concentration dependence, but it is approximately as follows:

- 400-500°C (La,Sr)(Co,Cu,Cr,Fe)O3
- 500-600°C (La,Sr)(FeO3)
- 750-850°C (La,Sr)MnO3
- 1400-1500°C (La,Sr)CrO3

The results of these studies show that the concentration of oxygen vacancies in air depends upon the B site elements present and increases according to the following order: Cr < Mn < Fe < Co < Cu. For example, at 500°C in air the oxygen vacancy content for La0.8Sr0.2MnO3, La0.6Sr0.4FeO3 and La0.6Sr0.4Fe0.8Co0.2O3 are 0, 1% and 5% respectively.

These results are very important for the SECA Industrial Team Members since they give a criteria for the selection of new materials for cathode development.

Introduction

Over the past few years, more and more work on the solid oxide fuel cells (SOFC’s) has been focused on the operation over the intermediate temperature (IT) regime (500-700°C), which seems mandatory if the cells are to be commercialized. Compared to the conventional high temperature cell operation (>800°C), operation in the intermediate temperature range imposes some rather restrictive requirements on both the electrolytes as well as the electrodes of the cell.
For the currently employed electrolytes (acceptor doped ceria or zirconia), a decrease in thickness to less than 10 microns appears to be sufficient for the first generation IT-SOFC’s. However this is not the case for both the anode and cathode where improvements in the performance of both electrodes must occur if the goals of the SECA program are to be met. Since this project is focused on the cathode, thus all discussions are directed at the cathode, but it is recognized that the anodes are of equal importance.

Currently \( \text{La}_{0.80}\text{Sr}_{0.20}\text{MnO}_3 \) (LSM) which is currently the preferred cathode material for SOFC operating temperatures of \( >800^\circ\text{C} \), has proven not to be completely suitable for use at temperatures below \( 700^\circ\text{C} \), probably due to its very low oxygen vacancy concentration which leads to cathodic overpotentials. In addition, LSM tends to react with zirconia forming electrically resistive interfacial layers between the electrodes and electrolyte. Iron and/or Co containing compounds appear to be better choices than LSM for use as cathodes in the IT regime because they have lower activation energy, smaller areal resistance, and higher oxygen vacancy level. However, research work is still needed to (1) understand the mechanism for the conductive and catalytic behavior and to set the criteria for selection of cathode materials, (2) develop a reliable and stable experimental method to measure oxygen vacancy concentration, oxygen ion conductivity, and catalytic behavior. The project has been aimed at providing the information required to address the above two important issues.

With only a few exceptions the project has followed very closely the original statement of project objectives which is partially reproduced as follows:

A. OBJECTIVES

The overall objectives of the SECA Core Technology Program are to:

(1) Generate new scientific and engineering knowledge to better enable SECA Industry Teams to develop low-cost solid oxide fuel cell power generation systems.

(2) Create technology breakthroughs to address technical risks and barriers that currently limit achievement of the SECA performance and cost goals for solid oxide fuel cell systems.

(3) Transfer new science and technology developed in the Core Technology Program to the SECA Industry Teams.

In Phase I of the Core Technology Program, recipients will investigate and evaluate the feasibility of the solution proposed and/or the merits of the scientific path of inquiry. Phase II projects shall seek to mature the science and technology developed to a sufficient level that it can be utilized by the SECA Industry Teams.

The overall objective of this program is to provide the fundamental background to enable SECA Industrial Team Members to select and develop oxide cathodes for the operation of solid oxide fuel cells in the intermediate temperature (500-700\(^\circ\text{C}\)). A number of experimental techniques will be used to address the specific obstacles within the program. The work expands our existing experimental techniques to the use of in situ diffraction and spectroscopic techniques that are sensitive to the oxygen and iron structural and chemical environment. Such measurements will
be coupled with the evaluation and determination of the catalytic properties of potential cathode oxides.

B. SCOPE OF WORK

The scope of work was to prepare carefully controlled cathode samples of various compositions and microstructure and perform fundamental measurements of their physical properties. The well-established characterization techniques which we have been using to characterize oxides (electrical conductivity, thermopower, thermogravimetric measurements, TEM, SEM, etc.) coupled with neutron scattering and Mössbauer spectroscopy have allowed us to accurately determine oxygen vacancy concentrations and to start developing models which predict both cathode compositions and temperature regimes which they should work well in SOFCs.

C. TASKS TO BE PERFORMED

TASK # 1.0 PREPARATION AND CHARACTERIZATION OF CATHODE MATERIALS

The performer will use previously developed cathode materials processing techniques to fabricate samples for the analytical effort described in the other tasks. The main cathode materials system will be the (La,Sr)(Fe,Co)O$_3$ series but additional systems can be pursued with DOE COR approval. Appropriate microstructure will be formed with special emphasis on controlled morphologies to facilitate examination of cathode physical properties. Such microstructure will include the preparation of epitaxial thin films on single crystal substrates such that the surface composition and/or dopant level of the substrate may be modified. Samples will be made available for collaborative research with surface scientists participating in DOE’s SOFC research program.

TASK # 2.0 IN SITU NEUTRON DIFFRACTION STUDIES

This task will resolve the crystal structure, magnetic moment and oxygen vacancy levels of low-dimensional cathode materials by in situ neutron diffraction.

1) Room temperature neutron and x-ray diffraction of cathode materials (with or without quenching from high temperature) will be performed.

2) In situ neutron and x-ray diffraction studies on the micrometer grain size specimens will be performed. Temperatures for those studies are from 500°C to 800°C with a step of 100°C; Gas environments include: O$_2$, air, Ar or N$_2$, CO/CO$_2$ mixtures and H$_2$/N$_2$ mixtures. The following will be sought: (1) Temperature dependent crystal structure at various oxygen activities; (2) Bonding angle changes between Fe and oxygen under changing of temperatures and oxygen activities; (3) Magnetic structure changes over a different temperatures and oxygen activities. These physical properties will be explored for state of the art cathode materials (such as LSF, LSCF) and compared with those of first generation materials (such as LSM).
The Mössbauer studies will be explored in two perspectives (1) in situ high temperature measurements and (2) quenched specimens from the highest temperatures beyond the in-situ capabilities. The sintered cathode materials (La$_{1-x}$Sr$_x$(Co,Fe)O$_3$ system) will be annealed at various temperatures (mostly from 800 to 1200°C) and oxygen activities (from 10-25 to 1 atm), and then quenched to room temperature to perform Mössbauer measurements. The magnetic properties will be explored as a function of Fe and Co stoichiometries and correlations with cathode electrochemical charge transfer activity will be sought.

1) Mössbauer measurements will be performed on all the powders in the temperature range room temperature to 800°C with various oxygen partial pressures. The isomer shift and quadrupole splitting will be measured.

2) Mössbauer will be employed to study the absorption of nanometer and micrometer cathode particles. The effects of the particle size on the isomer shift, quadrupole splitting and magnetic hyperfine will be studied.

3) The particle size dependent isomer shift, quadrupole splitting, and magnetic hyperfine field will be measured on the supported nanometer cathode particles (from 10 nm to 10 mm). The particle size results from Mössbauer will compared with the results from XRD and TEM.

The only variance from the SOPO is no overpotential measurements have been made. Some of these measurements will be made before Phase I is completed and will be continued in Phase II.

One additional update is that Pacific Northwest National Laboratory (PNNL) has invited UMR to form a Satellite Center to their High Temperature Electrochemistry Center to address materials problems (electrolyte, electrodes, sensors, interconnects and high temperature seals) associated with fuel cells. As a result we have requested funds for FY2005 through our congressional members. (The proposal which we submitted is included as Appendices A.) If this proposal is accepted, we should be forming an alliance with PNNL midyear of 2005.

Appendices B is a copy of the paper which Professor Anderson presented at a symposium in his honor at the 105th Annual Meeting of the American Ceramic Society held in Nashville, TN on April 27-30, 2005.

Results and Discussion

1. SUMMARY OF RESULTS

(The details of our research are contained in section 2 and in the previously submitted Topical Report so will only be summarized here)

(1) Techniques developed using Neutron scattering and Mössbauer Spectroscopy allow the determination of oxygen vacancy content to within 5%. Analysis of magnetic spectra allows the accuracy to be improved to ~1%. Using these techniques we established that the oxygen vacancy content at 500°C in air for LSM, LSF and LSCF are 0, <0.5% and
5% respectively. Since the oxygen ion conductivity is directly related to the vacancy content, we expect that at 500°C, both LSM and LSF should have much lower ionic conductivity than LSCF. Oxygen vacancies at high temperature (>500°C) are generated by thermally activated processes.

(2) The electrical conductivity in air shows that a maximum occurs in the conductivity which is dependent upon the particular cations that occupy the B site in the perovskite lattice. These data are very significant since this maximum occurs because of the compensation of carriers by oxygen vacancies. As the temperature increases, say from room temperature, the electrical conductivity increases because of the exponential temperature dependence of the mobility. The mobility term is essentially carrier concentration independent, so as the temperature increases and oxygen vacancies start to form and the carrier (holes) content begins to decrease, the product of the mobility and conductivity, which is not surpassed until the temperatures become high enough for the mobility term to completely dominate the conductivity.

Why is this important? It is important since this maximum gives the temperature below which oxygen vacancy contents become insignificant. These data suggest that at 500°C, only perovskites which contain Fe, Co or Cu on their B site can be expected to contain > 0.5% oxygen vacancies.

(3) Oxygen permeation measurements on LSF in air at 500°C indicate that the oxygen ion conductivity is in the order of $10^{-4}$ S/cm. Since under those conditions, the total electrical conductivity is about 200 S/cm, the ionic transport number for oxygen can not be $>10^{-5}$. This means that under these conditions, the mixed conductivity is very small and significant cathode overpotentials can be expected. This suggests that the determination of the relationship between ionic conduction and cathodic overpotential may be important to our understanding of the behavior of SOFC cathodes.

2. Tasks Accomplished

Task 1.0 Preparation and Characterization of Cathode Materials

Some of the measurements of electrical conductivity as $f(T, P_{O_2})$ for $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ and $La_{0.6}Sr_{0.4}FeO_3$ are shown in figure 1. As can be seen both the ferrite compositions show a significant drop in conductivity as the oxygen activity decreases from 0.2 atm. This decrease does not occur for $La_{0.8}Sr_{0.2}MnO_3$ until the oxygen activity decreases below $10^{-8}$ atm. The inference from these data is that the ferrite compositions have substantially more oxygen vacancies than the manganite. This is borne out by the ND studies.
The electrical conductivity data of La$_{0.6}$Sr$_{0.4}$FeO$_3$ f(T) have been fitted to a model which shows the influence of oxygen vacancies on the total electrical conductivity (figure 2).

Figure 3 illustrates that the temperature where the maximum electrical conductivity in air occurs is dependent upon the cations which occupy the B site in the perovskite lattice. These data are very significant since this maximum occurs because of the compensation of carriers by oxygen vacancies:

$$[\text{holes}] = [S']_{La} - 2[V_{o}^{**}]$$
The electron conductivity is given by the relation

\[ \sigma = e \mu [\text{holes}] \]

where \( e \) is the change on the electron and \( \mu \) is the mobility of holes. Thus for temperatures lower than the conductivity maximum oxygen vacancies no longer can form and the carrier concentration is fixed (figure 2). The significance of this that in the temperature region, the concentration of oxygen vacancies is fixed to a value determined by the temperature of the maximum in the conductivity.

Properties – Defect Chemistry
The Role of Temperature

- Maximum conductivity
  For Mn, Fe, Co, and Cu compounds

- Mechanism for \( \sigma_{\text{max}} \)
  \( \text{Vo}^{\text{oos}} \) compensate \( p = \text{[SrLa]} - 2 \text{[Vo]} \)

- Temperature shifting
  \( T_{\text{cr}} > T_{\text{Mn}} > T_{\text{Fe}} > T_{\text{Co}} > T_{\text{Cu}} \)

This is the minimum temperature at which significant oxygen vacancy concentrations can equilibrate under oxidizing conditions. This minimum has some acceptor concentration dependence, but as is shown in figure 3 is approximately as follows:

- 400-500°C (La, Sr)(Co, Cu, Cr, Fe)O3
- 500-600°C (La, Sr)(FeO3)
- 750-850°C (La, Sr)MnO3
- 1400-1500°C (La, Sr)CrO3

The current results of these studies show that the concentration of oxygen vacancies in air depends upon the B site elements present and increases according to the following order: Cr < Mn < Fe < Co < Cu. For example, at 500°C in air the oxygen vacancy content for La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\), La\(_{0.6}\)Sr\(_{0.4}\)FeO\(_3\), and La\(_{0.6}\)Sr\(_{0.4}\)Fe\(_{0.8}\)Co\(_{0.2}\)O\(_3\) are 0, 1%, and 5% respectively.

The importance of these results to the SECA Industrial Teams is that it gives them guidance as to the temperature region that they should expect a given perovskite composition to function well as a cathode.

One of our goals has been to make ionic conductivity measurements on the perovskite compositions which we are studying. We have been trying to do this by impedance measurements, but have had little success. We have been successful in making oxygen
permeation measurements. Our initial results on La\(_{0.6}\)Sr\(_{0.4}\)FeO\(_3\) (LSF) are discussed in Appendices C.

The permeation results are very close to those reported in the literature. The values of the ionic conductivity are subject to the choice of models. At the moment, we are performing some experiments to delineate which model is correct. For LSF in air at 500°C (with < 1% oxygen vacancies) the ionic conductivity (oxygen ion) can be expected to be in the order of 10\(^{-4}\)-10\(^{-3}\) s/cm. Under these conditions the electronic conductivity is about 200 s/cm. This means that the oxygen ion transport number is < 10\(^{-5}\). This means that under these conditions, the mixed conductivity is very small so significant cathode over potentials should be expected. The determination of the relationship between ionic transport number and cathodic parameters was planned to be unraveled in the Phase II project. Hopefully, this work can be continued in the near future in other programs.

**Task 2.0 In Situ Neutron Diffraction (ND) Studies**

The determination of oxygen vacancy concentration by neutron diffraction has been a major goal in this project. After analyzing a number of spectra. We arrived at the conclusion that Rietveld analysis of the spectra leads to values with an uncertainty of about ±5%. For the Fe containing compositions, the use of the magnetic spectra the uncertainty is reduced to about ±1%, (see Figure 4).

![Figure 4](image)

Figures 5 and 6 show the oxygen vacancy concentrations determined by ND and Mössbauer. These data show that the Fe containing compositions contain a significant concentration of oxygen vacancies even in an air atmosphere.

Figure 7 compares the conductivity parameters and oxygen vacancy content at 500°C in air for La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\), La\(_{0.6}\)Sr\(_{0.4}\)FeO\(_{3-\delta}\) and La\(_{0.6}\)Sr\(_{0.4}\)Fe\(_{0.8}\)Co\(_{0.2}\)O\(_{3-\delta}\). As can be seen, even at this low
temperature, LSCF contained nearly 2% vacancies ($\delta=0.05$). This is a significant finding that should relate to performance as a cathode.

Figures 8-12 show the relationships between oxygen vacancy and Fe valence state. These data should be important for our understanding of the behavior of ferrite compositions as cathodes.

Reports that give details on these studies are included in Appendices D.
Comparison between 
La$_{0.80}$Sr$_{0.20}$MnO$_{3-\delta}$, La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ and La$_{0.60}$Sr$_{0.40}$Fe$_{0.80}$Co$_{0.20}$O$_{3-\delta}$ at 500°C in Air

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<th>LSM</th>
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<td>$E_a$ (eV)</td>
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<td>$\mu_b$ (cm$^2$/v s)</td>
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<td>3-\delta</td>
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<td>2.997</td>
<td>2.95</td>
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Figure 7

Fe valence state and [$V^\circ\circ_\circ$] vs. 3-\delta for L6SF – ND Studies

Figure 8

Fe valence state and [$V^\circ\circ_\circ$] vs. 3-\delta in La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ for L6SF – Mössbauer Studies

Assumptions:
- Neutrality condition
- Only Fe$^{3+}$ and Fe$^{4+}$ exist if $\delta < 0.2$ in La$_{0.80}$Sr$_{0.20}$FeO$_{3-\delta}$

Figure 9

Figure 10
Task 3.0  In Situ Mössbauer Spectroscopy Studies

In Situ measurements started on air quenched specimens of La$_{0.6}$Sr$_{0.4}$FeO$_3$. Figure 11 and 12 are examples of the spectra. The Neel temperature appears to be a function of the oxygen vacancy concentration. This is under investigation.

![Figure 11](image)

![Figure 12](image)

Reports giving details on these studies are included in Appendices E.

Conclusions

The combination of all of the experimental techniques we have employed has allowed us to determine oxygen vacancy concentrations in our selected perovskites both rapidly and precisely. (Details of these studies are contained in Appendices F-M) The most important results are summarized as follows:

- Neutron diffraction studies show that there is an excellent correlation between magnetic moment data and oxygen vacancy concentration.
- The measurements of electrical conductivity as $f(T, P_{O2})$ for La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$ and La$_{0.6}$Sr$_{0.4}$FeO$_3$ have been completed. The ferrite compositions show significant drop in conductivity as the oxygen activity decreases from 0.2 atm. This decrease does not occur for La$_{0.8}$Sr$_{0.2}$MnO$_3$ until the oxygen activity decreases below $10^{-8}$ atm. The inference from these data is that the ferrite compositions have substantially more oxygen vacancies than the manganite. This is borne out by the ND studies.
- The electrical conductivity data of La$_{0.6}$Sr$_{0.4}$FeO$_3$ $f(T)$ have been fitted to a model which shows the influence of oxygen vacancies on the total electrical conductivity.
Data shows that the oxygen vacancy content at 500°C in air for La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$FeO$_3$ and La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ are 0, 1% and 5% respectively. This is a significant finding that should relate to performance as a cathode.

Experimental and modeling work has progressed so that minimum temperatures for significant vacancy formation can be determined. These are:

- 400-500°C (La,Sr)(Co,Cu,Fe)O$_3$
- 500-600°C (La,Sr) FeO$_3$
- 750-850°C (La,Sr) MnO$_3$
- 1400-1500°C (La,Sr) CrO$_3$

Initial ND runs indicate that La$_{0.6}$Sr$_{0.4}$FeO$_3$ does not equilibrate at 500°C in air. That is, no significant changes in oxygen vacancy concentration were observed.

Oxygen permeation measurements indicate that for LSM at 500°C in air the ionic number is $<10^{-5}$.

**How Well Did Phase I Research Meet Its Objectives?**

Essentially 3 tasks were to be performed:

- Preparation and characterization of cathode materials
- In Situ Neutron Diffraction Studies
- In Situ Mössbauer Spectroscopy Studies

All 3 tasks were completed. The only variance from the SOPO is no overpotential measurements have been reported. Some of these measurements are currently being made and a significant quantity of data has been accumulated and will be subjects of future reports and programs.

**Importance of Phase I Results to SECA Industrial Teams**

- The knowledge of the relationship between oxygen vacancy content, electrical conductivity, and the particular cation on the B site of the perovskite give the SECA Industrial Teams guidance as to the temperature region that they should expect a given perovskite composition to function well as a cathode.
- An understanding of the relationship of oxygen vacancy content and ionic transport number to the cathodic overpotential is very important for the selection of appropriate cathode materials. This knowledge is just starting to be generated and will hopefully be fully determined in future research.
Appendices A through M
Appendix A

“High Temperature Fuel Cell Materials Center”
University of Missouri-Rolla
Requested Action

| Amount | $4.5 million |
| Legislation | FY04 Energy and Water Appropriations |
| Agency | ____________________ |
| Account | ____________________ |
| Program | ____________________ |

SUMMARY

The Electronic Materials Applied Research Center (EMARC) at the University of Missouri-Rolla (UMR) is requesting $4.5M in FY2004 appropriations through the Department of Energy (DOE) [Office of Fossil Energy, Distributed Power Systems—Fuel Cells, Advanced Research] for research and development related to the advancement of the fuel cell technology required to meet the nation’s future energy needs.

NEED

In his 2003 State of the Union Address, President Bush announced a $1.2 billion program to reverse America’s growing dependence on foreign oil by developing the technology needed for commercially viable hydrogen-powered fuel cells - a way to power cars, trucks, homes and businesses that produces no pollution and no greenhouse gases. The President’s Hydrogen Initiative will invest $720 million in new funding over the next five years to develop the technologies and infrastructure needed to produce, store, and distribute hydrogen for use in fuel cell vehicles and electricity generation. Combined with the FreedomCAR (Cooperative Automotive Research) Initiative, President Bush is proposing a total of $1.7 billion over the next five years to develop hydrogen-powered fuel cells, hydrogen infrastructure and advanced automotive technologies.

In his SOTU speech, President Bush focused on the development of hydrogen powered fuel cells for use primarily in transportation as a replacement of the internal combustion engine. The major obstacles to attaining the goals of the President’s Hydrogen Initiative are related to the cost of producing hydrogen (~4x that of gasoline), the development of adequate hydrogen storage systems and the creation of affordable fuel cells (current costs ~10x that of internal combustion engines).

Among various natural energy resources, coal is one of the most abundant and inexpensive resource from which coal gas and hydrogen can be produced. Instead of burning coal like a conventional power plant, a coal gasification system breaks coal apart into a gaseous mixture. Coal gas consists mainly of carbon monoxide, CO and
hydrogen, \( \text{H}_2 \). CO is usually the main constituent with a \( \text{H}_2/\text{CO} \) ratio of typically 3/7. The key advantage of solid oxide fuel cells (SOFC) is that the fuel cell does not require high purity hydrogen to generate electrical power. Hence, recent R&D activities on SOFC are geared towards creating **affordable** hydrogen fuel cells.

The DOE’s Solid-State Energy Conversion Alliance (SECA) which is part of the DOE Vision 21 Program, which shares many of President Bush’s energy goals. SECA’s mission is to ensure our long-term energy needs by developing advanced energy conversion devices which are fuel flexible, highly efficient, and environmentally kind, including devices which can be powered by fossil fuels as well as hydrogen. Fuel cells have been identified as the best technology to utilize our abundant fossil fuels for the energy sources, and DOE has brought together the National Energy Technology Laboratory (NETL) and Pacific Northwest National Laboratory (PNNL) to address the problem of developing coal-based fuel cells. DOE has also formed at PNNL the High Temperature Electrochemistry Center (HiTEC), whose mission is to identify and address the key research issues which address the technical and economic barriers to the use of fuel cells in transportation, portable power, stationary, and distributed generation applications.

In order address these multidisciplinary barriers, HiTEC is starting to team with selected Universities throughout the nation to form Satellite Centers each of which has specific expertise to address the limiting problems.

Currently, HiTEC has formed a Satellite Center with Montana State University to address problems related to coal gasification and is seeking to form an alliance with UMR to address fuel cell stack materials problems (electrolyte, electrodes, sensors, interconnects and high temperature seals), as well as power conversion problems associated with fuel cells. In the future, HiTEC expects to include the University of West Virginia (coal gasification) and University of Alaska-Fairbanks (membrane and power management) as Satellite Centers.

The goal in the formation of Satellite Centers is that they will not be in competition (neither technically nor financially) with one another, but will compliment one another and as a group will develop the research needed to overcome these complex issues and barriers.

**REQUESTED ACTION**

EMARC is requesting $4.5M in FY2004 to conduct the research and development of the materials and power electronics required to provide both efficient and economic fuel cells. In addition these funds will accelerate education and research activities on materials for fuel cells and will help provide the infrastructure at UMR which will allow the formation of a new Satellite Center affiliated with the HiTEC at PNNL.

Specifically, this coal-based initiative will:

- Provide auxiliary power for transportation which will eventually assist with the propulsion in hybrid systems. For trucks the fuel cells will lead engine and replacing it with a fuel cell, then running all belt-driven functions (such as oil pump, fan, fuel pump, air conditioner, etc) electrically with power from the fuel cell. This will improve the fuel efficiency by as much as 20%.
- Allow the direct utilization of fossil based fuels (such as coal, gasoline, natural gas, diesel, jet fuel, alcohol, propane, butane, etc) to power the fuel cell without the necessity of converting it to a high purity hydrogen source. This will overcome one of the major obstacles in the development and to the commercial acceptance of fuel cells, which is the need to use high purity hydrogen as a fuel. This will both decrease the cost of fuels (highly refined hydrogen is not needed) as well as allow the use of our existing fuel distribution and storage systems.
- Speed up the commercialization and utilization of fuel cell technologies which will assist the nation into achieving energy independence and solutions to global warming.
- Develop novel power conversion and management technologies suitable for integrating fuel cells into hybrid electric vehicles, and 42V vehicle electrical systems.

INSTITUTIONAL UNIQUENESS

The researchers at EMARC have over 25 years continuous funding in the research and development of oxides which are used as components in the solid oxide fuel cells. This activity has been supported by federal agencies (NSF, DOE, ONR) and by companies and institutes (Praxair, BP/Amoco, General Electric, Gas Research Institute) with a total cumulative funding in excess of $10M. This support has allowed UMR to publish over 150 technical papers, develop more than 10 patents, graduate over 25 students who are working in the area of electrical ceramics and to achieve an international reputation in the area of education and research in electrical ceramics as well as making it a leader in the development of oxide components for the high temperature fuel cells.

CONCLUSION

This combination of expertise and research capabilities uniquely positions UMR to be a key player in the DOE Vision 21 Program. The access of the proposed funds will allow UMR to become a Satellite to the HiTEC at PNNL which will enhance the nation’s position in the development of affordable advanced coal-based fuel cells that are efficient, environmentally friendly and economical.
Appendix B

“Defect Chemistry of (La, Sr)MnO₃ and (La, Sr)(Fe, Co)O₃”

Harlan U. Anderson
Electronic Materials Applied Research Center
University of Missouri-Rolla

Presented at the 105th Annual Meeting of the American Ceramic Society
Nashville, TN
April 27-30, 2003
Defect Chemistry of 
(La, Sr)MnO$_3$ and (La, Sr)(Fe, Co)O$_3$

H. U. Anderson

Electronic Materials Applied Research Center
University of Missouri-Rolla
Rolla, MO 65401

Acknowledgements

A word of Thanks to the Division Sponsors
(Electronic, Basic and Nuclear)
and the organizers of this symposium
(Dr’s Sundaram, Manthiram and Kumta)

I am most gratified by the honor of this symposium
What I present today came from the efforts of a number of hard working students and research colleagues. For fear of leaving someone out, I will not list you separately, but want to express my gratitude for the honor and opportunity of working with each of you.

I also wish to thank the agencies, national labs and companies for supplying the funding to support my research activities.

My introduction to the perovskite type oxides began when I started working at Sprague Electric Co. whose interest was the development of ceramic capacitors. My work there was centered around the perovskite type oxides with an emphasis on the titanates and zirconates.
After entering the academic world, I expanded my interests to include conducting oxides, p-type perovskite oxides

- Primarily, Rare earth containing structure
- Chromite, manganite, ferrite, and cobaltite
- Defect Chemistry
- Synthesis

What I discovered was that the perovskite type oxides are wonderful chemistry labs

- Site occupancy determined mainly by ionic size. One can be fairly certain about the lattice site location of a particular cation
- Electronic conductivity ($\sigma$) determined by B site ion
- Ionic conductivity results from oxygen vacancies
**ABO₃ Perovskites**

<table>
<thead>
<tr>
<th>Typical A site host cations</th>
<th>La⁺³⁺ (1.14Å)</th>
<th>Y⁺³⁺ (0.92Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd⁺³⁺ (1.04Å)</td>
<td>Pr⁺³⁺ (1.16Å)</td>
</tr>
<tr>
<td></td>
<td>Gd⁺³⁺ (1.11Å)</td>
<td>Sm⁺³⁺ (1.00Å)</td>
</tr>
<tr>
<td>A site dopants</td>
<td>Sr²⁺ (1.12Å)</td>
<td>Ca²⁺ (0.99Å)</td>
</tr>
<tr>
<td>All acceptors</td>
<td></td>
<td>Ba²⁺ (1.34Å)</td>
</tr>
<tr>
<td>Typical B site host cations</td>
<td>Cr³⁺ (0.65Å) (also valence 6+)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn³⁺ (0.66Å) (also valence 2+ and 4+)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe³⁺ (0.67Å) (also valence 2+)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co³⁺ (0.63Å) (also valence 2+)</td>
<td></td>
</tr>
<tr>
<td>Typical B site dopants cations (only acceptors Listed)</td>
<td>Ca²⁺ (0.99Å)</td>
<td>Mn²⁺ (0.80Å)</td>
</tr>
<tr>
<td></td>
<td>Co²⁺ (0.72Å)</td>
<td>Mg²⁺ (0.65Å)</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺ (0.69Å)</td>
<td>Cu²⁺ (0.72Å)</td>
</tr>
</tbody>
</table>

**Applications of ABO₃**

- Capacitors
- Electrodes
- Gas Separation Membranes
- Sensors
Properties – Defect Chemistry
The Role of Temperature

1. Maximum conductivity
   For Mn, Fe, Co, and Cu compounds

2. Mechanism for $\sigma_{\text{max}}$
   $V_0$'s compensate $p$
   
   \[ p = [\text{SrLa}] - 2[V_0] \]

3. Temperature shifting
   $T_{cr} > T_{Mn} > T_{Fe} > T_{Co} > T_{Cu}$

---

Properties – Defect Chemistry
The Role of Oxygen Activity

Log conductivity vs. log(pO₂/atm)

- $La_{0.80}Sr_{0.20}MnO_3$ (1000°C),
- $La_{0.80}Sr_{0.20}FeO_3$ (1000°C),
- $La_{0.80}Sr_{0.20}Co_{0.20}Fe_{0.80}O_3$ (1000°C),
- $La(Mg_{0.10}Cr_{0.90})O_3$ (1200°C),
- $La_{0.95}Sr_{0.05}Ga_{0.80}Cr_{0.20}O_3$ (1000°C)
Comparison between LSM, LSF and LSCF at 500°C in Air

<table>
<thead>
<tr>
<th></th>
<th>LSM</th>
<th>LSF</th>
<th>LSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_p$ (S/cm)</td>
<td>104</td>
<td>173</td>
<td>340</td>
</tr>
<tr>
<td>$E_h$ (eV)</td>
<td>0.095</td>
<td>0.17</td>
<td>0.087</td>
</tr>
<tr>
<td>$\mu_h$ (cm$^2$/v s)</td>
<td>0.19</td>
<td>0.16</td>
<td>0.31</td>
</tr>
<tr>
<td>3-$\delta$</td>
<td>3</td>
<td>2.997</td>
<td>2.95</td>
</tr>
</tbody>
</table>

The Simplifications

- $\text{A}^{2+}\text{B}^{4+}\text{O}_3$
  - 1. Electron conductor (n type)
  - 2. Oxygen ionic conductors

- $\text{A}^{3+}\text{B}^{3+}\text{O}_3$
  - 1. Hole conductor (p type)
  - 2. Oxygen ionic conductors

- Mobility generally activated
Defect Chemistry of Perovskite-type Oxides (ABO$_3$)

- Consider
  - A$^{+3}$
  - B$^{+3}$
  - Divalent acceptor (I)

For simplicity, assume
- No defect association
- Fully ionized oxygen vacancies, V$_O^{**}$
- No interstitial defects
- A/B = 1

Basic Defect Reaction for p-Type Oxides

- **Intrinsic Electronic**
  \[ \text{nil} = e^+ + h^+ \]
  \[ K_i = n_p = \exp\left(\frac{-\Delta G_i}{kT}\right) \]

- **Stoichiometric Schottky**
  \[ \text{nil} = V_A^{**} + V_B^{**} + 3V_O^{**} \]
  \[ K_s = [V_C^t]^3[V_O^{**}]^1 \]

- **Oxygen Excess**
  \[ \frac{3}{2}O_2 = V_A^{**} + V_B^{**} + 3O_6^{+} + 6h^+ \]
  \[ K_i = [V_C^t]^3 p^6 p_0^{-3/2} \]

- **Oxygen Deficient**
  \[ O_5 = V_O^{**} + 2e^- + \frac{1}{2}O_2 \]
  \[ K_{V_o} = [V_O^{**}] n^3 p_0^{1/2} \]

**Neutrality Condition**
\[ [I^+] + 6[V_C^t] + n = p + 2[V_O^{**}] \]
From these basic equations, the overall behavior of the defects in ABO$_3$ can be mapped out as function of temperature, oxygen activities and acceptor concentration.

Two method for solving resulting equations:

1) Divide into region of particular neutrality conditions
2) Do not use limiting conditions, but solve the global equation using the overall neutrality relations.

Results using simplified neutrality conditions!

Region I – VI
VI
Decomposition
(B⁺⁺ to B⁺⁺)

V
Reduction
(B⁺⁺ to B⁺⁺)

IV
III
II
I

\[ \text{[V'O']} \]
\[ \text{[V'O']} = [I'] \]
\[ \text{[V'O']} = [I'] \]
\[ \text{[V'O']} = \text{pO}_2^{1/2} \]
\[ \text{[V'O']} \propto \text{pO}_2^{1/8} \]

\[ \log([\text{VO}^••], n, p) \]

\[ \log(pO_2) \]

Oxygen Content

HIGH [V'O'] REGIONS

Log([V'O'], n, p)

\[ n \propto p \]

\[ \sigma \propto p \]

\[ \text{HIGH} [\text{V'O'}] \text{ REGIONS} \]

Table of constant “m” in \([ \text{[V'O']} \), n, p \propto \text{pO}_2^m\)

<table>
<thead>
<tr>
<th></th>
<th>VI</th>
<th>V</th>
<th>IV</th>
<th>III</th>
<th>II</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>1/6</td>
<td>1/4</td>
<td>1/4</td>
<td>0</td>
<td>3/16</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>-1/6</td>
<td>-1/4</td>
<td>-1/4</td>
<td>0</td>
<td>-3/16</td>
<td></td>
</tr>
<tr>
<td>[V'O']</td>
<td>-1/6</td>
<td>0</td>
<td>~ -1/2</td>
<td>-1/2</td>
<td>-1/8</td>
<td></td>
</tr>
<tr>
<td>Neutrality condition</td>
<td>[ B_o = n = 2[V'O'] ]</td>
<td>[ 2[V'O'] = [I_{RE}] ]</td>
<td>[ p = \frac{[I_{RE}]}{2[V'O']} ]</td>
<td>[ p = [I_{RE}] ]</td>
<td>[ p = 3[V'I'] + 3[V'B'] ]</td>
<td></td>
</tr>
</tbody>
</table>

*: Marked are majority carrier(s)

Dissociation Activities for Some Binary oxides

<table>
<thead>
<tr>
<th>Reaction</th>
<th>800°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃ ⇒ Cr</td>
<td>10⁻²² atm</td>
<td>10⁻²² atm</td>
</tr>
<tr>
<td>CoO ⇒ Co</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁵</td>
</tr>
<tr>
<td>Cu₂O ⇒ CuO</td>
<td>10⁻²</td>
<td>10⁻²</td>
</tr>
<tr>
<td>CuO ⇒ Cu</td>
<td>10⁻⁵</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>CuO ⇒ Cu₂O</td>
<td>10⁻⁸</td>
<td>10⁻⁸</td>
</tr>
<tr>
<td>FeO ⇒ Fe</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁵</td>
</tr>
<tr>
<td>Fe₂O₃ ⇒ FeO</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁵</td>
</tr>
<tr>
<td>Fe₂O₃ ⇒ Fe₂O₄</td>
<td>10⁻⁵</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>MnO ⇒ Mn</td>
<td>10⁻¹⁴</td>
<td>10⁻¹⁴</td>
</tr>
<tr>
<td>Mn₂O₃ ⇒ MnO</td>
<td>10⁻¹⁰</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>Nb₂O₅ ⇒ Nb</td>
<td>10⁻²⁵</td>
<td>10⁻²⁴</td>
</tr>
<tr>
<td>Nb₂O₆ ⇒ Nb₂O₅</td>
<td>10⁻²⁵</td>
<td>10⁻²⁴</td>
</tr>
<tr>
<td>MnO ⇒ MnO</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁴</td>
</tr>
<tr>
<td>MnO₂ ⇒ MnO</td>
<td>10⁻¹⁰</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>MnO₃ ⇒ MnO₃</td>
<td>10⁻¹⁰</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>Cr₂O₃ ⇒ Cr</td>
<td>10⁻²³ atm</td>
<td>10⁻²³ atm</td>
</tr>
</tbody>
</table>

Approximate oxygen activity where regions III, IV, and V begin at 1000°C

<table>
<thead>
<tr>
<th>Composition</th>
<th>Region III (atm)</th>
<th>Region IV (atm)</th>
<th>Region V (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(La, Sr)TiO₃₋δ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaVO₂₋δ</td>
<td>&lt; 10⁻¹⁸</td>
<td></td>
<td>&lt; 10⁻¹⁸</td>
</tr>
<tr>
<td>LaCrO₃₋δ</td>
<td>&lt; 10⁻¹⁸</td>
<td>&lt; 10⁻¹⁸</td>
<td>&lt; 10⁻¹⁸</td>
</tr>
<tr>
<td>LaCrₓ₄₋ₓMgₓ₂O₃₋ₓ</td>
<td>10⁻¹¹</td>
<td>&lt; 10⁻¹⁸</td>
<td>10⁻¹⁸</td>
</tr>
<tr>
<td>LaₓSrₓTiO₃₋δ</td>
<td>10⁻¹¹</td>
<td>&lt; 10⁻¹⁸</td>
<td>10⁻¹⁸</td>
</tr>
<tr>
<td>LaMnO₃₋δ</td>
<td>10⁻¹¹</td>
<td>10⁻¹⁸</td>
<td>10⁻¹⁸ – 10⁻¹⁷</td>
</tr>
<tr>
<td>LaₓSrₓMnO₃₋ₓ</td>
<td>10⁻¹¹</td>
<td>10⁻¹⁸</td>
<td>10⁻¹⁸</td>
</tr>
<tr>
<td>LaₓSrₓFeO₃₋ₓ</td>
<td>10⁻¹¹</td>
<td>10⁻¹⁷</td>
<td>10⁻¹⁷</td>
</tr>
<tr>
<td>LaₓSrₓCoO₃₋ₓ</td>
<td>10⁻¹¹</td>
<td>10⁻¹⁷</td>
<td>10⁻¹⁷</td>
</tr>
<tr>
<td>LaₓSrₓFeₓCoO₃₋ₓ</td>
<td>10⁻¹⁴</td>
<td>10⁻¹⁷</td>
<td>10⁻¹⁷</td>
</tr>
<tr>
<td>LaₓSrₓFeₓO₃₋ₓ</td>
<td>&gt; 10⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaₓSrₓCoO₃₋ₓ</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Solutions to the “Global” Equation

\[ \sigma = N \cdot \mu \cdot q = \left[ \frac{\sqrt{1 + 8 \cdot AOG \cdot B} - 1}{4 \cdot AOG} \right] \cdot \left[ \frac{\mu_0}{T} \exp \left( - \frac{E_b}{kT} \right) \right] \cdot q \]

\[ AOG = \frac{K_{AOG,0}}{K_{AOG}} \cdot \exp \left( - \frac{E}{kT} \right) \cdot p_{O_2}^{1/2} = A \cdot p_{O_2}^{1/2} \]

\[ B = \left[ \text{Sr}_{0.4} \right] \]

Simulation of \( \log(N) \) and \( \log(\sigma) \) vs. \( \log(pO_2) \) from the Global equation

\[ \sigma = N \cdot \mu \cdot q = \left[ \frac{\sqrt{1 + 8 \cdot AOG \cdot B} - 1}{4 \cdot AOG} \right] \cdot \left[ \frac{\mu_0}{T} \exp \left( - \frac{E_b}{kT} \right) \right] \cdot q \]

XDZ and HUA, unpublished
Conclusions

1. A defect chemistry model for the oxidation-reduction behavior of p type perovskite oxides was developed.

2. The model explains the electrical conductivity of the chromites.

3. In order to explain the behavior of Mn containing perovskites, both site percolation and thermally activated disproportionation of $2\text{Mn}^{3+} - \text{Mn}^{2+} + \text{Mn}^{4+}$ must be added to the model.

4. The (La,Sr)(Co, Fe)O$_3$ system follows the model and becomes very oxygen nonstoichiometric (10-30%) prior to dissociation.
Appendix C

“Oxygen Permeation Test”

Toshio Suzuki, Piotr Jasinski, and Harlan U. Anderson
University of Missouri-Rolla
**Experimental**

Figure 1 shows the experimental apparatus for oxygen permeation test. Detailed experimental conditions are listed on Table I. Argon gas was used as carrier gas to the mass spectrometer and the flow rates were controlled by a mass flow controller. The oxygen permeation \( J_{O2} \) through the sample in the carrier gas (Ar) can be determined using the mass spectrometer, which can detect the oxygen contents in the gas. The intensity of oxygen molecular \( I_{O2} \) from the mass spectrometer is proportional to the amount of oxygen in the carrier gas \( J \gg J_{O2} \):

\[
I_{O2} = a \frac{(J_{O2} + J_{O2,c})}{J}, \quad (1)
\]

where \( a, J, J_{O2,c} \) are constant, carrier gas flow rate and the oxygen content in the carrier gas (as a flow). Since \( J_{O2,c} \) is proportional to \( J \) \( (J_{O2,c} = bJ) \), Eq. 1 can be rewritten as

\[
I_{O2} = a \frac{J_{O2}}{J} + ab. \quad (2)
\]

By plotting the intensity of \( O_2 \) as a function of an inverse of carrier gas flow rates \( J \), the oxygen permeation \( J_{O2} \) can be determined from the slope of the curve.

Leakage of oxygen can be detected by checking the nitrogen content in the carrier gas. If there is a leakage, nitrogen content should also change as a function of flow rate. Checking of leakage in
this system was conducted in room temperature. For the flow rate range from 50 to 150 cc/min, no obvious leakage was observed as show in Fig. 2 as well as no permeation of oxygen in room temperature.

Table I. Experimental Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>(La, Sr)FeO$_3$ pellet 2.4 mm thick, area 0.3 cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ detection</td>
<td>Quadrupole Mass Spectrometer, AMETEK</td>
</tr>
<tr>
<td>Temperature</td>
<td>800 – 850°C</td>
</tr>
<tr>
<td>P$_{O_2}$ gradient</td>
<td>Ar (P$<em>{O_2}$=8.5*10$^{-5}$ atm) / Air (P$</em>{O_2}$= 0.2 atm)</td>
</tr>
<tr>
<td>Carrier gas flow rates (f)</td>
<td>50 ~ 150 cc/min (Room Temperature)</td>
</tr>
<tr>
<td>Sealant</td>
<td>Ag paste</td>
</tr>
</tbody>
</table>

Figure 2. Mass spectrometer intensity as a function of argon flow rate through the sample at room temperature.
Results and discussions

Figure 3 shows the intensity of oxygen as a function of $1/J$. As can be seen, lines are straight as model predicted (Eq. 2) and interception, which shows the amount of oxygen in the carrier gas, are almost same value and fits to the result shown in Fig.2. From these slopes, oxygen permeation rates can be determined. The ratio of oxygen amount and the intensity ($a$ in Eq. 1) was determined separately.

Figure 4 shows the oxygen permeation rates in an Argon / Air gradient for LSF. The activation energy for the permeation was about 1.1 eV, which were close to that of (La, Sr) (Fe, Co)O$_3$ system [1].

The oxygen permeation is mainly sum of two effects, the bulk diffusion and the surface exchange of oxygen ion. For perovskite material specimen with thickness of 1 mm, the bulk diffusion is limiting factor at 800°C for oxygen permeation[2]. Therefore, the permeation date in this condition can be used to determined the bulk conductivity of specimens.

![Figure 3. Oxygen intensity as a function of $1/J$.](image-url)
Oxygen Permeation rates \( (J_{O2}) \) can be describe using the conductivity of materials as [3]

\[
J_{O2} = \frac{RT}{16F^2} \int_{P_{O2}}^{P_{O2}'} t_i t_e \sigma d(\ln P_{O2})
\]  

(3)

where \( R, F, L, t_i, t_e, \sigma_i \) are the gas constant, Faraday constant, thickness of sample, ionic and electronic transference number and total conductivity.

When the electronic conductivity of material is much higher than the ionic conductivity, or the ionic transference number \( (t_i) \) is very small, Equation 1 can be rewritten as

\[
J_{O2} = \frac{RT}{16F^2} \int_{P_{O2}}^{P_{O2}'} \sigma d(\ln P_{O2})
\]  

(4)

\[\log(J_{O2}, \text{mole cm}^{-2} \text{s}^{-1})\]

\[\frac{1}{T}, \text{K}^{-1}\]

Figure 4. Oxygen permeation rates in an Argon / Air gradient for LSF.
From Equation 4, the ionic conductivity can be determined using the oxygen permeation data, however, one must know the $P_{O2}$ behavior of the ionic conductivity. Typically, the ionic conductivity can be described as a function of $P_{O2}$,

$$\sigma_i = \sigma_o P_{O2}^n.$$  \hspace{1cm} (5)

Using Eq. 5, Equation 4 becomes,

$$J_{O2} = \frac{RT}{16F^2 L} \sigma_o \left( P_{O2}^{\prime \prime \prime} - P_{O2}^{\prime \prime} \right) \quad (n \neq 0)$$ \hspace{1cm} (6)

and

$$J_{O2} = \frac{RT}{16F^2 L} \sigma_o \ln \frac{P_{O2}^{\prime \prime \prime}}{P_{O2}^{\prime \prime}} \quad (n = 0).$$ \hspace{1cm} (7)

When $n=0$, $P_{O2}$ behavior is independent of $P_{O2}$ and $\sigma_i = \sigma_o$. From Equations 6 and 7, it is possible to estimate the value of $n$ by measuring $J_{O2}$ with using different carrier gas (i.e. 0.1%$O_2$ content gas). The ratio between those two $J_{O2}$ values can be written as

$$\frac{J_{O2}(P_{O2}^{\prime \prime \prime}, P_{O2}^{\prime \prime})}{J_{O2}(P_{O2}^{\prime \prime}, P_{O2}^{\prime})} = \frac{P_{O2}^{\prime \prime \prime} - P_{O2}^{\prime \prime}}{P_{O2}^{\prime \prime} - P_{O2}^{\prime}} \quad (n \neq 0),$$ \hspace{1cm} (8)

and

$$\frac{J_{O2}(P_{O2}^{\prime \prime \prime}, P_{O2}^{\prime \prime})}{J_{O2}(P_{O2}^{\prime \prime}, P_{O2}^{\prime})} = \ln \frac{P_{O2}^{\prime \prime \prime}/P_{O2}^{\prime \prime}}{P_{O2}^{\prime \prime}/P_{O2}^{\prime}} \quad (n = 0).$$ \hspace{1cm} (9)

The left hand side of Equations 8 and 9 can be determined from experiment and depends on the value of $P_{O2}$ and $n$. If $n=0$, the experimental results should follow Eq. 9 and if not, $n$ can be found by plotting Eq. 8 as a function of $n$.

As an example, the ionic conductivity for LSF is calculated assuming that $n=0$ ($\sigma_i$ is independent of $P_{O2}$), -1/2 and –1/4. Figure 5 shows the ionic conductivity as a function of temperature determined from Eqs. 6 and 7 in air. As can be seen, the values can be varied one order of magnitude when the $P_{O2}$ behavior is different.

Further investigation will be continued to determine $P_{O2}$ behavior of the ionic conductivity by suggested method above.
Figure 5. Ionic conductivity for LSF in Air for different $n$.

Reference

Appendix D

“Neutron Diffraction Determination of Oxygen Vacancy Concentration in Perovskites”

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Neutron diffraction determination of oxygen vacancy concentration in perovskites

W.B. Yelon, Q. Cai
W.J. James, J. Yang, X.D. Zhou, H.U. Anderson

The cross section for coherent scattering of neutrons by atoms is a nuclear property, not dependent on the number of electrons. Consequently, the sensitivity of neutron scattering to light atoms such as oxygen is far greater than of x-ray scattering. Thus, it is well known that powder neutron diffraction coupled with Rietveld refinement can be used to determine the oxygen vacancy concentration in many oxides. However, the precision of such a determination has not been fully tested, especially at low vacancy content. In addition, many perovskite oxides exhibit magnetic ordering, and we have shown that in $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ the ordering temperature and room temperature magnetic moment are a sensitive function of the vacancy concentration. Neutron diffraction is a very sensitive direct probe of the magnetic moment, which may, therefore, be used as an indirect probe of the vacancy concentration. In addition, the unit cell volume (which may be determined either by neutron or x-ray diffraction) is a potential probe of the vacancy concentration. Extensive experiments have been undertaken on $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (L6SF) and limited data have been collected on several other related materials including $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (L8SF), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (L6SF8C) and $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ (L4SF) to determine the relative sensitivities of the direct determination of oxygen vacancy concentration from Rietveld refinement of the neutron data to determination of magnetic moment or unit cell volume. It is found (for L6SF) that the room temperature magnetic moment is the most sensitive probe of the vacancy concentration while at higher concentrations either the direct determination or the cell volume may be used (and should probably be combined) to yield accurate concentrations. For other samples such as L8SF, the room temperature moment is already large at room temperature, due to the higher ordering temperature, but diffraction measurements at elevated temperature (~200°C) can be employed to increase the sensitivity at low vacancy concentration.

Although the high La samples investigated were expected to have R-3C symmetry, it was found that a lower symmetry trigonal space group P-3C1 gives improved fits to the data including the matching of a peak not fitted in the R-3C symmetry, and a more reasonable dependence of the vacancy concentration on the heat treatment. The magnetic moment and unit cell volume, however, are found to be essentially independent of the choice of crystallographic model.

For a given La/Sr/Fe/Co composition, all samples were taken from the same stock, prepared by a polymer method. They were subsequently heat treated in air at various temperatures up to 1500°C and rapidly quenched to room temperature. For the L6SF system data had also been collected in an earlier study on samples annealed at 1000°C in three different CO/CO$_2$ mixtures (90/10, 50/50 and 10/90). Results from those samples (with higher vacancy concentrations) appear to extrapolate well from the air annealed results.

Results:

A) The room temperature magnetic moment and unit cell volume: correlation with vacancy concentration
1) L6SF

The sample L6SF, La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$, was heat treated in 100°C steps from 700°C to 1500°C. The results of the neutron refinement are given in table 1. For an untreated sample and the sample heated only to 700°C, the refinement results show the oxygen sites to be fully occupied while the vacancy concentration gradually increases as the temperature is raised, reaching a maximum of 6.5% at 1500°C. Refinement using the R-3C space group calculates oxygen excess at the lowest temperature, an implausible finding. At the same time, refinement of the same data in the P-3C1 space group gives realistic occupancy and improved goodness of fit parameters. Figure 1 shows part of the data for the 1000°C heat treatment and the fitted curves using the two different space groups. There is an observed peak at about 41º that is not modeled in R-3C. This peak is fitted in P-3C1. In this space group there are 2 inequivalent Fe and La/Sr sites. One site has a multiplicity of 4, while the second has a multiplicity of 2. Examination of the refined results show that the z coordinate of the La/Sr atoms shift about .07Å from the ideal (R-3C) position at 1000°C, while the Fe atoms shift about 0.02Å. The oxygen atoms are split into 3 sites with a theoretical multiplicity of 12. Two of these lie in crystallographically similar environments (relative to a trigonally distorted cubic parent cell) while the third is in a different site. However, these are expected to be only ½ full in the fully stoichiometric compound. There are, thus 4 O atoms with one Fe-O distance (forming a square plane), and 2 O atoms at a different distance in each Fe centered oxygen octahedra. Because there is a high correlation between the occupancies of each of these sites, unconstrained refinements of the occupancy of each site leads to a small over-population of one site, reasonable total occupancy, and a large statistical uncertainty on the total occupancy. If, however, the occupancy of each site is constrained to be less than or equal to 0.5, and the two basal oxygen atoms are constrained to have equal occupation, the goodness-of-fit measures increase negligibly while the statistical uncertainty on the total occupancy is dramatically reduced to approximately 0.5%, a value that appears to be consistent with the scatter in the data plotted versus heat treatment temperature (fig. 2) or against magnetic moment. Up to about 1200°C there is a significant distortion of the lattice from cubic, while above this temperature the distortion is quite small (~0.06º) and may be the result of magnetoelastic forces, i.e., the strong magnetic ordering leads to a small distortion of the lattice, balancing the gain in magnetic energy against the loss of lattice energy.

The magnetic moments on the two Fe sites were constrained to be equal, and the room temperature moment was found to increase from 1.3µ$_{B}$ for the untreated sample to 1.4µ$_{B}$ for the 700°C specimen to 3.4µ$_{B}$ for the 1500°C specimen (Fig. 3). The cause of this increase will be discussed in the next section. The uncertainty in the magnetic moment is estimated to be less than 1% of the total moment, significantly less than the error in the direct determination of the vacancy concentration. The small increase in moment between the untreated and 700°C samples probably reflects the production of a small vacancy concentration, outside the limit of the direct determination.

The unit cell volume increases monotonically as the treatment temperature increases, by a total of 4.8Å$^3$ from the lowest to the highest temperature (Fig. 4). The uncertainty in this determination is estimated to be about 0.04Å$^3$ suggesting that it, too, can be a good metric for the determination of vacancy concentration. However, these results are relative (unlike the
moment, which is absolute) due to uncertainty in wavelength, sample position, etc, and therefore determination of the volume of a single specimen cannot be used to estimate vacancy concentration. The small downturn in volume at the highest temperature appears to be an artifact, since data on the samples treated in reducing atmosphere with vacancy concentration up to 11% show a continued increase in volume that extrapolates well from lower concentration.

Fig. 5 shows the magnetic moment and unit cell volume as a function of vacancy concentration. It appears that, in this range, the magnetic moment refinement shows the smoothest behavior and may well be the most reliable indirect measure of that concentration.

2) L6SF8C

Data for the samples of L6SF8C, La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-δ}$ have been studied over the range of heat treatment 700°C –1200°C. As with the L6SF system the space group P-3C1 gives better results than R-3C and the same unfitted peak at about 41° is observed and fitted by the P-3C1 space group. The sample treated at 700°C shows a very small fitted vacancy concentration, approximately 2/3%. At 900°C this increases to 2% and at 1100°C it is found to be approximately 4% (Fig. 2). Between 1100°C and 1200°C no change (within statistical uncertainty) in vacancy concentration is seen. Higher temperature treatments will be needed to determine if this is close to the limiting concentration or an artifact. At all temperatures the vacancy concentration is modestly higher than observed in the L6SF sample (without Co). The magnetic moment for the 700°C sample is found to be only 0.62$\mu_B$, indicating that the Neel temperature for this sample is only slightly above room temperature. The moments increase strongly with increasing treatment temperature (Fig. 6) reaching 2.2$\mu_B$ for the 1100°C and 1200°C samples. The smaller value of the moment compared to the L6Sf specimens is, at least, partly the result of the smaller Co moment. As was observed for the vacancy concentration, the magnetic moment does not differ significantly for the 1100°C and 1200°C samples. The unit cell volume for these samples (Fig. 7) shows a similar trend as for the L6Sf samples, increasing strongly with vacancy concentration up to about 2-2.5% vacancy and then varying more slowly at higher concentration.

Although more data are needed for this system, it appears that the magnetic moment can be reliably used to track vacancy concentration up to about 3% (and perhaps higher), while the unit cell volume may be a more useful metric for higher temperature treatments.

3) L8SF

Only limited data has thus far been collected on the L8SF series La$_{0.8}$Sr$_{0.2}$FeO$_{3-δ}$, for heat treatment at 900°C, 1000°C and 1500°C. The space group for all of these samples is orthorhombic, Pbnn, with 4 formula units per unit cell. The La/Sr atoms are on only one site as are the Fe atoms. The oxygen atoms, however, are on two sites with multiplicities 8 and 4. The samples treated at the two lower temperatures show no oxygen vacancies, only a small change in magnetic moment from 2.966$\mu_B$, to 3.048$\mu_B$, and a small increase in cell volume from 240.48Å$^3$ to 240.63 Å$^3$. Data for the highest temperature treatment show a 1% vacancy concentration and a magnetic moment of 3.3$\mu_B$, but the cell volume still shows almost no change, increasing to 240.96 Å$^3$. It is apparent that it is much more difficult to produce oxygen vacancies in this sample than in the L6S series. In addition, it is clear that the Neel
temperature for all of these samples is well above room temperature and thus, the effect of vacancy concentration on the room temperature magnetic moment is modest. The magnetic moment could be made to be a more sensitive measure of vacancy concentration by carrying out these measurements at a higher temperature. This is clearly not precluded by the effect of the higher measuring temperature on the vacancy concentration, since the data clearly show that measurement up to at least 500ºC is likely to have minimal effect. It should be quite easy to determine the optimum measuring temperature by following the temperature dependence of the magnetization and choosing one where the moment (for low temperature heat treatment) is in the neighborhood of 1µB. Then one might expect to see the moment increase strongly with vacancy concentration.

4) Others
A limited amount of data has been collected on L4SF and on some other samples. The published crystal structure for L4SF does not appear to be correct and the correct space group must be determined before reliable measurement of the vacancy concentration can be performed. Data for the other samples thus far measured are too fragmentary for meaningful analysis.

B) Direct determination of vacancy concentration from the saturation magnetic moment

For the ferrites with high La (50% or more), it is reasonable to assume that all of the Fe atoms are in the 3+ or 4+ charge states. If the saturation magnetic moments for these two ions are significantly different, then a determination of the saturation moment (measurement at low temperature) can provide a direct determination of the ratio of the two species and, thus, of the stoichiometry. For the tool to be more useful than the correlation studies discussed in part A above, however, it is important to confirm that the moments for each charge state are not significantly affected by the La/Sr ratio. Figure 8 shows the saturation moments, determined from neutron powder diffraction measurements at 10K, for several samples of L6SF, as a function of oxygen deficiency. The highest deficiency, δ = 0.2 corresponds to a nearly pure Fe3+ state, while the extrapolation to δ = -0.3, corresponds to a pure 4+ charge state. Over this range the moment changes from near zero for the 4+ charge state to 3.8µB for the 3+ state. The behavior is, as expected, linear with vacancy concentration and is large enough that the vacancy concentration can be determined more accurately, by this method than by direct crystallographic refinement.

The data of figure 8 refer only to L6SF. If we assume, however, that the moments for the two charge states are the same for the L8SF system, we find, once again, excellent agreement between moment and refined vacancy concentration. Furthermore, we have measured a room temperature moment for LaFeO3 of 3.8µB. Since the Neel temperature of this material is quite high, the room temperature result is expected to be close to the saturation value. These results confirm the applicability of this method to the range of materials of interest here.

At the present time measurement of the saturation moment requires mounting the sample in a closed cycle refrigerator, cooling to temperature and rewarming, a process that takes a minimum 24 hours. This could be significantly speeded up by the acquisition of a top-loading He cryostat for neutron powder diffraction studies.
Discussion:
The strong correlation between room temperature magnetic moment and vacancy concentration may, at first sight appear surprising, but in this system the changes in crystallography and in chemistry both act on the magnetic interactions in order to yield this effect. The magnetic interactions between Fe atoms, leading to magnetic ordering in this type of oxide, are predominantly superexchange; exchange that is mediated by polarization of the oxygen atoms lying between the Fe near neighbors. This interaction is maximum (and antiferromagnetic) when the Fe-O-Fe bonds are linear. As the angle decreases from 180º to around 150º the interaction first decreases and then passes through zero to become ferromagnetic. We have previously shown that in the L6SF system, the Fe-O-Fe angle increases from about 163º to 173º as the vacancy concentration reaches around 7%. This increase strongly raises the magnetic ordering temperature $T_N$. The earlier results were based on refinements in the R-3C space group, and the structural details using the improved P-3C1 model have not yet been studied. In addition to the geometrical factor, the distribution of 3+ and 4+ ions is expected to play a large role in the exchange. Since the Fe$^{4+}$ions have small or zero moments, the exchange interactions in the system are expected to be dominated by the Fe$^{3+}$- Fe$^{3+}$ interactions. These will obviously increase markedly as the Fe$^{3+}$ concentration increases with increasing oxygen vacancies.

The magnetization, as a function of temperature follows the Brillouin curve: saturated at low temperature and decreasing slowly up to about 70% of $T_N$ and more rapidly as $T_N$ is approached. Thus, for untreated L6SF, where the Fe-O-Fe angle is small, and the Fe$^{4+}$ concentration large, $T_N$ is low and the room temperature moment is small. Eventually, however, $T_N$ increases to 500ºC or higher and the room temperature moment is little affected by the change in superexchange and $T_N$. However, the same effect that leads to the variable saturation moment (the ratio of low moment Fe$^{4+}$ and high moment Fe$^{3+}$) will dominate the room temperature moment when the ordering temperature is high. Since the Fe atoms are antiferromagnetically ordered, this effect cannot be observed using bulk magnetic measurements, but can easily be seen with the neutron diffraction measurements. When the composition reaches La$_{0.6667}$Sr$_{0.4}$FeO$_{2.8}$, i.e. 6.667% vacancies, it is expected that the system will reach its maximum average moment. Beyond this point Fe$^{2+}$ is expected to appear, also with a smaller moment than Fe$^{3+}$, and the room temperature moment would then be expected to decrease. Indeed this trend was seen in the CO/CO$_2$ reduced samples.

There are a number of advantages in using the magnetic moment as a measure of the vacancy concentration. The saturation moment gives an absolute determination without establishing the room temperature curves, while the room temperature moment may be quickly and reliably determined and used if the correlations have been established. The uncertainty in the vacancy concentration is about 0.5%, while these results give a maximum vacancy concentration of 6.5% for L6SF and less for other samples. The uncertainty in magnetic moment is 2% at low vacancy concentration, decreasing to less than 1% when the moment is large. In addition, it is necessary to collect full data sets in order to accurately refine the vacancy concentration, while it is possible to use partial data sets including only the low angle region of the data and still extract accurate moment values. Such data may be collected in as little as 1 hour, with minimal sample preparation prior to measurement. Thus, the vacancy concentration should be known, by this indirect determination, to a precision of 1% or 2% over the range of interest. Of course, at very high vacancy concentration, the direct determination will become more precise, while the
magnetic measurements will be less so, due to saturation. This may be overcome by measuring at elevated temperature. The optimum choice remains to be determined.

The unit cell volume is also a useful correlate for the vacancy concentration. The reported statistical error is about .04Å³ although the scatter in the data suggests that the actual uncertainty may be somewhat larger. There can be systematic error in this determination if the space group symmetry is not correct, or, as may be the case of the L6Sf sample treated at 1200ºC, if the sample consists of more than one phase, due to incomplete equilibration. As previously discussed, however, the determination of volume may be affected by sample positioning during measurement, (for both neutrons and x-rays) or other experimental issues, less likely to affect the moment determination.

On the other hand, collection of full neutron data sets allows all three determinations to be carried out simultaneously, as the refinement adjusts all of these quantities in fitting the measured data. Furthermore, these determinations are essentially independent. The unit cell volume is based only on peak position and not peak intensity, and uses the full data set. The magnetic refinement is based primarily on the intensity of the low angle reflections, while the vacancy concentration affects the intensities at all angles and especially uses the high angle data. Thus use of neutron diffraction provides redundancy and cross checks on the determination.

Conclusions:
Neutron diffraction measurements on samples quenched from high temperature appear to be a reliable, redundant method for determining the vacancy concentration in perovskites. For many of the materials of interest, the room temperature magnetic moment can provide data at least as accurate as the direct determination from the crystallography (Rietveld refinement) and from the change in unit cell volume. The saturation moment is an even more powerful (if experimentally more difficult) result that gives determination of the vacancy concentration.

In the near future in situ neutron diffraction measurements will also be carried out. To the extent that these are performed above the magnetic ordering temperature, this parameter will not be useful, but those measurements will still be able to directly determine the vacancy concentration and unit cell volume. They will be of particular value in establishing the kinetics of equilibration at high temperature, by making short sequential measurements. The MURR neutron powder diffractometer is particularly well suited to this purpose, since it spans 20º (20), collecting the scattered intensity over this range. The high penetration of neutron through many materials allows the construction of a furnace with high temperature-variable atmosphere capabilities. At the present time, one such furnace is being modified to accommodate the types of powder sample appropriate for these studies.
Table 1: Refinement about L6SF series. Model 1: r-3c Oxygen occupied 18e only. Model 2: r-3c oxygen occupied 36f only.
Model 3: r-3c, oxygen occupied 18e and 36f both.

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<td>0.476(2)</td>
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<td>7.18</td>
<td>6.56</td>
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<td>3</td>
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<td>13.55558(123)</td>
<td>359.685(42)</td>
<td>0.476(2)</td>
<td>0.507(3)</td>
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<td>13.55236(111)</td>
<td>359.511(38)</td>
<td>0.475(2)</td>
<td>0.493(4)</td>
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<td>3.413(22)</td>
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<td>0.493(4)</td>
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<td>3.413(22)</td>
<td>6.38</td>
<td>6.04</td>
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</tr>
</tbody>
</table>
Figure 1. Neutron Diffraction pattern refined with different space groups.

Figure 2. Oxygen deficiency vs. quenching temperature for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ and $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$. 
Figure 3. Magnetic Moment vs. Quenching temperature for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ and $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$. 

$\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$

$\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$
Figure 4. Unit cell volume vs. quenching temperature for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$.

Figure 5. Magnetic moment and unit cell volume vs. oxygen deficiency for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$. 
Figure 6. Magnetic moment vs. quenching temperature for $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$.

Figure 7. Unit cell volume vs. quenching temperature for $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$.
Figure 8. Oxygen occupancy vs. saturation moment (10K) for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$. 

Experimental Data

Linear Fit
In-Situ studies of high temperature oxygen absorption-desorption

Neutron diffraction is the ideal tool for in-situ studies at high temperature because the high penetrating power of the neutron allows for construction of environmental enclosures with multiple walls, heat shields and heating elements. The design chosen for the present studies is based on earlier work on hydrogen (deuterium) absorption in Ti-Al alloys at temperatures up to about 700ºC. Some modifications have been made to that furnace to allow for still higher temperatures.

The sample in variable gaseous environments is contained in a central 2” diameter quartz tube, which leads through a graded seal to a glass-kovar seal and stainless steel top. This is welded to a top flange that seals to the top of the vacuum enclosure. The sample, inside the quartz enclosure is powdered to a coarse mesh and held inside a basket of PT gauze approximately 5mm diameter by 50 mm length. The porosity of the gauze allows gas contact to the sample. Thermocouples are located a several positions inside the quartz tube to monitor sample temperature, top and bottom as well as the Kovar seal to assure that its limit is not surpassed.

The sample is heated by a mantle wound of Super-Kanthal wire which completely encloses the quartz tube. Four concentric heat shields surround the mantle, the innermost of Ta and the remaining three of stainless steel. Heat shields are also located above and below the mantle. The walls of the vacuum surrounding are Al, and at 900ºC the maximum wall temperature is about 140ºC.

Attenuation of the neutron beam by the thick (~1/2”) mantle is found to be about 40%, while the remaining elements of the system attenuate another 10%. This is found to be acceptable, but could be further improved by replacing the present mantle by one with a ¾” wide opening in the incident beam path, thereby reducing the total loss to about 30%.

The radial collimator system of the neutron diffractometer excludes scattering from the quartz tube above about 20º (2Θ), but below this angle broad amorphous scattering can be observed. Fortunately, none of the Bragg peaks of the ferrite sample lie in this low angle region with the present neutron wavelength, 1.488Å.

Two sets of measurements have been carried out with the present setup, using room air as the gaseous environment. The first of these examined the loss of oxygen as a function of temperature in La_{0.6}Sr_{0.4}FeO_{3-δ}, starting with material that had been heated to 1000ºC and slowly cooled to room temperature, producing a sample with near full oxygen occupancy (δ≈0). Results of these measurements are given in Table 1.
Table 1: L6SF Slowly Cooling: P-3c1 refinement, oxygen atoms are at three 12g:

<table>
<thead>
<tr>
<th>File</th>
<th>Temp</th>
<th>a (Å)</th>
<th>err</th>
<th>C (e)</th>
<th>err</th>
<th>$\chi^2_0$</th>
<th>$\alpha$ (°)</th>
<th>err</th>
<th>Total(o)</th>
<th>err</th>
<th>B(o)</th>
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<tr>
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<td>13.4784 7</td>
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<td>5.53312</td>
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<tr>
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<td>26</td>
<td>13.5228 8</td>
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<td>5.54701</td>
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<td>13.5473 8</td>
<td>169</td>
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<tr>
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<td>35</td>
<td>13.5615 3</td>
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<td>60.10</td>
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<td>102</td>
<td>364.526</td>
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<td>2.40</td>
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</table>

Between room temperature and about 250ºC the sample shows no change in oxygen occupation, while for higher temperatures the occupation slowly drops, and approaches the limit of 2.8 ($\delta=0.2$) observed in samples quenched from temperatures above 1000ºC. The observation of low oxygen at a somewhat lower temperature may be reasonable if the samples quenched from 800-1000ºC reabsorbed some oxygen during removal from the furnace.

The unit cell volume of this sample increases by nearly 10Å³ over this temperature range, and the rhombohedral angle $\alpha$ decreases from 60.31° to 60.10°. The data indicate that the sample remains slightly distorted from cubic, which would have an $\alpha$ exactly equal to 60.00°.

The second sample studied had the same composition but was rapidly quenched from 1500ºC and thus began with a significant oxygen deficiency ($\delta=0.2$). Heating this sample to 500ºC produced a lattice expansion but no significant increase in the oxygen occupancy. This result appears to contradict TGA data that shows a significant oxygen uptake above 250ºC and has not yet been reconciled. Although the neutron refinement of total oxygen has limited accuracy, information should also be available through a careful analysis of the unit cell volume as a function of temperature, since the creation of vacancies increases the cell volume (as does a temperature increase). Thus the volume change of the slow cooled sample should be much larger than that of the quenched sample, as the temperature is raised.
Appendix E

“Mössbauer Study of the Hyperfine Interactions and Valence States of Fe in La$_{0.6}$Sr$_{0.4}$FeO$_3$
Quenched at Different Temperatures”

J.B. Yang, X.D. Zhou, W.J. James, and H.U. Anderson
University of Missouri-Rolla

Q. Cai, and W.B. Yelon
University of Missouri-Columbia
Report on: Mössbauer study of the hyperfine interactions and valence states of Fe in 
La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched at different temperatures

J.B. YANG, X.D. ZHOU, Q. CAI, W.J. JAMES, W.B. YELON, H.U. ANDERSON

Mössbauer spectroscopy is the recoil-free emission and resonant absorption of the $\gamma$-rays in a solid. The technique of Mössbauer spectroscopy is a very sensitive and accurate way of gathering information about the chemical bonding, valence state, and the structural, magnetic, time-dependent and dynamical properties of chemical systems. For iron-57 Mössbauer spectroscopy, an energy difference of about $10^{-8}$ eV can be observed. The hyperfine interactions between electrons and nuclei are of the order $10^{-8}$eV and hence may be observed in Mössbauer spectra. Fe$^{57}$ Mössbauer spectroscopy has a remarkably high ratio of the line width ($10^{-8}$eV) to the transition energy (14.4 keV), of the order $10^{-12}$.

There are three parameters which can be obtained from Mössbauer spectra. (1) The isomer shift (IS), arises from the interaction energy of the part of the electronic cloud inside the nucleus with the nuclear charge. The isomer shift provides direct information about the electron density at the nucleus and this can often be interpreted to give unequivocal information about the valence state of the ion under study. (2) The quadrupole splitting (QS), arises from the fact that the nucleus is not perfect spherical, but may be ellipsoidal, either elongated or flattened. The electrostatic force between the surrounding ligands, assumed to be negatively charged, and the nonspherical part of the nuclear charge tend to make the nuclear axis point to the ligands. (3) The hyperfine field (HF), due to magnetic hyperfine interactions arise from the coupling of the nuclear magnetic moments with the effective magnetic field at the nucleus, and results in a splitting of the nuclear ground and excited states. Using these parameters (IS, QS, HF) obtained from Mössbauer spectra, the valence state, structural, and magnetic interaction can be effectively studied, and compared to other experimental data, such as neutron diffraction (magnetic moments, magnetic and crystal structures), and magnetic measurements (magnetic properties). Here we have used Mössbauer spectroscopy to study the valence state and hyperfine interactions of La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched at different temperatures.

Fig. 1 shows the Mössbauer spectra of La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures. The Mössbauer spectra were obtained at room temperature on a constant-acceleration spectrometer with a Co$^{57}$ source and was calibrated at room temperature with $\alpha$-Fe foil. Very complex spectra were observed which come from a rapid electron exchange between Fe ions in the quenched samples. The spectra have been fit with two sextets for samples quenched from 1000-1500°C. One single line and one Voigt peak-shaped sextet were used to fit the spectra of the untreated and 800°C quenched samples. For the 900°C treated sample, due to a large distribution of hyperfine parameters, two Voigt peak-shaped sextets and one single line were used.
The fitted hyperfine parameters are listed in Table I. Isomer shifts of the un-treated and 800°C quenched samples are nearly what could be expected for valence states of Fe^{3+} and Fe^{4+}. The relative ratio of Fe^{3+} and Fe^{4+} ions of the untreated sample obtained from relative areas of the Mössbauer spectra is 64:36, indicating a nearly zero oxygen vacancy in these compounds. The ratio of Fe^{3+}/Fe^{4+} is 70:30 for the 800°C quenched sample which indicates oxygen vacancies have increased in the compound. As the quench temperature becomes higher than 900°C, the Fe^{4+} spectrum disappears (Fe^{4+} normally is non-magnetic with a single line). It is evident that the magnetic sextets become dominant and all peaks of the spectra become sharper when the quench temperature increases to 1300°C. This indicates an increase in the Fe magnetic ordering temperature and suggests a structural transformation in the sample. Neutron diffraction studies has confirmed an increase of the magnetic ordering temperature with increasing quench temperature, and also a structural transformation from distorted cubic to cubic.

Because Mössbauer spectra of quenched samples show a rapid electron exchange between the Fe ions, an average valence state of Fe will be used to describe the Fe ions. Therefore, average IS and HF values have been used to study the valence state and hyperfine interaction in these compounds. As shown in figure 2(a), the average HF increases with the increasing quench temperature and reaches the saturated value at a temperature of 1400°C. The hyperfine field is composed of contact, orbital, and dipolar contributions: HF=HC+HL+HD. High spin Fe^{3+} has a spherical distribution of the electric charge due to the orbital configuration, t_{2g}^3 e_g^2 and therefore only HC contributes to the HF (~11T per unpaired electron in the 3d shell). Accordingly, the HF changes from 22 T to 49 T for unquenched and 1500°C quenched samples, respectively, which indicates the unpaired electrons to be nearly 5.0, a valence state of Fe^{3+} for the 1500°C quenched samples. If the HC is the major contributor to the HF, the HF can be converted to a magnetic moment using a conversion factor. The right vertical scale Fig 2(b), gives the magnetic moments as computed from the magnetic hyperfine fields using a factor of 14.7T/µB. It is clear that the magnetic moments do agree very well with those obtained from neutron diffraction data.

Fig. 2(c) shows the average IS of the Fe ions dependence on the quenching temperature. The IS steadily increases with quenching temperature. Since the isomer shift provides direct information about the electron density at the nucleus, we have attempted to derive information about the valence states of Fe ions in these compounds. In figure 3, we plot the dependence of the isomer shift on the average valence states of Fe in La_{1-x}Sr_x FeO_3. (Here, data from S. E. Dann et al., J. Solid State Chem. 109 (1994)134 were used). They prepared La_{1-x}Sr_x FeO_3 (0<=x<=1.0) under high pressure O_2 at 900 °C, and then slow cooled the samples. The samples show no oxygen vacancies, excepting the x=0.8 and 0.9 samples, less than 1% vacancy. Using a polynomial fit of the IS versus average valence states of Fe in these compounds, the average IS can be phenomenologically expressed as:

<IS>=3.269-1.461*x+0.166*x^2,

where x is the average valence state of the Fe. Applying the expression to the average IS of the quenched La_{0.6}Sr_{0.4} FeO_{3-δ}, the average valence states of the Fe and the oxygen vacancy content δ are obtained and shown in Fig 2. (d) and (e). It is found that the valence state of Fe changes from 3.36 to 3.04, suggesting that the Fe valence states change from a mixture of Fe^{3+}
and Fe$^{4+}$ to about 96% Fe$^{3+}$ as quenched from 1500 °C. The change in the valence state of Fe results in an increase in both the hyperfine field and magnetic moment for the quenched samples. The oxygen content $\delta$ changes from 0.02 to 0.18 per formula after quenching at 1500 °C. The oxygen contents $\delta$ obtained from Mössbauer spectra are again consistent with those obtained from the neutron diffraction refinements (See Fig 2.(e)).

The quadrupole splitting (QS) of the Fe ions decreases as the quench temperatures increase to 1200 °C, which indicates a crystal symmetry transformation from distorted-cubic to cubic, and shows nearly no splitting when the cubic pervoskite structure is attained.

Table I. Hyperfine parameters of La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures in the air. Hyperfine Field (HF) is in Tesla; Quadrupole Splitting (QS) and Isomer shift (IS) are in mm/s.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>IS(mm/s)</th>
<th>QS(mms)</th>
<th>HF(T)</th>
<th>Ratio (%)</th>
<th>Average &lt;IS&gt;</th>
<th>Average &lt;HF&gt;</th>
<th>Average &lt;QS&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treated</td>
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<td>-0.06(38)</td>
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</tr>
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<td>A 0.292(18)</td>
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<td>0.232(60)</td>
<td>22.5(27)</td>
<td>-0.06</td>
</tr>
<tr>
<td>900</td>
<td>A 0.340(28)</td>
<td>-0.23(31)</td>
<td>32.9(23)</td>
<td>49.9</td>
<td>0.256(18)</td>
<td>26.5(19)</td>
<td>-0.12</td>
</tr>
<tr>
<td>B* 0.197(10)</td>
<td>0.39(56)</td>
<td>27.1(15)</td>
<td>46.2</td>
<td>0.261(20)</td>
<td>30.1(18)</td>
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</tr>
<tr>
<td>C* 0.090(1)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
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</tr>
<tr>
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<td>73.1</td>
<td>0.359(6)</td>
<td>49.5(1)</td>
<td>0.03</td>
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</table>

In conclusion, we have shown that by measuring the isomer shift, hyperfine field and quadrupole splitting of the Fe ions in the La$_{0.6}$Sr$_{0.4}$FeO$_3$ compounds quenched at different temperatures, the valence states and the hyperfine interaction of Fe atoms, as well as the oxygen content in these compounds can be obtained. By combining the Mössbauer spectroscopy and neutron diffraction techniques, we can provide much detail and reasonably accurate information regarding oxygen vacancy concentration, valence states, and structural transformations. Furthermore, the in situ high temperature Mössbauer spectra provide direct information of the crystal dynamics and valence state dynamical information, studies of which are now in progress.
Fig. 1 Mössbauer spectra of La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures.
### Magnetic moment from neutron diffraction

<table>
<thead>
<tr>
<th>Quench Temperature (°C)</th>
<th>Magnetic Moment (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.20</td>
</tr>
<tr>
<td>1000</td>
<td>0.25</td>
</tr>
<tr>
<td>1200</td>
<td>0.30</td>
</tr>
<tr>
<td>1400</td>
<td>0.35</td>
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### Magnetic moment from Mossbauer spectra

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<th>Magnetic Moment (μB)</th>
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<tbody>
<tr>
<td>800</td>
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</tr>
<tr>
<td>1000</td>
<td>0.25</td>
</tr>
<tr>
<td>1200</td>
<td>0.30</td>
</tr>
<tr>
<td>1400</td>
<td>0.35</td>
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</table>

### Average isomer shift (mm/s)

<table>
<thead>
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<th>Average Isomer Shift (mm/s)</th>
</tr>
</thead>
<tbody>
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<td>1200</td>
<td>1.10</td>
</tr>
<tr>
<td>1400</td>
<td>1.15</td>
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</table>

### Average hyperfine field (T)

<table>
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<th>Average Hyperfine Field (T)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.00</td>
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<tr>
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<tr>
<td>1200</td>
<td>3.20</td>
</tr>
<tr>
<td>1400</td>
<td>3.30</td>
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</table>

### Average valence state of Fe

Using $<\text{IS}> = 3.26929 - 1.46141 \times X + 0.16582 \times X^2$ to obtain $X$ the valence state of Fe in La$_{0.6}$Sr$_{0.4}$FeO$_3$.

### Oxygen vacancy

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<tr>
<td>1000</td>
<td>0.05</td>
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<tr>
<td>1200</td>
<td>0.10</td>
</tr>
<tr>
<td>1400</td>
<td>0.15</td>
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---

**Fig. 2(a)** Average hyperfine field of Fe in La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures.

**Fig. 2(b)** Average magnetic moment of Fe in La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures.

**Fig. 2(c)** Average isomer shift of La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures.

**Fig. 2(d)** Average valence of Fe for La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures.

**Fig. 2(e)** Oxygen vacancy for La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched from different temperatures.
Report 2: Mössbauer study of the hyperfine interactions and valence states of Fe in La$_{0.6}$Sr$_{0.4}$FeO$_3$ quenched at different temperatures

The isomer shift (IS), arises from the interaction energy of the part of the electronic cloud inside the nucleus with the nuclear charge. The isomer shift provides direct information about the electron density at the nucleus and this can often be interpreted to give unequivocal information about the valence state of the ions. The Mössbauer spectra were obtained at different temperatures on a constant-acceleration spectrometer (Co$^{57}$ source) which was calibrated at room temperature with α-Fe foil. The La$_{0.6}$Sr$_{0.4}$FeO$_3$ samples are prepared by a liquid mixing method. The as–prepared sample was heat treated at different temperatures (700-1500°C) for 24h and cooled to room temperature.

Figs. 1-4 show the Mössbauer spectra of as-prepared and heat-treated La$_{0.6}$Sr$_{0.4}$FeO$_3$ measured under argon at different temperatures. The spectrum changes from a sextet to a singlet as the measuring temperature increases from room temperature to high temperature for the heat-treated samples (Figs. 2-4) indicating a magnetic ordering transition (antiferromagnetic ordering temperature). The Néel temperatures obtained from Mössbauer spectra are shown in Fig. 5. The Néel temperature increases from 30°C for the as-prepared sample, to 420°C for the 1500°C heat treated sample. The increase of the Néel temperature is due to the increase of the exchange interaction between Fe-Fe arising from changes in the valence state of Fe as a consequence of the heat treatment (see last report). It is found that the valence state of Fe changes from 3.36 to 3.04, suggesting that the Fe valence states change from a mixture of Fe$^{3+}$ and Fe$^{4+}$ to about 96% Fe$^{3+}$ as quenched at 1500°C. The change in the valence state of Fe results in an increase in both the hyperfine field and magnetic moment for the quenched samples. The oxygen content $\delta$ changes from 0.02 to 0.18 per formula after quenching at 1500°C.

The fitted isomer shifts of the non-treated sample at room temperature are nearly what would be expected for valence states of Fe$^{3+}$ and Fe$^{4+}$. The relative ratio of Fe$^{3+}$ and Fe$^{4+}$ ions of the untreated sample obtained from the relative areas of the Mössbauer spectra is 64:36, indicating a nearly zero oxygen vacancy in these compounds at room temperature. The room temperature IS of the 1500 °C heat-treated samples indicates an average Fe valence state of Fe$^{3+}$. The line width of the spectrum becomes smaller as the measured temperature increases.
This indicates a faster hopping between the Fe$^{3+}$ and Fe$^{4+}$ at higher temperature. Therefore, an average valence is exhibited at high temperature for these compounds.

Fig. 6 is the IS of the non-treated sample measured at different atmospheres versus the temperature. As we can see, the IS measured under argon is larger than those measured under air and O$_2$ at temperatures above 500°C, suggesting an Fe valence change in different atmospheres with different oxygen partial pressure. This change is significant at temperature above 700°C.

Figs. 7(a)-(d) show the IS of heat-treated La$_{0.6}$Sr$_{0.4}$FeO$_3$ measured at different temperatures. As compared to the non-treated sample, the IS of heat-treated samples shows a higher value at the same measured temperature, which is attributed to the higher amount of oxygen vacancies in these compounds. Both neutron diffraction and Mössbauer studies have confirmed that the valence state of Fe changes from 3.36 to about 3.04 after heat treatment at 1500°C.

**Further work:** In order to obtain meaningful information of the valence states of Fe, the dependence of the IS on temperature and valence states must be calibrated with a standard sample. Therefore, a standard sample with a certain structure and known valence states (La$_{1-x}$Sr$_x$FeO$_3$) will be prepared and used to calibrate the Mössbauer spectra. In the meantime, temperature and time-dependent spectra will be used to study the dynamical properties of these compounds, such as diffusion of oxide ion vacancies, vacancy ordering, magnetic ordering and, charge density etc. By combination with structural and compositional information from high temperature neutron diffraction data, an analysis of the Fe valence state in the perovskite at high temperature can be achieved.
Fig. 1 Mössbauer spectra of as-prepared La$_{0.6}$Sr$_{0.4}$FeO$_3$ measured at different temperatures under argon atmosphere.
L6SFO 1000 °C quench

Fig 2 Mössbauer spectra of La$_{0.6}$Sr$_{0.4}$FeO$_3$ heat-treated at 1000 °C measured at different temperatures under argon atmosphere.
Fig 3 Mössbauer spectra of La$_{0.6}$Sr$_{0.4}$FeO$_3$ heat-treated at 1400 °C measured at different temperatures under argon atmosphere.
Fig 4 Mössbauer spectra of La$_{0.6}$Sr$_{0.4}$FeO$_3$ heat-treated at 1500 °C measured at different temperatures under argon atmosphere.
Fig 5 Neel temperature of La$_{0.6}$Sr$_{0.4}$FeO$_3$ heat-treated at different temperatures
Fig. 6 Isomer shifts of non-quenched La$_{0.6}$Sr$_{0.4}$FeO$_3$ measured at different temperatures under different atmospheres.
Fig. 7 Isomer shifts of heat-treated La$_{0.6}$Sr$_{0.4}$FeO$_3$ measured at different temperatures under argon atmospheres.
Appendix F

“Cathode Materials for IT SOFC”

Harlan U. Anderson
University of Missouri-Rolla

Presented at the SECA Core Technology Program Review
Sacramento, CA
February 19, 2003
Cathode Materials for ITSOFC
DE-FC26-02NT41563
U.S. Department of Energy

Harlan U. Anderson
(Electronic Materials Applied Research Center) EMARC
University of Missouri-Rolla
Rolla, MO 65409

Presented at
SECA Core Technology Program Review
Held at Radisson Hotel Sacramento
Sacramento, CA

February 19, 2003

Contributors

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Abstract

The overall objective of this study is to gain a fundamental understanding of the parameters and characteristics which are related to SOFC cathode performance in the 500-700°C range. Initially, we are focusing on determining why Co and/or Fe containing perovskites perform better than Mn based perovskites. This is being accomplished by comparing the electrical conductivity, defect structure and cation valence states of these perovskite compositions. Early results show that one of the primary differences in these oxides is the levels of oxygen vacancy concentrations present at a given temperature and oxygen activity. This suggests that the degree of mixed ionic and electronic conductivity is directly related to the cathode overpotential.
**Outline**

- Issues Addressed
- Objectives
- Approach
- Results to Date
- Importance to Goals of SECA
- Future Work

---

**Technical Issue Addressed**

- Overpotential of LSM is too high to operate SOFC at $T < 800^\circ C$
- Need for cathode materials with overpotential low enough to operate in the 500-700$^\circ C$ range.
- The question to be answered is: What are the properties that a cathode must possess to successfully operate at $T < 750^\circ C$?

---

**Research Objective**

- The overall objective of this study is to gain a fundamental understanding of the parameters and characteristics which are related to SOFC cathode performance in the 500-700$^\circ C$ range. That is, what material parameters must an oxide have to possess to perform well as a cathode?
- And with this knowledge develop an appropriate cathode material.
- We are focusing on answering the question of why Co and/or Fe containing compositions perform better than (La,Sr)MnO$_3$?

- The primary goal will be to compare the electrical conductivity, defect structure and cation valence states of the (La,Sr)(Fe,Co)O$_3$ compositions to those of La$_{0.8}$Sr$_{0.2}$MnO$_3$ as function of temperature and oxygen activity.
- These results will be compared to the overpotential measured on electrode/YSZ electrolyte structures.
- To test the hypothesis that the cathode overpotential is related to the oxygen vacancy concentration and the cation valence states in the cathode.
This will be done by:

- Preparing powders and dense specimens of:
  \[ \text{La}_{0.8} \text{Sr}_{0.2} \text{MnO}_3 \]
  \[ \text{La}_2 \text{Sr}_4 \text{FeO}_4 \]
  \[ \text{La}_{0.8} \text{Sr}_{0.2} \text{Fe}_{0.8} \text{Co}_{0.2} \text{O}_3 \]

- Characterizing each composition using:
  
  - XRD
  - TGA
  - Electrical Conductivity
  - Neutron Diffraction
  - Mössbauer Spectroscopy

The determination of oxygen deficiency is of important for evaluation of oxides for use as cathodes. In addition to chemical analysis and TGA; two techniques are employed:

1. **Neutron Diffraction** not only resolves structural and magnetic properties, but also allows an accurate and rapid determination of oxygen deficiency levels;

2. **Mössbauer spectra** allow studies on the valence state of Fe, therefore an **in situ** spectroscopy study of the reaction between the ferrite cathode and oxygen is feasible.

Our studies plus other results suggest that ferrite compositions are candidates for use as cathodes in IT SOFCs.

---

**Results to Date**

- Compositions Prepared:
  \[ \text{La}_{0.8} \text{Sr}_{0.2} \text{MnO}_3 \]
  \[ \text{La}_2 \text{Sr}_4 \text{FeO}_4 \]
  \[ \text{La}_{0.8} \text{Sr}_{0.2} \text{Fe}_{0.8} \text{Co}_{0.2} \text{O}_3 \]

- Determination of Oxygen Vacancy Content

  - Electrical conductivity
  - TGA
  - Neutron Diffraction (RnT)
  - Mössbauer Spectroscopy (RnT)

- Electrical Conductivity in Air
  
  - Measurements
  - Simulation
  - Fe Local Chemistry

---

**The University of Missouri Research Reactor Center – (MURR)**

- Neutron Powder Diffractometer (HR)
- Neutron Reflectometer
- Residual Stress Diffractometer
- Triple Axis Spectrometers
- SQUID Magnetometer
- Deep Level Transient Spectrometer Monochromators
- Neutron Irradiation ...
The Merits of Neutron Diffraction on Studies of the Perovskite-Type Cathodes

- Neutrons have unique scattering amplitudes and scattering is not dominated by heavy atoms;
- Neutron cross sections are isotope dependent;
- Neutron energies are comparable to elementary excitations (phonons and magnons). Thus, inelastic scattering substantially changes the neutron energy (wavelength);
- Neutrons have a magnetic moment and can probe the magnetic structures and excitations through a strong interaction;
- Neutrons are scattered by the nuclei (except for magnetic scattering). Thus the form factor is flat.

Typical Neutron Diffraction Performed at Room Temperature

1: Nucleus Bragg position
2: Magnetic position

Néel temperature of LSF is around RT, therefore magnetic peak contribution is weak in ND pattern.

High Néel Temperature and Strong Magnetic Contribution in Quenched La$_{0.60}$Sr$_{0.40}$FeO$_{3-δ}$

Quenched temperature: 1500°C
Annealing time: 24 hours

Magnetic contribution only

Space group of P – 3c1 improved ND refinement

(a) Refined with P-3c1 space group
(b) Refined with R-3c space group

The green marks are the Bragg peak positions of each phase. Specimen was quenched in air at 1000°C and ND was performed at RT.
3-δ vs. $\mu_B$ for La$_{0.60}$Sr$_{0.40}$FeO$_{3-δ}$ quenched at various temperatures

- Saturation moments for all specimens
- Fe$^{2+}$ (moment $= 2.8 \mu_B$)
- Only Fe$^{3+}$ contributes to antiferromagnetic moment in this system

Oxygen Content determined by TGA and ND for LSM, LSF and LSCF

- La$_{0.60}$Sr$_{0.40}$FeO$_{3-δ}$ (ND)
- La$_{0.60}$Sr$_{0.40}$FeO$_{3-δ}$ (TGA)
- La$_{0.60}$Sr$_{0.40}$MnO$_{3-δ}$

Oxygen Content (3-δ) for Quenched La$_{0.60}$Sr$_{0.40}$FeO$_{3-δ}$

- Neutron Diffraction
- Mössbauer

Specimens were annealed for 24 hours
Quenched temperature was in the range from 800°C to 1500°C

Log($\sigma$) vs. Log($pO_2$) for LSM, LSCF and LSF

- La$_{0.60}$Sr$_{0.40}$FeO$_{3-δ}$
- La$_{0.60}$Sr$_{0.40}$Co$_{0.20}$Fe$_{0.80}$O$_{3-δ}$
- La$_{0.60}$Sr$_{0.40}$MnO$_{3-δ}$
Conductivities of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-\delta}$

Temperature dependent of $\sigma$ for LSM, LSCF and LSF

Simulation of $\sigma$ for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ in air, ($V_0$ from ND)

Comparison between $\text{La}_{0.60}\text{Sr}_{0.20}\text{MnO}_{3-\delta}$, $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$, and $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$ at 500°C in Air

\[ \sigma = C[Sr_{1-x}] \mu_q \text{ at } T < 500°C \]
\[ = (C[Sr_{1-x}] - 2V_0^{**}) \mu_q \text{ at } T > 600°C \quad C \sim 0.4 \]
Mössbauer Studies

Specimen without quenching
- Singlet spectrum
- Neel temperature ~ RT
- Fe²⁺ 60%, Fe⁴⁺ 40%
- Quenched Temp. = 1500°C
- Sextet spectrum
- Neel temperature > RT
- Fe²⁺ two local chemical environments

Assumptions:
- Neutrality condition
- Only Fe²⁺ and Fe⁴⁺ exist if δ < 0.2 in La₀.₆₆Sr₀.₄₀FeO₃-δ

Fe valence state and \([V_0^{oo}]\) vs. 3-δ in \(La_0.66Sr_{0.40}FeO_{3-δ}\)

Fe valence state and \([V_0^{oo}]\) vs. 3-δ for L6SF – ND Studies

Fe valence state and \([V_0^{oo}]\) vs. 3-δ for L6SF – Mössbauer Studies
**Future Work**

- Complete current studies
- Perform *in situ* studies
- Select candidate for Cathodes
- Determine cathode/electrolyte over potentials of selected candidates
Appendix G

“Neutron Diffraction Studies of the Cathode for IT SOFCs”

J.B. Yang, X.D. Zhou, W.J. James, and H.U. Anderson
University of Missouri-Rolla

Q. Cai, Z. Chu, and W.B. Yelon
University of Missouri-Columbia
Acknowledgements

The work is supported by the Department of Energy under contracts of DE-FC26-02NT41563 and UAF99 – 0038.
Fuel Cells: electrochemical devices that convert a fuel's energy directly to an electrical energy.

Advantages of Fuel Cells
- Improved Environment and Energy Security
- Directly Convert Energy without Combustion
- Significant Energy Efficiency
- Clean, Quiet and Negligible Emission of Pollutions
- Fuel Availability Promotes Energy Security
- Reliable and Durable Plants

Traditional: Heat energy to mechanical energy (as with a turbine), and finally turning mechanical energy into electricity (e.g. using a dynamo).

Fuel cells: chemically combine the molecules of a fuel and oxidizer without burning.

Applications:
- Stationary, Transportation
- Portable, Space and Military

http://www.llnl.gov/str/Mitlit.html

Fuel Cell Application: Intermediate Temperature (IT) regime (500°C – 700°C) operation seems mandatory if the cells can be commercialized

Applications:
- Stationary, Transportation
- Portable, Space and Military

IT operation:
1. Commercialization for house or plant
2. DOE goal: <$400/kW @ 2010

IT SOFC Problems and Solutions: Challenges for Materials Scientists

Materials selection
- Cathode
- Anode
- Electrolyte
- Interconnection

Materials Design
- Low dimension
- Composites
- Porosity
- Orientation

Cell Design
- Thin Electrolyte
- Interfacial layer

Induced Problems
- Compatibility
- Thermal Expansion
- Reaction
- Duration

(1) an extremely strict material selection, which allows the similar electrode kinetics and internal resistance as those at high temperature; (2) feasible techniques to build those devices so that each component in the SOFC can function efficiently.
Areal Specific Resistance (ASR) of the Electrolyte

Discussions:
If the electrolyte contributes to half of the ASR, at 600°C, \( t < 20 \mu m \), at 500°C \( t < 10 \mu m \).

At 0.7V, if power density is 1 W/cm², the total areal specific resistance of the cell should be less than 0.21 \( \Omega \text{cm}^2 \).

Cathode Materials – Perovskite Type Oxides

Property characterization of cathodes (Objective: high cond, low overpotential, sufficient electrode kinetics
A: Interfacial Resistance
B: Ionic and Electronic Cond
C: Oxygen reduction mechanism, Spectroscopy (SIMS, Mössbauer, FTIR, NMR etc), Neutron/XRD Diff, Microscopy

Cathode Materials for IT SOFCs

Cathode properties:

Materials Chemistry:
Oxygen self-diffusion coefficient;
Oxygen surface exchange coefficient;
\( V_{\text{ave}} \), local chemical environment of B site ion, interaction with oxidant (O₂);
Composition …

Structure
Tortuosity (\( \tau \)), Porosity (\( \eta \)); Specific surface area, composite connectivity …

Compatibility
Thermal expansion coefficient
Reaction with the electrolyte

\[
R_{\text{Chem}} = \frac{1}{T} \left(1 - \varepsilon \right) aC_0^2D^k
\]

\( R_{\text{chem}} \): chemical reaction induced R, \( D^k \): oxygen self-diffusion coefficient (cm² s⁻¹); k:
\( C_0^2 \): concentration (mol cm⁻³); \( \varepsilon \): fractional porosity; a: surface area/unit volume;

\textbf{Object}: search for the materials with large \( D^k \) value, for example \( > 10^{-6} \text{cm}^2 \text{s}^{-1} \) @ 500°C
The Merits of Neutron Diffraction on Studies of the Perovskite-Type Cathodes

- Neutrons have unique scattering amplitudes and scattering is not dominated by heavy atoms;
- Neutron cross sections are isotope dependent
- Neutron energies are comparable to elementary excitations (phonons and magnons). Thus, inelastic scattering changes the neutron energy (wavelength) substantially;
- Neutrons have a magnetic moment and can probe the magnetic structures and excitations through a strong interaction.
- Neutrons are scattered by the nuclei (except for magnetic scattering). Thus the form factor is flat.
Typical Neutron Diffraction Pattern

More distorting rhombohedral or cubic for these quenched at pO2 < 10^-13 atm.

Oxygen Vacancy Levels, Fe – O – Fe Angles, and Néel Temperatures vs. pO2

Oxygen vacancy level and B-site atom valence state change vs. dopant level
Cell Volume and Magnetic Moment per Fe of Quenched La\textsubscript{0.60}Sr\textsubscript{0.40}FeO\textsubscript{3-δ}

- Cell volume increases from 355.72 (without quenching) to 359.51 (at 1500°C)
- Magnetic Moment increases from 1.3 $\mu_B$ to 3.4 $\mu_B$
- Oxygen vacancy level increases with quenching temperature

Mössbauer Studies

Specimen quenched at 800°C
- Singlet spectrum
- Néel temperature ~ RT
- Fe$^{3+}$ 68%, Fe$^{4+}$ 32%

Specimen quenched at 1500°C
- Sextet spectrum
- Néel temperature > RT
- Fe$^{3+}$ two local chemical environments

$\delta$ in quenched La\textsubscript{0.60}Sr\textsubscript{0.40}FeO\textsubscript{3-δ} vs. Magnetic Moment

- Quenched Temp. = 1500°C
- Quenched Temp. = 800°C
- Singlet spectrum
- Néel temperature ~ RT
- Fe$^{3+}$ 68%, Fe$^{4+}$ 32%

- Sextet spectrum
- Néel temperature > RT
- Fe$^{3+}$ two local chemical environments
At high temperature, the loss of oxygen generates oxygen vacancies, which compensate the major carriers, $h^+$. Therefore, there exists the highest conductivity around 600°C to 700°C.

Studies (particularly in situ) of Neutron Diffraction with Mössbauer Spectroscopy, Impedance Spectroscopy, and Second Ion Mass Spectroscopy (SIMS), can resolve the structural, electrical, magnetic and catalytic properties of the cathodes.
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<th>QS</th>
<th>HF</th>
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**Graphical Data:**

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Appendix H

“Utilization of Neutron Diffraction and Mössbauer Spectroscopy in the Studies of the Cathode for SOFCs”

J.B. Yang, X.D. Zhou, W.J. James, and H.U. Anderson
University of Missouri-Rolla

Q. Cai, and W.B. Yelon
University of Missouri-Columbia

Submitted to Solid State Ionics
Abstract

Neutron diffraction and Mössbauer spectroscopy were used to characterize the perovskite type cathodes, in terms of the crystal structure, oxygen occupancy, magnetic moment, and Fe valence state. It was found that a lower symmetry trigonal space group P-3C1 gives improved fits to the data including the matching of a peak not fitted in the R̅3c symmetry. A significant lattice distortion from rhombohedral to cubic was observed in La₀.₆₀Sr₀.₄₀FeO₃₋δ quenched from 1200°C, Average Fe valence states are ~ 3.04 and 3.36 for La₀.₆₀Sr₀.₄₀FeO₃₋δ quenched from 1500°C and 700°C respectively. Results from neutron diffraction and Mössbauer spectroscopy indicated that (1) in the specimen without quenching, there was not significant oxygen vacancy, (δ = 0) and ratio of Fe³⁺ over Fe⁴⁺ is 6/4; and (2) in the sample quenched from 1500°C, δ was ~ 0.2 and Fe exhibited a valence state ~ 3⁺.

1. Introduction

Search for the new generation of the cathode used in intermediate temperature (IT) solid oxide fuel cells (SOFCs) is of great importance because the areal specific resistance (ASR) of the cathode, currently being used, is too large to be considered 1, 2. One technique to improve the cathode is to tailor its microstructure, for example its porosity, torosity, composite connectivity etc; the other technique is to design the cathode to be mixed ionic and electronic conductor (MIECs) 3. Neutron diffraction is a powerful tool to characterize these new cathode oxides because it resolves not only the crystal structure, but also the magnetic properties and the oxygen vacancy concentration 4-6. Compared to x-ray diffraction, neutron diffraction possess couple of significant advantages, including: (1) The sensitivity of neutron scattering to light atoms such as oxygen is far greater than of x-ray scattering because the coherent scattering of neutrons is only determined by the nucleus and independent upon the number of electrons and (2) Neutron has a magnetic moment can probe the magnetic structures and excitations through a strong interaction. Most of the perovskite type oxides (ABO₃) used as the cathodes are magnetic oxides because of the unpaired electron(s) of B site ions, such as Mn³⁺, Fe³⁺ and Co³⁺. Moreover, Fe local chemistry, particularly valence state and bonding between Fe and O, is of great importance in that it is directly related to the electronic conductivity, reaction between oxygen and the cathode and cathode stability. Mössbauer spectroscopy is a sensitive technique for the studied in terms of the chemical bonding, valence state, and magnetic properties of Fe containing systems (Ferrites). The isomer shift of Mössbauer spectra provides unequivocal information of the valence state of Fe.

2. Experimental

The modified Pechini method was used to synthesize nanocrystalline particles, which were calcined at various temperatures to prepare powders. 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 5º-105º (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. Mössbauer spectra were measured using a
source of $^{57}$Co in Rh matrix with a conventional constant accelerated driver. Standard $\alpha$ - Fe was used to calibrate the spectrometer with the isomer shift relative to $\alpha$ - Fe at 300K.

3. Results and Discuss

3.1 Typical neutron diffraction pattern and refinement

Figure 1 illustrates typical room temperature neutron diffraction patterns of La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ (L6SF) quenched from 1500°C. The inserted figure is on the sample without quenching. The most obvious difference between the two patterns is a much stronger low angle (~ 19°) peak in Fig. 1, which is contributed by the magnetic interaction only. In order to achieve detailed information about magnetic moment, magnetic and crystal structure, refinement of the neutron diffraction data was carried out using the FULLPROF program. Previous studies showed that the refinement using the R$\bar{3}$c space group could resolve oxygen content. Very recently, it was found that refinement in the trigonal space group P-3C1 on the same data resulted in an improvement of the fit parameters, which in turn gave more realistic oxygen occupancy. For example, an observed peak at about 41° for the specimen quenched from 1000°C is not modeled in R$\bar{3}$c, which can be fitted in P-3C1. The magnetic moment and unit cell volume, however, are found to be essentially independent of the choice of crystallographic model. Because there is a high correlation between the occupancies of each of these sites, unconstrained refinements of the occupancy of each site leads to a small over-population of one site, reasonable total occupancy, and a large statistical uncertainty on the total occupancy.

3.2 Crystallographic Structure

From all the quenched samples, similar patterns as shown in Fig. 1 were observed, showing them to be single phase. Crystal structure at various quenching temperature is shown in Figure 2, in which $a^*$ represents $a/\sqrt{2}$ and $c^*$ is $c/2\sqrt{3}$. The symmetry of L6SF quenched from 600 to 1200°C at room temperature remains as rhombohedral (space group R$\bar{3}$c). The rhombohedral splitting of the peaks becomes not obvious for the specimens quenched from $T > 1200^\circ$C, which indicates a significant lattice distortion from the rhombohedral cell to the cubic cell. This distortion becomes small (~0.06°) in samples quenched from $T > 1300^\circ$C. The unit cell volume increases monotonically as the quenching temperature increases, by a total of 3.8Å$^3$ from 355.72Å$^3$ (without quenching) to 359.52Å$^3$ (quenched from 1500°C). The uncertainty in this determination is estimated to be about 0.04Å$^3$ suggesting that increasing of unit cell volume (~1.1%) was resulted from increasing of oxygen vacancy concentration and ionic radius of Fe ion, which in turn can be a good method for the determination of vacancy concentration.

3.3 Local Chemistry of Fe and Magnetic moments

3.3.1 Magnetic interaction

La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ exhibits an antiferromagnetic – paramagnetic transition, hence the magnetic moments on the two Fe sites are constrained to be equal, and the room temperature moment was found to increase from 1.3$\mu$B for the sample without quenching to 3.4$\mu$B for the
1500°C specimen. The reason for increasing magnetic moment mainly is due to the distribution of 3+ and 4+ ions. Since the Fe$^{4+}$ ions have small or zero moments, the exchange interactions in this system are expected to be dominated by the Fe$^{3+}$ - Fe$^{3+}$ interactions. These will obviously increase markedly as the Fe$^{3+}$ concentration increases with increasing oxygen vacancies. The magnetization of La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ as a function of temperature follows the Brillouin curve: saturated at low temperature and decreasing slowly up to about 70% of $T_N$ and more rapidly as $T_N$ is approached. Thus, for unquenched L6SF, where the Fe-O-Fe angle is small, and the Fe$^{4+}$ concentration large, $T_N$ is low and the room temperature moment is small. $T_N$ increases to ~410°C for the specimen quenched from 1500°C, therefore the room temperature moment is little affected by the change in superexchange and $T_N$. However, the same effect that leads to the variable saturation moment (the ratio of low moment Fe$^{4+}$ and high moment Fe$^{3+}$) will dominate the room temperature moment when the ordering temperature is high. Since the Fe atoms are antiferromagnetically ordered, this effect cannot be observed using bulk magnetic measurements, but can easily be seen with the neutron diffraction measurements. When the composition reaches La$_{0.60}$Sr$_{0.40}$FeO$_{2.8}$, it is expected that the system will reach its maximum average moment. Beyond this point Fe$^{2+}$ is expected to appear, also with a smaller moment than Fe$^{3+}$, and the room temperature moment would then be expected to decrease. Indeed this trend was seen in the CO/CO$_2$ reduced samples.

3.3.2 Fe valence state

The relative ratio of Fe$^{3+}$ and Fe$^{4+}$ ions for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ without quenching obtained from relative areas of the Mössbauer spectra is 64:36, indicating a nearly zero oxygen vacancy in these compounds. This ratio changes to 70:30 for the specimen quenched from 800°C, showing an increase of oxygen vacancy concentration. As the quench temperature becomes higher than 900°C, the Fe$^{4+}$ spectrum disappears (Fe$^{4+}$ normally is non-magnetic with a single line) and the magnetic sextets become dominant. The spectra of the specimens quenched from $T > 1200°C$ are particularly sharp, which represents an increase in the Fe magnetic ordering temperature and suggests a structural transformation in the sample. It is found that the valence state of Fe changes from 3.36 to 3.04, suggesting that the Fe valence states change from a mixture of Fe$^{3+}$ and Fe$^{4+}$ to about 96% Fe$^{3+}$ as quenched at 1500°C. The change in the valence state of Fe results in an increase in both the hyperfine field and magnetic moment for the quenched samples. The oxygen content $\delta$ changes from 0.02 to 0.18 per formula after quenching at 1500°C. The oxygen contents $\delta$ obtained from Mössbauer spectra are again consistent with those obtained from the neutron diffraction refinements.

Since the isomer shift provides direct information about the electron density at the nucleus, we have attempted to derive information about the valence states of Fe ions in these compounds. By using the average IS of the quenched La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$, the average valence states of the Fe is shown in Figure 3. It is found that the valence state of Fe changes from 3.36 to 3.04, suggesting that the Fe valence states change from a mixture of Fe$^{3+}$ and Fe$^{4+}$ to about 96% Fe$^{3+}$ as quenched at 1500°C. The change in the valence state of Fe results in an increase in both the hyperfine field and magnetic moment for the quenched samples. The quadrupole splitting (QS) of the Fe ions decreases as the quench temperatures increasing ($T > 1200°C$), which indicates a crystal symmetry transformation from distorted-cubic to cubic, and shows nearly no splitting when the cubic perovskite structure is attained.
Conclusions:

Neutron diffraction and Mössbauer spectroscopy were used to characterize the La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$, a cathode candidate for the intermediate temperature solid oxide fuel cells. Crystal structure, magnetic moment and Fe valence state were studied on the specimens quenched from 700°C to 1500°C. It was found that a lower symmetry trigonal space group P-3C1 gives improved fits to the data including the matching of a peak not fitted in the R$\bar{3}$c symmetry. A significant lattice distortion from rhomboedral to cubic was observed in the sample quenched from $T > 1200^\circ$C. Average Fe valence state and saturated magnetic moment are $\sim 3.04$ and 3.7$\mu$B respectively for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ quenched from 1500°C, indicating that $\delta$ is $\sim 0.2$. In the specimen without quenching, average Fe valence state and low temperature magnetic moment are $\sim 3.4$ and 2.4$\mu$B and the fraction of Fe$^{3+}$ is $\sim 60\%$, therefore $\delta$ is $\sim 0$, which indicates a full oxygen occupancy.

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References:

Figure 1. Neutron diffraction of La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ quenched from 1500°C. The inserted figure is the low angle part of the sample without quenching.

Figure 2. Lattice parameter of La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ quenched from various temperatures.
Figure 3. Plot of Fe average valence state and fraction of Fe$^{3+}$ and Fe$^{4+}$ in La$\textsubscript{0.60}$Sr$\textsubscript{0.40}$FeO$_{3-\delta}$ quenched from various temperatures.
Appendix I

“Determination of Oxygen Deficiency and Simulation of Conductivities – \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta} \)”

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Abstract

Oxygen content (3-δ) for La₀.₆₀Sr₀.₄₀FeO₃-δ was determined by analyzing measurements of powder neutron diffraction and Mössbauer spectroscopy. A full stoichiometry (δ ~ 0) for La₀.₆₀Sr₀.₄₀FeO₃-δ without quenching and δ ~ 0.2 for the specimen quenched from 1500°C were determined by Rietveld refinement of neutron diffraction results, which simultaneously resolves the magnetic moments. The saturated magnetic moments (measured at 10K) provided a direct determination of the ratio of Fe³⁺ over Fe⁴⁺, which was also measured by Mössbauer spectroscopy. Oxygen content was thus determined from the ratio of Fe³⁺/Fe⁴⁺. Oxygen vacancy concentration was considered in the determination of the total carrier concentration, which resulted in a maximum conductivity for La₀.₆₀Sr₀.₄₀FeO₃-δ around 600°C in air.

1.0 Introduction

Electrical conductivity and oxygen deficiency are two of the critical factors for the materials used as oxygen separation membranes and solid oxide fuel cell cathode. Ferrite compositions are currently being widely used, particularly the perovskite-type ferrites, La₁-xSrₓFeO₃-δ (LSF) [1-3]. The perovskite-type oxides encompass a large variety of chemical compositions that contribute to their diverse and unique properties, in which La₀.₈₀Sr₀.₂₀FeO₃-δ [2] and La₀.₆₀Sr₀.₄₀FeO₃-δ [3] are of particular interest because they possess low cathode overpotentials in solid oxide fuel cells. The low cathode overpotential results from fast oxygen reduction, high oxygen ion diffusion and/or high oxygen vacancy concentration, which are also important for oxygen transport through dense membranes. Hence, these oxides find applications for oxygen reduction in syngas reactors or solid oxide fuel cells. These applications require a sufficient oxygen vacancy concentration that allows oxygen to dissociate and transport in the cathodes or membranes. Therefore, it is of great importance to determine oxygen vacancy level and to understand the mechanism for the oxygen vacancy generation. Thermogravimetric analysis (TGA) is a directly way of measuring oxygen vacancy level, which has been widely used to characterize oxygen vacancy concentration, with significant success on several compounds, such as mangnites [4], ferrites and cobaltites [5]. The drawbacks for TGA are equilibrium time and base line for the stoichiometric compositions. Thus, other indirect techniques have been utilized in literature, including chemical titration [6], Columbic titration and neutron diffraction [7]. Chemical titration resolves a fraction of different valence state, for example Fe³⁺ and Fe⁴⁺, from which oxygen content can be calculated based on charge balance in the compound. In principle, other experiments that are able to distinguish the fraction of Fe³⁺ and Fe⁴⁺ can be used to indirectly determine oxygen content.

The most advantageous merit for neutron diffraction when determining oxygen content is that the cross section for coherent scattering of neutrons by atoms is a nuclear property, which is not dependent on the number of electrons [8]. Thus, neutron scattering is sensitive to light atoms (such as oxygen) and oxygen content can be determined by coupling powder neutron diffraction with Rietveld. Moreover, neutron has a magnetic moment, which allows us to study the LSF series that exhibit anti-ferromagnetic ordering [7]. Previous results [7] showed that the room temperature magnetic moment was a function of oxygen content in reduced LSF specimens. The unit cell volume (which may be determined either by neutron or x-ray diffraction) is a potential probe of the vacancy concentration. On the other hand, collection of full neutron data sets allows
all three determinations to be carried out simultaneously, as the refinement adjusts all of these quantities in fitting the measured data. Mössbauer spectroscopy has been employed to successfully study Fe valence state in LSF, from which the fraction of Fe$^{3+}$ and Fe$^{4+}$ can also result in oxygen content. These techniques are essentially independent, which therefore can provide cross checks on the oxygen content. It is the intent of this paper to determine oxygen contents of La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ quenched from 700 – 1500°C by neutron diffraction and Mössbauer spectroscopy. A simply defect chemistry model was used to simulate the electronic conductivity for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ by considering the compensation between majority carrier (holes) and oxygen vacancies.

2.0 Experimental

The modified Pechini method was used to synthesize nanocrystalline particles, followed by calcining, uni-axially pressing and sintering. Electrical conductivity was measured by a four-probe method in the temperature range 150 – 1000°C. Neutron diffraction was performed at room temperature on the sintered and quenched specimens. A conventional constant accelerated driver was used to measure Mössbauer spectra with a $^{57}$Co as the source. The spectrometer was calibrated by using $\alpha$ - Fe at room temperature.

3.0 Results and Discussion

3.1 Determination of oxygen vacancy concentration

Figure 1 shows a plot of 3-\(\delta\) vs. quenching temperature for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$. A datum of ~3 for the specimen without quenching is shown in Figure 1 as well. Oxygen content was directly determined from refinements of neutron diffraction results. A value around 2.8 was observed for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ quenched from 1500°C, whereas full stoichiometry (\(\delta \sim 0\)) was determined for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ without quenching. From charge neutrality principle, Fe is in the valence state of 3+ for La$_{0.60}$Sr$_{0.40}$FeO$_{2.8}$ and Fe exhibits an average valence state of 3.4 for La$_{0.60}$Sr$_{0.40}$FeO$_{3.0}$. Therefore, the magnetic moments are expected to be different for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ with various $\delta$ values. The magnetic moment and oxygen content can be determined independently by Rietveld refinement of neutron diffraction data. A strong correlation between oxygen deficiency and magnetic moment has been observed, which indicates that this technique is powerful and fast to resolve the oxygen content in perovskite type ferrites. The saturation moments for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ were determined from neutron powder diffraction measurements at 10K, as a function of 3-\(\delta\). In this study, the highest deficiency (\(\delta = 0.2\)) corresponds to a nearly pure Fe$^{3+}$ state and in the full stoichiometric (\(\delta = 0\)) composition, the fraction Fe$^{3+}$ is 60% and that of Fe$^{4+}$ is 40%. If the saturation magnetic moments for these two ions are significantly different, then a determination of the saturation moment (measurement at low temperature) can provide a direct determination of the ratio of the two species and, thus, of the stoichiometry. The magnetic moment for La$_{0.60}$Sr$_{0.40}$FeO$_{2.8}$ is $\sim 3.8 \mu B$, which is a typical moment for Fe$^{3+}$ in LaFeO$_3$ system. The magnetic moment for La$_{0.60}$Sr$_{0.40}$FeO$_{3.0}$ is $\sim 2.3 \mu B$ ($\sim 3.8 \mu B \times 60\%$). The magnetic moment is as expected, linear with vacancy concentration and can be used to determine oxygen content by direct crystallographic refinement.
There are a number of advantages in using the magnetic moment as a measure of the vacancy concentration. The uncertainty in magnetic moment is 2% at low vacancy concentration, decreasing to less than 1% when the moment is large. In addition, it is necessary to collect full data sets in order to accurately refine the vacancy concentration, while it is possible to use partial data sets including only the low angle region of the data and still extract accurate moment values. Thus, the vacancy concentration should be known, by this indirect determination, to a precision of 1% or 2% over the range of interest. Of course, at very high vacancy concentration, the direct determination will become more precise, while the magnetic measurements will be less so, due to saturation. This may be overcome by measuring at elevated temperature.

Oxygen deficiency can also be determined by Mössbauer studies. Because Mössbauer spectra of quenched samples show a rapid electron exchange between the Fe ions, an average valence state of Fe will be used to describe the Fe ions. Therefore, average IS and HF values have been used to study the valence state and hyperfine interaction in these compounds, from which the average Fe valence was achieved for each specimen. Oxygen content was then calculated, as shown in Figure 1.

Isomer shifts of the un-treated and 800 °C quenched samples are nearly what could be expected for valence states of Fe$^{3+}$ and Fe$^{4+}$. The relative ratio of Fe$^{3+}$ and Fe$^{4+}$ ions of the untreated sample obtained from relative areas of the Mössbauer spectra is 64:36, indicating a nearly zero oxygen vacancy in these compounds. The ratio of Fe$^{3+}$/Fe$^{4+}$ is 70:30 for the 800 °C quenched sample which indicates oxygen vacancies have increased in the compound. As the quench temperature becomes higher than 900 °C, the Fe$^{4+}$ spectrum disappears (Fe$^{4+}$ normally is non-magnetic with a single line). It is evident that the magnetic sextets become dominant and all peaks of the spectra become sharper when the quench temperature increases to 1300 °C. This indicates an increase in the Fe magnetic ordering temperature and suggests a structural transformation in the sample.

3.2 Simulation of electrical conductivity

The electrical conductivity is determined by the majority carrier concentration, hole hopping mobility, oxygen vacancy concentration and oxygen ion mobility. It is, therefore, very critical to experimentally determine these parameters and to develop a fundamental understanding the mechanisms of vacancy generation.

The total electrical conductivity, $\sigma$, follows Eq. (1)

$$\sigma = N \mu q$$  \hspace{1cm} (1)

where $\mu$ is the mobility, $q$ is the carrier charge and $N$ is the carrier concentration. Because of the much higher mobility of the electrons or holes than that of oxygen ions, the total conductivity in ferrites is dominated by hole conduction. The carrier concentration, $N$ is:

$$N = [\text{Sr}_{La}] - 2[V_{O}^{**}]$$  \hspace{1cm} (2)
The accurate determination of oxygen deficiency allows us to understand and simulate the electrical conductivities. Figure 2 illustrates a plot of the electronic conductivity as a function of temperature for La\textsubscript{0.60}Sr\textsubscript{0.40}FeO\textsubscript{3-δ} in air. A maximum conductivity was observed, which is similar to other p-type perovskite type conductors.

Oxygen vacancy concentration ([V\textsubscript{o}**]) is much less than the dopant concentration ([Sr\textsubscript{La}]) at relatively low temperature (T < 500°C), the electronic conductivity, therefore, can be repented as:

\[ \sigma = N \mu q = [Sr\textsubscript{La}] \mu q, \] (3)

The mobility term (\(\mu\)) in Eq. (1) is determined by the diffusion of the majority carriers in the lattice of sensor materials, which can be expressed as:

\[ \mu = \frac{\mu_0}{T} \exp\left(-\frac{E_h}{kT}\right) \] (4)

Therefore, plotting of ln(\(\sigma T\)) vs. 1/T in the low temperature region will resolve \(E_h\).

At high temperature (T > 600°C), the loss of oxygen generates oxygen vacancies, which compensate the major carriers (holes) and the total carrier concentration is then decreased (Eq. 2). The maximum conductivity resulted from the balance between decreasing the total carrier concentration and increasing the mobility. Therefore, there exists the highest conductivity around 600°C, which can be expressed as:

\[ \sigma = N \mu q = ([Sr\textsubscript{La}] - 2[V\textsubscript{o}**]) \mu q \]

\[ = [Sr\textsubscript{La}] \mu q - 2[V\textsubscript{o}**] \mu q \] (5)

The total conductivity can then be modeled by employing oxygen vacancy concentrations determined from neutron diffraction (Figure 2). When the T < 500°C,

\[ \sigma = \frac{1.76 \times 10^6}{T} \exp\left(\frac{-1983}{T}\right) \] (6)

and when T > 500°C,

\[ \sigma = \frac{1.76 \times 10^6}{T} \exp\left(\frac{-1983}{T}\right)(1 - 10^{-21} \times [V\textsubscript{o}**]) \] (7)

Conclusions:

Neutron diffraction and Mössbauer spectroscopy were used to determine oxygen deficiency for La\textsubscript{0.60}Sr\textsubscript{0.40}FeO\textsubscript{3-δ}. A full stoichiometry (\(\delta \sim 0\)) for La\textsubscript{0.60}Sr\textsubscript{0.40}FeO\textsubscript{3-δ} without quenching and \(\delta \sim 0.2\) for the specimen quenched from 1500°C were directly determined by
Rietveld refinement of neutron diffraction results. The saturated magnetic moments (measured at 10K) from neutron diffraction provided a determination of the ratio of $\text{Fe}^{3+}$ over $\text{Fe}^{4+}$ that was also measured by Mössbauer spectroscopy. Oxygen content was thus determined from the ratio of $\text{Fe}^{3+}/\text{Fe}^{4+}$, which was consistent with that from refinement. Oxygen vacancy concentration was considered in the determination of the total carrier concentration, which resulted in a maximum conductivity for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ around 600°C in air.

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References:

Figure 1. Oxygen occupancy ($3-\delta$) vs. quenching temperature for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$. A datum of ~3 for the specimen without quenching is shown as well.

Figure 2. Experimental and simulating conductivity vs. $1/T$ for La$_{0.60}$Sr$_{0.40}$FeO$_{3-\delta}$ as a function of temperature in air.
Appendix J

“Charge Disproportionation and Ordering in La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$”

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Abstract

The perovskite \( \text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3 - \delta \) was investigated by neutron diffraction, magnetic and Mössbauer spectroscopy measurements. \( \text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3 - \delta \) undergoes magnetic ordering at \( T = 190 - 200 \text{K} \) accompanied by charge disproportionation. Magnetic peaks due to charge ordering are observed below 200K. The charge ordering is gradually developed below 200 K along with a charge disproportionation, \( \text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+} \). \( \text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3 - \delta \) shows an antiferromagnetic structure at low temperature. Magnetic moments of about 3\( \mu_B \) and 1.3\( \mu_B \) were obtained from the neutron diffraction data refinement for \( \text{Fe}^{3+} \) and \( \text{Fe}^{5+} \) at 15K, respectively. These values are significantly lower than those reported by Battle et al. for \( \text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{2.98} \). Mössbauer spectra indicate that a full charge ordering might be reached below 20K with no \( \text{Fe}^{4+} \).

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I. INTRODUCTION

Perovskite compounds of the type RE$_{1-x}$A$_x$BO$_{3-\delta}$, where RE is rare earth, A is Ba, Ca or Sr, B is Fe, Mn, Co or Ni are of considerable importance, due to their interesting electronic, magnetic and catalytic properties [1–8]. Depending on their compositions, they show a variety of magnetic and electronic phenomena, including ferromagnetic, antiferromagnetic, charge and orbital ordering. Among them, charge ordering (CO) transitions have been found to occur in La$_{1-x}$Sr$_x$FeO$_3$ (x=2/3), using Mössbauer spectroscopy measurements [9]. Neutron powder diffraction on the same compound by Battle et al. [10] indicated a CO sequence of Fe$^{5+}$Fe$^{3+}$Fe$^{5+}$Fe$^{3+}$Fe$^{5+}$... along the body diagonal [111] with respect to the ideal perovskite structure. The magnetic moments were 3.6$\mu_B$ for Fe$^{3+}$, and 2.7$\mu_B$ for Fe$^{5+}$ at 50 K. A structural modulation accompanying the CO transition has been confirmed by electron microscopy [11]. Charge ordering is also observed in some other R$_{1/3}$Sr$_{2/3}$FeO$_3$ compounds with R=Pr and Nd [12–15]. The charge ordering normally was interpreted as the separation of a charge state into two different states as 2d$^n$=d$^{n-1}$+d$^{n+1}$, where n is an integer. Takano et al. [16] proposed a nonintegral oxidation state of iron in these materials as Fe$^{4+}$⇌Fe$^{4-\lambda}$+Fe$^{4+\lambda}$. Recently, J. Matsuno et al. [17] suggested that the charge disproportionation can be correctly described as 2d$^5$ L → d$^5$ L$^2$+d$^5$ rather than 2d$^4$ → d$^3$+d$^5$, where L denotes a hole in the oxygen 2p band. It has been shown that the charge disproportionation might be purely electronically driven and that the ordering of the oxygen holes plays an important role in La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ [18]. Although a neutron diffraction study has been reported for the La$_{1/3}$Sr$_{2/3}$FeO$_{2.98}$ compound at 50K and room temperature [10], no systematic study of the dependence of the crystal and magnetic properties of La$_{1/3}$Sr$_{2/3}$FeO$_3$ with temperature has been reported. Neutron diffraction can directly detect magnetic ordering and the structural modulation related to charge ordering; therefore it is of considerable interest to investigate the relationship among the structural, magnetic and charge ordering in this system.

In this study, we report on the structural and magnetic properties of La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ using data obtained from neutron diffraction, Mössbauer spectroscopy and magnetic mea-
measurements. The effect of temperature on the structural, magnetic properties and hyperfine interactions in this compound has been studied.

II. EXPERIMENTAL

The liquid-mix process was used to prepare La$_{1/3}$Sr$_{2/3}$FeO$_3$. An aqueous nitrate solution containing all the ingredient cations for each La$_{1/3}$Sr$_{2/3}$FeO$_3$ composition was prepared from reagent-grade metal nitrates or carbonates. The cation content of each individual metal salt was determined by conversion to the respective oxide. A viscous polymeric precursor formed, when a mixture of citric acid and ethylene glycol (in 1:1 molar ratio) was mixed with nitrate solution at about 75°C upon evaporation of water and heating at 250°C. The resulting porous resin intermediate was then pulverized and calcined at 800 °C for 6-8 h to yield oxide powders whose crystalline size was typically 50-500nm. The powders were pressed at 207 MPa to form a dense bar. The bar was sintered at 1000-1200 °C for 24 hours in air and slowly cooled to room temperature. Powder x-ray diffraction using Cu-$K_\alpha$ radiation indicated that the symmetry of the samples remained rhombohedral (space group R3c) at room temperature. The magnetization curves of the samples were measured using a SQUID magnetometer in a field of up to 6 T from 1.5 K to 300 K. The powder neutron diffraction experiments were performed at the University of Missouri-Columbia Research Reactor (MURR) using neutrons of wavelength $\lambda=1.4875$ Å. The data for each sample were collected over 24 h at 290 K between 2θ angles of 5 and 105 degrees on approximately 1g of fine powders placed in a thin wall vanadium container. Refinement of the neutron diffraction data was carried out using the FULLPROF program [19], which permits multiple phase refinement as well as magnetic structure refinements. The Mössbauer spectra were measured using a conventional constant accelerated driver with a $^{57}$Co (50 mCi) source in a Rh matrix. The spectrometer was calibrated using $\alpha$-Fe and the isomer shift (IS) relative to $\alpha$-Fe at room temperature.
III. RESULTS AND DISCUSSION

X-ray diffraction patterns of La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ powders were obtained at a scanning speed of 0.2°/min. The sample is single phase and the symmetry of the samples remains rhombohedral (space group R$\overline{3}$c). In order to study the temperature dependence on the crystal and magnetic structure, powder neutron diffraction was employed to distinguish the phase transition, and to determine the magnetic structure. Fig. 1 shows typical neutron patterns of the sample measured at different temperatures. At room temperature, all peaks of the pattern can be indexed by a unit cell $a=5.477$ Å and $c=13.397$ Å, space group R$\overline{3}$c in the hexagonal setting as reported by Battle et al. [10]. Below 200 K, there are three extra peaks appearing at about 6.38, 19.17 and 26.50°, which arise from the magnetic ordering. Accordingly, the nuclear structure was refined using space group R$\overline{3}$c from 10 K to room temperature. The lattice parameters of the La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ powders obtained from neutron diffraction data refinement at different temperatures are shown in Fig. 2. As can be seen from the curve, the lattice parameters $a$ and $c$ remain almost constant below 120K, and a fluctuation around 180 K is observed which corresponds to charge disproportionation and magnetic ordering. Above 200 K, the lattice parameters increase almost linearly. It is suggested that there is an abrupt change of lattice parameters due to the charge disproportionation and ordering. This indicates that the spin-lattice coupling becomes prominent at low temperature due to charge disproportionation and magnetic ordering. This may be the reason as to why the lattice parameters remain nearly constant in value below 200 K. We do not observed any structural distortion along with the charge ordering. This agrees well with Battle's results [10]. Theoretical calculations [17] have shown that lattice distortion is not necessary for charge disproportionation to occur in La$_{1/3}$Sr$_{2/3}$FeO$_3$. It is found that charge disproportionation is purely electronically driven and that the ordering of the oxygen holes plays an important role in the charge-disproportionated states of La$_{1/3}$Sr$_{2/3}$FeO$_3$ [18].

The magnetic peaks can be indexed using the same unit cell, but in a space group P$\overline{3}$c1 as used Battle et al. [10]. However, as the magnetic peaks appearing in the neutron
diffraction pattern showed the easy axis of magnetization to be in the basal plane, (in the xy plane of the structure rather than along the z-axis, thus removing the 3 symmetry) we refined the magnetic structure using space group P1, which provides more flexibility in refining the model. It is noticed that the symmetry of the crystal structure might be lower than R3c due to the distortion of the structure. Space group R3c can give reasonable refinement because of the small distortion of the crystal structure. The unit cell of the magnetic structure is the same as that of the crystalline structure, which has six iron atoms in the positions (0,0,0), (1/3,2/3,1/6), (2/3,1/3,1/3), (0,0,1/2), (1/3,2/3,2/3) and (2/3,1/3,5/6) with a charge sequence of Fe$^{5+}$Fe$^{3+}$Fe$^{3+}$Fe$^{5+}$Fe$^{3+}$Fe$^{3+}$.... In the refinement, the magnetic moments of the iron atoms were constrained as two groups (Fe$^{5+}$ and Fe$^{3+}$) to form an antiferromagnetic structure and the absolute values of the magnetic moments were kept the same for each group. The magnetic moments entirely lie in the basal plane. Several magnetic spin configurations were used to refine the magnetic structure. The magnetic spin configuration of 5+(↑)3+(↓)3+(↓)5+(↓)3+(↓)3+(↑) gives the lowest $\chi^2$ and the best refinement. The coupling between Fe$^{3+}$ and Fe$^{5+}$ is ferromagnetic; on the other hand the coupling between Fe$^{3+}$ and Fe$^{3+}$, and between Fe$^{5+}$ and Fe$^{5+}$ is antiferromagnetic. The data refinement shows that the intensity of the first peak at 6.38° depends on the Fe$^{3+}$ and Fe$^{5+}$ charge ordering and magnetic ordering, and the peaks at 19.17 and 26.50° arise from antiferromagnetic ordering at temperatures below 200K. The intensities of these three peaks decrease as the temperature increases. They disappear at temperatures between 186K and 194K. This is consistent with the magnetic ordering transition temperature [13,20], which is also confirmed by our magnetic measurements. The Néel temperature of the compound is about 190 K, which is a response to the charge disproportionation and ordering. The refined magnetic moments of Fe$^{3+}$ and Fe$^{5+}$ at different temperatures are shown in Fig. 3. The magnetic moment of Fe$^{3+}$ is about 3$\mu_B$ at 15K and decreases gradually to 1.7 $\mu_B$ at 180K, and the magnetic moment of Fe$^{5+}$ changes slightly from 1.3$\mu_B$ at 15K to 1.1 $\mu_B$ at 180K. Above 200K, both magnetic moments drop to zero. Our magnetic moments are smaller than those reported by Battle et al [10]. If the moments are fixed to their values, the
calculated first peak, which is not shown in their neutron diffraction pattern, mismatches significantly with the experimental data both in the P\textsubscript{3}c1 and P1 space groups. Thus it is possible that their exclusion of the first magnetic and charge ordering peak may have lead to higher magnetic moments in their refinement.

Fig. 4 shows the temperature dependence of the magnetization measured in a magnetic field of 5 kOe. A kink at about 180 K is found in the curve, corresponding to the Néel temperature of this compound [13,20]. A ferromagnetic component is observed in the curves. This might arise from a tilting of the magnetic moment of Fe in the magnetic structure. This has been observed in some antiferromagnetic systems, where a parasitic ferromagnetic component appears in an antiferromagnetic structure [21–23]. The appearance of a weak ferromagnetic moment is not unexpected in the space group when the magnetic moments are not parallel to the c-axis [24,25]. No magnetic impurity was detected in the neutron diffraction and Mössbauer spectra measurements.

Fig. 5 is the Mössbauer spectra of La\textsubscript{1/3}Sr\textsubscript{2/3}FeO\textsubscript{3−δ} measured at different temperatures. The hyperfine parameters of the spectra are listed in Table I. The hyperfine field and isomer shift are shown in Fig. 6. Using a least-squares computer program, two sets of Lorentzian sextet lines due to the Fe\textsuperscript{3+} and Fe\textsuperscript{5+} were fitted to the Mössbauer spectra at 20K. Another sextet due to the Fe\textsuperscript{4+} was used to fit the spectra from 80 to 200 K. There is a single line of the Fe\textsuperscript{4+} above 180K. The Mössbauer spectra consist of two single lines at, and above, 200K. The isomer shifts of the subspectra indicate that one is Fe\textsuperscript{3+} and the other Fe\textsuperscript{4+} at room temperature. The ratio of Fe\textsuperscript{3+}/Fe\textsuperscript{4+} is about 35:65 corresponding to the stoichiometry of La\textsubscript{1/3}Sr\textsubscript{2/3}FeO\textsubscript{2.99} at room temperature. The amount of Fe\textsuperscript{4+} decreases from 65% to 5% as the temperature decreases from room temperature to 80 K. The charge disproportionation appears below 200K, wherein the Fe\textsuperscript{4+}, Fe\textsuperscript{5+}, and Fe\textsuperscript{3+} valence states coexist. At 20K, the ratio of Fe\textsuperscript{3+} to Fe\textsuperscript{5+} is about 2:1 due to the complete charge ordering. The hyperfine field of Fe changes very slowly below the Néel temperature, and quickly drops to zero at 200K, a trend similar to that of the magnetic moments. This provides further evidence of charge disproportionation. There are some Fe\textsuperscript{4+} states appearing in the compound below
the Néel point which indicates charge ordering to be incomplete. This may be the reason that the charge ordering peak in the neutron diffraction pattern is very broad and exhibits asymmetric features.

Since Fe$^{4+}$ has very small magnetic moments at low temperatures, its presence in the compound decreases the average magnetic moment of Fe, and disturbs the charge ordering. It is found that charge ordering is sensitive to the homogeneity, defect, vacancy and chemical composition as well [26,27]. Sample was prepared with a conventional solid reaction method by Battle et al as compared to our liquid-mixing method sample, which will have different grain size, homogeneity, defects and oxygen vacancies. This may change the electron-electron interaction, magnetic interaction, and electron-lattice interaction in realizing charge ordering. This might be another reason why different magnetic moments have been observed in this system.

IV. SUMMARY

Based on neutron diffraction, Mössbauer spectroscopy and magnetic measurements, it is found that magnetic ordering and charge disproportionation appear at a temperature below 200K in La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$. However, charge ordering develops slowly along with the charge disproportionation. A fully charge ordering appears to occur below 20 K in polycrystalline La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$. We clearly observed a neutron diffraction peak around 6.38 degree due to the magnetic and charge ordering below 200 K. Further, magnetic moments of Fe$^{3+}$ and Fe$^{5+}$ are 3.0 and 1.3 $\mu_B$ at 15K.

V. ACKNOWLEDGMENTS

The financial support of the National Science Foundation for grant DMR-9614596, the Defense Advanced Research Projects Agency for grant DAAG 55-98-1-0267 and the support by DOE under DOE contract #DE-FC26-99FT400054 are acknowledged.
REFERENCES

### TABLES

**Table I.** Refinement parameters of La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ at different temperatures. x, y, z are the fractional position coordinates. a, c are the lattice parameters. V is the unit cell volume. B is the temperature factor. $\chi^2$ is $[R_{wp}/R_{exp}]^2$ where $R_{wp}$ is the residual error of the weighted profile.

<table>
<thead>
<tr>
<th></th>
<th>T</th>
<th>15K</th>
<th>80K</th>
<th>160K</th>
<th>180K</th>
<th>200K</th>
<th>RT</th>
</tr>
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<tbody>
<tr>
<td>a(Å)</td>
<td></td>
<td>5.4717(2)</td>
<td>5.4711(2)</td>
<td>5.4722(6)</td>
<td>5.4708(2)</td>
<td>5.4726(3)</td>
<td>5.4769(2)</td>
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<tr>
<td>V(Å$^3$)</td>
<td></td>
<td>346.39</td>
<td>346.35</td>
<td>346.71</td>
<td>346.46</td>
<td>346.97</td>
<td>348.03</td>
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<tr>
<td>O, 18e,x</td>
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<td>0.4780(2)</td>
<td>0.4775(2)</td>
<td>0.4770(4)</td>
<td>0.4783(2)</td>
<td>0.4793(4)</td>
<td>0.4816(7)</td>
</tr>
<tr>
<td>B(Å), Fe,6b</td>
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<td>0.43(5)</td>
<td>0.09(5)</td>
<td>0.36(4)</td>
<td>0.21(2)</td>
<td>0.23(4)</td>
<td>0.29(6)</td>
</tr>
<tr>
<td>B(Å), O,18e</td>
<td></td>
<td>1.26(5)</td>
<td>1.07(7)</td>
<td>1.20(1)</td>
<td>1.02(2)</td>
<td>1.08(2)</td>
<td>1.10(8)</td>
</tr>
<tr>
<td>B(Å), La(Sr),6a</td>
<td></td>
<td>0.48(4)</td>
<td>0.21(2)</td>
<td>0.51(5)</td>
<td>0.38(1)</td>
<td>0.34(3)</td>
<td>0.58(3)</td>
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<td>$\chi^2$(%)</td>
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<td>2.3</td>
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<td>2.0</td>
<td>4.5</td>
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</table>

**Table II.** The hyperfine field($B_{hf}$), isomer shift(IS), quadrupole splitting(QS), and relative intensity(Int.) of La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>T</th>
<th>$B_{hf}$</th>
<th>IS</th>
<th>QS</th>
<th>Int.</th>
<th>$B_{hf}$</th>
<th>IS</th>
<th>QS</th>
<th>Int.</th>
<th>$B_{hf}$</th>
<th>IS</th>
<th>QS</th>
<th>Int.</th>
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</thead>
<tbody>
<tr>
<td>$Fe^{3+}$</td>
<td></td>
<td>(K)</td>
<td>(mm/s)</td>
<td>(mm/s)</td>
<td>(%)</td>
<td>(T)</td>
<td>(mm/s)</td>
<td>(mm/s)</td>
<td>(%)</td>
<td>(T)</td>
<td>(mm/s)</td>
<td>(mm/s)</td>
<td>(%)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.258(1)</td>
<td>35</td>
<td>0.064(4)</td>
<td>65</td>
<td>38.9(2)</td>
<td>0.335(3)</td>
<td>0.002(3)</td>
<td>29</td>
<td>180</td>
<td>0.164(4)</td>
<td>47</td>
<td>23.2(2)</td>
</tr>
<tr>
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<td>0.322(2)</td>
<td>42</td>
<td>0.091(3)</td>
<td>58</td>
<td>130</td>
<td>0.367(4)</td>
<td>-0.022(1)</td>
<td>63</td>
<td>45.3(3)</td>
<td>0.173(4)</td>
<td>11</td>
<td>24.9(1)</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.387(1)</td>
<td>-0.026(3)</td>
<td>65</td>
<td>7.0(1)</td>
<td>0.193(2)</td>
<td>0.345(2)</td>
<td>5</td>
<td>50</td>
<td>25.7(3)</td>
<td>0.025(2)</td>
<td>0.032(1)</td>
<td>30</td>
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<tr>
<td></td>
<td>20</td>
<td>0.393(2)</td>
<td>-0.036(1)</td>
<td>67</td>
<td>26.6(1)</td>
<td>-0.035(2)</td>
<td>-0.016(1)</td>
<td>33</td>
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</tr>
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</table>
FIGURES

FIG. 1. Neutron diffraction patterns of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3-\delta$ at different temperatures. (In the first pattern, 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). *CO indicates the charge ordering peak.

FIG. 2. The lattice parameters of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3-\delta$ at different temperatures.

FIG. 3. The refined magnetic moments of $\text{Fe}^{3+}$ and $\text{Fe}^{5+}$ at different temperatures for $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3-\delta$

FIG. 4. The temperature dependence of the magnetization for $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3-\delta$

FIG. 5. The Mössbauer spectra of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3-\delta$ at different temperatures.

FIG. 6. The hyperfine fields and isomer shifts of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3-\delta$ at different temperatures.
Yang et al., Fig. 1
Yang et al., Fig. 2

Yang et al., Fig. 3
Yang et al., Fig. 4

\[ M \text{ (emu/g)} \]

\[ T_N', T_{CO} \]

\[ \text{La}_{2/3}\text{Sr}_{2/3}\text{FeO}_3 \]

\[ H = 5 \text{ kOe} \]
Yang et al., Fig. 5
Yang et al., Fig. 6
Appendix K

NATO
Advanced Research Workshop
“Mixed Ionic Electronic Conducting (MIEC) Perovskites for Advanced Energy Systems”
Keiv

Harlan U. Anderson, Xiao-Dong Zhou and Fatih Dogan
University of Missouri-Rolla
DEFECT CHEMISTRY OF MIXED IONIC/ELECTRONIC P-TYPE OXIDES

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Abstract: The p-type perovskite structure oxides are finding use in a number of energy related applications. In particular they are being used as cathodes in fuel cells as well as dense oxygen separation membranes. The defect concentration and defect mobility determine the electrical properties. Since both of these are dependent upon the operating temperature and oxygen activity, it is important to understand how an oxide equilibrates with its environment. In this paper, a defect chemistry model for the oxidation-reduction behavior of p-type perovskites is reviewed with formulations in the (La, Sr)(Cr, Mn, Co, Fe)O$_3$ system being used as examples.

Key words: (La, Sr)(Cr, Mn, Cr, Co)O$_3$ perovskite, oxidation-reduction, electrical conductivity, oxygen vacancies.
1. INTRODUCTION

The perovskite or pseudo-perovskite structure class of oxides is very important since many of them are utilized in electrochemical processes. The structure is basically cubic with the general formula of ABO$_3$ in which A, the large cation site, may be an alkali, alkaline earth, or rare earth ion, and B, the small cation site, a transition metal cation. The large cations are in 12 fold coordination with oxygen while the small cations fit into octahedral positions. Since these two sites are very different in size, the occupancy of these sites is determined primarily by ionic size rather than valency, so it is possible to substitute selectively for either the A or B ion by introducing isovalent of aliovalent cations. This gives the materials scientist an opportunity to alter the properties of a given oxide by substituting different cations onto either the A or B site. The main criteria which must be followed is the ionic radius of a substitution cation must be close (with ~15%) to a cation for which it substitutes without regard to valency.

In the early 1950's, Verwey and et al. (1) observed that when substitutions are made on to the perovskite lattice, if the valence of the substituting ion is different (i.e., it is aliovalent) from that required by the site, then the charge imbalance and overall charge neutrality will be maintained by the formation of electrons, holes or charged vacancies. The compensation process creates carriers which can take part in electrical conductivity. Thus, depending upon whether the basic oxide is a p- or n-type conductor, the substitution of either acceptors or donors, can increase or decrease the carrier concentration. This is very important because it has lead to a number of devices, such as NTC resistors, PTC resistors, electrodes for electrochemical devices, etc.

When a perovskite which contains transition metal ions on the B site is heated to a sufficiently high temperature that it can equilibrate with the ambient oxygen activity, reversible changes in the oxygen content occur as the oxygen activity is varied. This behavior occurs with both p- and n-type perovskites and represents a compensation mechanism in addition to that presented by Verwey and et al. (1). This can cause the neutrality condition to change from electronic to ionic or visa versa.

Thus to completely understand the defect behavior in the perovskite oxides which contain transition metal cations, it is necessary to include the equilibration reaction with the ambient temperature and oxygen activity in addition to the influence of aliovalent effects. This occurs with all perovsites, but for the sake of brevity, in this review only acceptor doped p-type oxides will be considered with appropriate examples included.

2. DEFECT CHEMISTRY

As noted previously, the perovskite oxides can be represented by ABO$_3$ where the charge related to the A and B sites is +6 with the valence of the B site cation ranging from +3 to +5. In the discussion here, both the A and B sites will be +3 which covers a number of the rare earth perovskites which are important for electrical conductivity and
magnetic applications. For simplicity, the following assumptions are made: 1) the A to B site ratio is one, with the A site occupied by a trivalent rare earth and the B site is occupied by trivalent transition metal ions: Cr, Fe, Mn, Co or mixtures thereof; 2) only fully ionized oxygen vacancies are present; 3) no defect association, 4) no interstitial defects and 5) a divalent acceptor ion, I, can substitute on either the A or B site with the A to B ratio remaining unity. These assumptions can be quite restrictive, but generally nonconformity to them does not affect the general predicted behavior, for example, when defect association occurs, carrier concentration will be altered, but the overall predicted behavior still is valid.

Based on these assumptions and that p-type disorder prevails in nonstoichiometric ABO₃ allows the development of a defect chemistry model. The procedure which is used is to: 1) list the basic defect reactions which can occur: intrinsic, stoichiometric, oxygen excess and oxygen deficient; 2) write the overall neutrality relation and 3) combine the resulting equations to yield a relationship which can be solved for particular temperature and oxygen activity regimes.

The equilibria of interest [using Kröger-Vink (2) notation]:

the Schottky defect reaction,

\[ nil = V_A^{\bullet\bullet} + V_B^{\bullet\bullet} + 3V_O^{\bullet\bullet} \]

\[ K_s = [V_C^{\bullet\bullet}]^2 [V_O^{\bullet\bullet}]^3 \]  

(1)

the intrinsic electronic defect reaction:

\[ nil = e^+ + h^+ \]

\[ K_i = np = \exp\left( -\frac{\Delta G}{kT} \right) \]  

(2)

the oxygen excess reaction

\[ \frac{3}{2} O_2 = V_A^{\bullet\bullet} + V_B^{\bullet\bullet} + 3VO^{\bullet}_{O_2} + 6h^+ \]

\[ K_i = [V_C^{\bullet\bullet}]^2 p^{6} P_{O_2}^{-3/2} \]  

(3)

the oxygen deficient reaction:

\[ O^{\bullet}_{O_2} = V_O^{\bullet\bullet} + 2e^+ + \frac{1}{2} O_2 \]

\[ K_{V_{O^\bullet}} = [V_O^{\bullet\bullet}]n^{2} p^{6} P_{O_2}^{1/2} \]  

(4)
From relations plus the relation for electroneutrality;

\[ [I^+] + 6[V_{C}^{"}] + n = p + 2[V_{O}^{"}] \]  

(5)

the basis equations can be developed to give the overall behavior of the defects in ABO₃ as a function of temperature, oxygen activity and acceptor concentration. Two methods can be used to solve the resulting equations: 1) divide into regions of particular neutrality conditions and solve for that particular region or 2) do not use limiting conditions, but allow a computer to make a numerical solution to the overall equation using the total neutrality condition. In this discussion, only particular solutions will be considered. The results on the global solution are being reported elsewhere (3).

Since the details of the development of the expressions for the defect equations have been previously reported, so only the results are given here (4). Figure 1 illustrates how the defect concentrations change with oxygen activity over six regions of limited neutrality conditions. (assuming the temperature is high enough for the attainment of thermodynamic equilibrium). Table I (4) shows the predicted oxygen activity dependence for the six regions.

![Diagram showing defect concentration in acceptor substituted ABO₃ as function of oxygen activity at constant temperature. The B site is occupied by a transition metal ion.](image)

**Figure 1:** Defect concentration in acceptor substituted ABO₃ as function of oxygen activity at constant temperature. The B site is occupied by a transition metal ion.

**Table I.** Table of constant “m” in \(([V_{O}^{"}], n, p \propto pO_{2}^{m})\) (4)

<table>
<thead>
<tr>
<th></th>
<th>VI</th>
<th>V</th>
<th>IV</th>
<th>III</th>
<th>II</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>1/6</td>
<td>1/4</td>
<td>1/4</td>
<td>0</td>
<td>3/16</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>-1/6</td>
<td>-1/4</td>
<td>-1/4</td>
<td>0</td>
<td>-3/16</td>
<td></td>
</tr>
<tr>
<td>([V_{O}^{&quot;}]) decomposition</td>
<td>-1/6</td>
<td>0</td>
<td>~1/2</td>
<td>-1/2</td>
<td>-1/8</td>
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</tr>
<tr>
<td>Neutrality condition</td>
<td>([B_{p}^{\prime}] = n = 2[V_{O}^{&quot;}])</td>
<td>(2[V_{O}^{&quot;}] = [I_{RE}^{\prime}])</td>
<td>(p = [I_{RE}^{\prime}] - 2[V_{O}^{&quot;}])</td>
<td>(p = [I_{RE}^{\prime}])</td>
<td>(p = 3[I_{I}^{\prime}] + 3[I_{B}^{\prime}])</td>
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</table>

**HIGH \([V_{O}^{\"}]\) REGIONS**
During the last 20 years, the electrical conductivity and oxygen vacancy concentration for a number of transition metal containing perovskite structure oxides have been investigated in our laboratory. The following examples represent several of the systems which have been studied. The overall results show that the overall defect chemistry is well represented by the simple approach shown above. Most of the exceptions result from defect association or by disproportionation reactions which are typical in Mn containing systems.

3. EXAMPLES

3.1 Chromites

Examples of the rare-earth chromites are contained in the studies by Flandermeyer (5) and Carini (6) who studied La(Mg,Cr)O₃ and (Y,Ca)CrO₃ respectively. Figures 2 and 3 show examples of their data which show that the simplified model fit their results quite well. In Flandermeyer's data, evidence of defect association was noted by Van Roosmalen et al. (7) who improved the fit of the experimental data to model by including association. This points out the importance of defect association, however, the simplified model described the overall behavior quite well.

![Figure 2: Moles oxygen weight loss per mole samples as a function of log PO₂ and dopant content at 1255°C. (5)](image)

![Figure 3: Log conductivity vs. Log PO₂ for Y₀.85Ca₀.15CrO₃ at various temperatures. The solid lines are calculated. (6)](image)
3.2 Manganites

Figure 4 shows results for \((\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3\) (8) which are typical for the Mn containing perovskites. The simplified model appears to fit the experimental data quite well. However, the model predicts a constant oxygen stoichiometry of 2.9 in region IV which does not occur. In order to account for the observed behavior, both Kuo (8) and Stevenson (9) had to invoke thermally excited disproportionation of Mn\(^{3+}\) to Mn\(^{4+}\) and Mn\(^{2+}\).

![Graph showing oxygen weight loss vs. Log PO\(_2\) for various Sr-dopant levels. The solid lines are calculated from model.](image)

Figure 4: Moles oxygen weight loss per mole sample vs. Log PO\(_2\) for various Sr-dopant levels. The solid lines are calculated from model. (8)

3.3 Ferrites

Compositions within the \((\text{La},\text{Sr})(\text{Fe},\text{Co})\text{O}_3\) family have been extensively studied because of their mixed electronic and ionic conductivity. Typical behavior of this system is shown in figures 5 and 6. (10) This family of compositions also follows the simplified model quite well, but as was the case of the manganites, region IV was not observed. This is probably due to continuous reduction of the cations on the B site. It is interesting to note that for most of the compositions, dissociation does not occur until the oxygen stoichiometry reaches the 2.4-2.7 range. This suggests that for the 40% Sr composition, oxygen vacancy content as high as 20% can be expected. This is the reason that high oxygen ion conductivity is observed.

![Graph showing oxygen content (moles) of \(\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3-x\) as a function of oxygen activity and Sr content (moles) at 1200\(^\circ\)C.](image)

Figure 5: Oxygen content (moles) of \(\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3-x\) as a function of oxygen activity and Sr content (moles) at 1200\(^\circ\)C. (10)
Figure 6: Electrical conductivity of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ as a function of oxygen activity equilibrated at different temperatures. (10)

4. CONCLUSIONS

a. A defect chemistry model for the oxidation-reduction behavior of p-type perovskite oxides which uses simplified neutrality conditions was developed.
b. The model explains the electrical conductivity of the chromites.
c. In order to explain the behavior of Mn containing perovskites, both site percolation and thermally activated disportionation of 2Mn$^{3+}$→Mn$^{2+}$ + Mn$^{4+}$ must be added to the model.
d. The (La,Sr)(Co,Fe)$_3$ system follows the model and becomes very oxygen nonstoichiometric (10-30%) prior to dissociation.

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REFERENCES

Appendix L

“Low Temperature Processing of Thin Film Electrolyte for Electrochemical Devices”

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Low Temperature Processing of Thin Film Electrolyte for Electrochemical Devices

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ABSTRACT

Thin film electrolyte processing has become a key issue for the development of electrochemical devices such as Solid Oxide Fuel Cells (SOFCs), since reducing resistance of the electrolyte is critical to enhance cell performance. In this study, yttrium stabilized zirconia (YSZ) thin film with thickness of 1-2 μm electrolyte has been prepared on dense and porous substrates using a combination of colloidal suspensions and polymer precursors at annealing temperatures < 1000°C. Use of processing temperatures < 1000°C minimizes interfacial reactions between electrolyte and anode/cathode materials. The conductivity of the thin film annealed at 900°C was measured and found to be the same as that of bulk YSZ and the processing temperature to obtain such conductivity was as low as 400°C.
Solid oxide fuel cells (SOFCs) are considered as being one of the important future energy sources [1]. Before these cells can become widely utilized, there are several problems that need to be solved. Among them are the interfacial reactions which occur between the anode/cathode and electrolyte which occur due to high temperature processing cause losses in the cell and limit performance of cell. There have been a number of reports which suggest that the solution to this problem if to introduce an interlayer to prevent the interfacial reaction [2]. On the other hand, this note offers perhaps a simpler solution, which is to decrease the processing temperature of the cell.

A low temperature thin film processing method (under 1000°C) for preparing dense, nanocrystalline electrolyte materials such as doped ZrO₂ and CeO₂ has been reported which uses the polymer precursor spin coating technique [3, 4]. The thickness of these films is <1 micron so the resistance of the electrolyte is low, thereby enhanceing the cell performance [5]. Because of these facts, low temperature thin film electrolyte processing has become a key issue for the development of SOFC. However, to apply the polymer precursor spin coating technique to SOFCs, there are several problems such as the difficulty for obtaining thick film above 1μm and limitation of application to only dense substrates. In this study, a combination of colloidal suspensions and polymer precursors has been used to prepare coatings on both porous and dense substrates which yield 1-2 μm thick dense films of yttrium stabilized zirconia (YSZ) film after annealing at temperatures < 1000°C.

The dense YSZ films were prepared by coating the surface of both dense sapphire and (La, Sr)MnO₃ porous substrates with a colloidal suspension which contained YSZ particles (size ~ 100 nm). After which, a polymer precursor solution which produces
YSZ upon heating, impregnated the colloidal coating. (The process is illustrated in Fig. 1). After drying, the composite coating is heated to temperatures < 400°C to convert the polymer phase to YSZ. A dense film can be obtained after a series of applications of the polymer precursor (the number of applications depends upon the solids content of the polymer precursor and the porosity of the colloidal film.) For the preparation of the YSZ polymer precursor, the details were discussed elsewhere [6]. Details of the preparation of the composite are withheld, due to a patent application.

Figure 2 shows SEM images (Hitachi S4700) of a YSZ film on a sapphire substrate for different annealing temperatures (400 and 950°C). As can be seen, the film thickness is around 1.5 μm, and YSZ particles are surrounded by a nanocrystalline continuous dense YSZ layer introduced by the polymer precursor. After annealing at 900°C, it is observed that the densification of continues in the YSZ layer and a dense nanocrystalline grain structure (100 ~ 200 nm) develops. One of advantages of the colloidal-polymer method is shown in Fig. 3. Figure 3 shows SEM images of a YSZ film on a porous substrate (annealing temperature = 900°C). This is a continuous defect-free dense YSZ layer of thickness ~ 2 μm. The thickness of the film can be easily controlled from 0.5 – 20 μm by changing the YSZ concentration in the YSZ colloidal suspension.

The electrical conductivity of the resulting YSZ films was studied using a Solartron 1260 frequency response analyzer with a 1296 Interface. Silver paste was used as electrodes and measurements were conducted in air over the temperature range from 400 to 800°C. The electrical conductivity of YSZ film (annealed 900°C) were calculated and shown in Fig. 4 as a function of temperature along with the values from the literature [7]. As can be seen, the conductivity of the films are close to that reported for bulk YSZ,
which shows the quality of the film prepared at low temperature. From these results, the area specific resistance of this YSZ thin film with 1.5μm thickness can be estimated and found to be 0.11 Ωcm² at 600°C, 0.6 Ωcm² at 500°C. Figure 5 compares the electrical conductivity of YSZ film prepared at 400°C by this technique to that using the polymer precursor process by itself [6] and dense YSZ prepared by the conventional tape cast technique, as a function of annealing temperature. For the tape cast technique, the same YSZ powder was used as that used to prepare the colloidal suspension. As can be seen, the annealing temperature needed to obtain the conductivity observed for dense YSZ depends upon the processing techniques with that required for colloidal-polymer method being the lowest at 400°C. Application of the colloidal-polymer method to other electrochemical devices can be expected to bring significant improvement of their performances.

Reference


Figure Captions

Figure 1: The schematic diagram of colloidal-polymer process.

Figure 2: SEM images of YSZ thin film on dense sapphire substrate annealed at (a) 400°C (b) 900°C.

Figure 3: SEM images of YSZ thin film on porous substrate annealed at 900°C (a) cross section (b) surface.

Figure 4: The electrical conductivity of the YSZ thin film on dense sapphire substrate annealed at 900°C.

Figure 5: The electrical conductivity of the YSZ thin film as a function of annealing temperature along with results from several processing techniques.
Fig. 2

(a) Annealing temperature 400°C.

(b) Annealing temperature 800°C.
(a) Cross section

(b) Surface

Fig. 3
Processing and characterization of yttrium-stabilized zirconia thin films on polyimide from aqueous polymeric precursors

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Abstract

Low-temperature deposition of dense, nanocrystalline yttrium-stabilized zirconia (YSZ) thin films on polyimide (PI) substrates is illustrated using an aqueous polymeric precursor spin-coating technique. The polymeric precursor uses low-cost materials, is water-soluble and the viscosity and cation concentrations can be easily adjusted in order to vary the film thickness from 0.02 to 0.3 μm. Due to the use of water as the solvent in the YSZ precursor and the hydrophobic nature of the PI surface, surface modification processes were utilized in order to improve the wetting characteristics. Surface modification of PI substrates using wet chemical and oxygen plasma techniques led to a decrease in the precursor contact angle, and ultimately allowed for uniform film formation on both bulk and thin film PI substrates. Scanning electron microscopy, transmission electron microscopy and UV/Vis absorption illustrate that near full-density nanocrystalline thin films of YSZ can be produced at temperatures as low as 350 °C. Thermogravimetric analyses illustrate that the PI substrate does not undergo any weight loss up to these temperatures.

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Keywords: Polyimide; Yttrium-stabilized zirconia; Polymeric precursor

1. Introduction

Polyimides (PI) are frequently used in microelectronic applications due to their high thermal stability, good mechanical properties and ease of processing. They are frequently used in circuit boards and multichip modules as well as insulators for pulsed power applications. Polymers coated with thin film materials are being used more frequently in capacitors, thermal barrier protection [1], ferroelectric liquid crystals, solar cells [2,3], flexible and transparent electronic conducting substrates [4], as well as in nonlinear optical applications. Processing of thin films on polymeric substrates can be difficult due to the temperatures needed in order to achieve the desired properties of the film. These processing temperatures can exceed the glass transition temperature or result in pyrolysis of the polymer substrate. PI has a glass transition temperature of approximately 400 °C, and thus increases the range of available processing temperatures.

PI surfaces are inherently hydrophobic and also have low adhesion strength with metallic and ceramic films. Thus, several surface modification techniques have been developed in order to improve the wetting characteristics and adhesion strength between PI and inorganic films. Chromic and perchloric acids were used [5] in order to increase the bonding strength between PI and epoxy and PI and copper thin films. The wetting angle of water on the PI surface changed from 82° to 55° and the adhesion strength was increased approximately twofold.

Deposition of other organic groups onto PI substrates also has been shown to increase the wetting characteristics and adhesion strength to inorganic films. Amino and cyano compounds have shown a large increase in the adhesion strength between PI and inorganic films [6–8]. In particular, plasma polymer deposition of acrylonitrile onto PI increases the adhesion strength of copper films by 4.3 times as compared with untreated PI. ArF laser and high fluence UV irradiation of a PI thin film in air have also been shown to greatly improve...
the wetting characteristics of water on PI [9]. The water contact angle changed from 45° to less than 10° following exposure to an ArF laser fluence of 40 mJ/cm² and subsequently treating with water.

Radio frequency oxygen plasma surface modification of PIs has been studied extensively [10–13]. It was shown [11] that the water contact angle of plasma-treated PI changes contact angle from 70° to less than 10° after a treatment time of 15 s. Surface modification has also been illustrated using a wet chemical technique utilizing strong bases such as NH₄OH, NaOH or KOH [14,15]. The strong bases react with an imide functional group to open the imide ring, resulting in amides and carboxylate salts. It has been shown that the water contact angle changes from 38° to 5° upon reaction of the PI with the strong bases.

After modification of the PI surfaces, many different techniques have been used in order to form ceramic films on these substrates. SiO₂ thin films were produced on PI using a sol–gel dip coating technique [16]. Reactive evaporation has been used to produce ITO films on modified PI [4]. Magnetron sputtering has been used in order to produce thin ZrO₂ films on RF oxygen plasma modified PI substrates [1]. Unfortunately, none of these techniques are highly cost-effective in a manufacturing environment.

A polymeric precursor spin-coating technique has been developed in our laboratory for the production of thin (0.02–3 μm thickness) oxide films on a variety of substrates [17–19]. These precursors have many advantages compared with other techniques such as the low cost of the starting materials, high water solubility of the polymer and low processing temperatures (typically <300 °C). In this study, the polymeric precursor technique has been applied to the processing of dense oxide thin films on PI substrates.

2. Experimental procedures

Polymeric precursors for depositing ZrO₂:16%Y (yttrium-stabilized zirconia, YSZ) thin films were prepared using a solution chemistry outlined previously [17]. Reagent grade ZrOCl₂ and Y(NO₃)₃ were used as the cation sources. These cation salts were dissolved in distilled water and thermogravimetrically standardized to obtain the exact cation contents in the solutions. The cation solutions were weighed according to the appropriate molar ratio, and mixed with tartaric acid and ethylene glycol. The resulting solution was heated and stirred at 70 °C for approximately 40 h, resulting in a polymeric solution that was homogeneous, precipitate-free and had a viscosity of 90 cps (as measured with a Brookfield viscometer at 25 °C). Filtering the precursor through a 0.45-μm glass fiber filter (Whatman, Inc.) removed any foreign material from the precursor.

Surface modifications of Kapton (DuPont, Inc.) PI substrates were accomplished using a wet chemical technique. Substrates approximately 10 cm² were trimmed from a large sheet and placed in hot ammonium hydroxide diluted to various concentrations with distilled water. Treatment temperatures, time and the ammonium hydroxide concentration were varied and the precursor wetting angles qualitatively measured in order to achieve good wetting characteristics.

Thin films of PI were produced on glass substrates using a spin-coating technique. PI precursor resin (PIRL III, Brewer Science, Inc.) was spun on cleaned glass substrates at 3000 rpm for 45 s, followed by drying the resin at 170 °C on a hot plate for approximately 5 min. The films were then fully polymerized at 350 °C for 10 min. Surface modifications of the PI thin films were accomplished using an RF oxygen plasma system. The RF power and exposure time were varied and the precursor wetting angles qualitatively measured in order to achieve the best wetting characteristics.

Thin films of YSZ on the modified PI substrates were produced by spin-coating the polymeric precursor on both the Kapton substrates as well as the PI thin film/glass substrates following surface modification. The YSZ precursor solution was applied to the surface and spun at 4000 rpm for 30 s. The wet polymeric precursor was then dried at 70 °C for 1 h followed by pyrolysis and oxide formation at 350 °C for 5 min.

A vacuum-chuck hotplate (CEE, Brewer Science, Inc.) was used during the initial 70 °C precursor drying on the Kapton substrates to prevent curling of the flexible substrate. Curling occurs when the wet precursor film evolves its solvent (water in this precursor system) and thus undergoes a large volume change. This large shrinkage of a continuous thin film induces a strain on the coated side of the substrate, which causes the flexible substrate to deform.

Cross-sectional SEM (Hitachi S4700 and JEOL S570) of YSZ/PI structures was done in order to find the film thickness as well as any defects such as delamination. A Cary 5 UV/Vis/NIR spectrophotometer was used to characterize as-deposited films of YSZ on the PI/glass composites. The YSZ film refractive index was modeled from these data over the wavelength range 300–700 nm. Using the Lorentz–Lorenz relationship, the density of the film was determined as a function of annealing temperature.

TEM (Philips EM430) of the YSZ/Kapton composites was done to determine the film morphology and grain size. Selected area electron diffraction was done during the TEM investigation to find the crystallographic phase of the YSZ film. Cross-sectional TEM samples of the YSZ/Kapton films were prepared using a freeze-fracture technique. Samples were placed in liquid nitrogen and fractured into small slivers and mounted on slotted copper grids using silver epoxy.
Thermogravimetric analysis (TGA, Cahn TG-1) was done on the YSZ precursor, the Kapton substrate and a 70 °C dried YSZ film on Kapton over the temperature range 25–800 °C. TGA data reveal information about the amount of solvent in the precursor, the wt.% of the oxide in the precursor, the oxide formation temperature, the Kapton decomposition temperature, as well as the wt.% of YSZ on the Kapton substrate. Planar TEM and electron diffraction of YSZ films after pyrolyzing the PI substrate at 800 °C was also accomplished in order to determine the YSZ crystallographic phase, grain size and grain morphology.

Auger electron spectroscopy and sputter depth profiling were also utilized in the characterization of these films. A Physical Electronics Model 545 Auger electron spectrometer was used in the capturing of the spectra. An electron beam accelerated at 3 kV with a current of 1 mA was used in the generation of the electrons. The films were sputtered using a 3-kV Ar beam using a gun current of 15 mA. The sputtering depth was calibrated using a standard 100-nm-thick Ta2O5 film on Ta metal. These standard samples were alternately sputtered and spectra taken every 2 nm, until the oxygen signal was minimized. The total YSZ film thickness achieved using Auger depth profiling was compared with SEM images, and the differences were found to be negligible.

3. Results and discussion

Heating and stirring the YSZ precursor at 70 °C for approximately 40 h resulted in a viscosity of approximately 90 cps, which was subsequently cooled before spin-coating. Fig. 1 is a TGA curve (heating rate=2 °C/min) for the precursor over the temperature range 25–800 °C. Initially, excess water as well as polyethylene glycol (PEG) are pyrolyzed, and the sample loses mass until approximately 250 °C. A slight plateau is evident from 250 to 300 °C, indicating that the film has pyrolyzed the entire PEG and only the 3-d network of tartaric acid cross-linked with the ethylene glycol and metal cations are still present in the film. Above 300 °C, another weight loss is observed, which is the tartaric polymer backbone pyrolyzing and giving way to the oxide. All of the organic material is removed from the precursor above 400 °C, leaving only the oxide behind. From the masses of the final oxide and starting precursor, a weight loss of 95% has been observed. As also seen in Fig. 1, the Kapton substrates begin to lose mass at temperatures greater than 450 °C. Thus, processing temperatures greater than approximately 400 °C (near the polymer glass transition temperature) should not be used.

Surface modification of the Kapton substrates using 1 M NH4OH in distilled water was done at 70 and 90 °C, as outlined previously. It was found that continuous films of the YSZ precursor could be formed on surface-modified substrates after reacting for 55 and 30 min, respectively. Similarly, the PI thin film on glass structure exhibited good precursor wetting characteristics following oxygen plasma treatments for 15 s at 300 W or 40 s at 150 W. Both surface treatment techniques illustrate similar results to previous investigations of wetting by water on PI following strong base and oxygen plasma surface treatments [11,14].

After a continuous film of YSZ precursor was formed on the modified substrates, the structures were allowed to dry. After the film had fully dried, the YSZ/Kapton structure was pyrolyzed thermogravimetrically in order to determine the difference between the burnout temperatures of the film and the substrate. The TGA curve of
the YSZ/Kapton composite (Fig. 1) illustrates that the YSZ film pyrolizes at temperatures lower than the substrate, thus allowing for processing of these films on PI substrates.

Although the YSZ precursor formed a continuous film on the surface of the PI and pyrolized before the substrate, the microstructural integrity of the structure should be characterized. Fig. 2 is a cross-sectional SEM image of a YSZ/Kapton composite fracture section. The composite was produced after modifying the substrate with 0.5 M NH₄OH at 70 °C for 30 min, depositing two layers of YSZ and annealing at 350 °C for 2 min after each deposition. As can be seen from this image, the YSZ film is 0.5 µm thick and there is no significant delamination between the YSZ and the Kapton.

Fig. 3a is a cross-sectional TEM image of a YSZ film on a Kapton substrate after annealing at 350 °C. As can be seen from this image, the film appears dense and has an average grain size of approximately 5 nm. Fig. 3b is a selected area diffraction pattern of the YSZ film cross-section. Indexing of the diffraction pattern rings near the transmitted spot is difficult due to the diffuse rings. Indexing the outer rings, however, matches well with fluorite-structured YSZ. These diffuse rings are due to the broadening associated with the nanocrystalline grain size of the YSZ film, a phenomenon which has been observed in both X-ray and electron diffraction [17].

In order to determine more exactly the crystallographic phase of the film, the YSZ remaining in the TGA crucible after annealing at 800 °C was placed on a 200 mesh copper TEM grid. Fig. 4a is a bright-field TEM image of the YSZ film after annealing at 800 °C. As can be seen, the YSZ grains grow from 5 nm at 350 °C.
(Fig. 3a) to approximately 35 nm at 800 °C. The film does not appear fully dense due to the thermal shock of the film upon imaging with a 300-kV electron beam in the TEM. Fig. 4b is a selected area diffraction pattern of the film in Fig. 4a. The pattern lines are much less diffuse than that in Fig. 3b, again illustrating the grain size impact on the diffraction characteristics.

UV/Vis transmittance spectra of the PI film/glass and YSZ/PI film/glass are shown in Fig. 5. The composite transmits greater than 90% from 500 to 700 nm, followed by absorption due to the PI at approximately 450 nm. The YSZ/PI film/glass transmittance spectra shows transmittance in the 80% range at 700 nm. The difference in the transmittance between the PI and the YSZ/PI is due to the reflection losses at the air/YSZ and YSZ/PI interfaces. Using the method described in detail by Heavens [20], the refractive index of the YSZ film can be calculated, given the refractive indices of the glass and PI materials, and assuming near zero extinction coefficient at the measured wavelength (633 nm in this case).

This is a good approximation due to the negligible absorption by the PI and YSZ (bandgap 5.9 eV) at this wavelength. Scattering due to the grain size of the YSZ film is highly unlikely because, according to Rayleigh scattering statistics, the loss in intensity is calculated to be 10^-9, and does not nearly account for the observed change in intensity. In order to account for the change in intensity due to scattering, the defect size must be on the order of 0.5 μm. As is evidenced in the field-emission SEM micrograph in Fig. 6a, there are no significant scattering sites of this size in the YSZ film. No delamination defects that may contribute to scattering losses are evident in the fracture cross-sectional FESEM image of the YSZ/PI/glass structures (Fig. 6b).

Ultimately, using the thickness of the YSZ film obtained from this SEM micrograph, the YSZ refractive index was calculated to be 2.12. The density of the YSZ film could then be calculated from the theoretical refractive index (zirconia = 2.2 [21]) and using the Lorentz–Lorenz relationship [22,23]. The optical density of the YSZ film is thus calculated to be 95% theoretical after processing at 350 °C.

Fig. 7 shows the results of the Auger electron spectroscopy depth profiling study for a single YSZ film deposited on the PI substrate, followed by annealing at 350 °C. A small amount of carbon is present in the YSZ film. This can be due to either incomplete pyrolysis of the polymer compound, which is unlikely from the TGA data, or due to contamination within the Auger system. The depth profile shows the change in Zr/C.

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**Fig. 5.** UV/Vis transmittance spectrum of as-deposited PI/glass and 0.5-μm YSZ/PI/glass composites. Both structures are highly transparent.

**Fig. 6.** Field emission SEM images of a YSZ/PI/glass structure (a) as-deposited surface and (b) cross-sectional fracture surface annealed at 350 °C. The YSZ film is approximately 0.3 μm thick and no delamination or cracking is observable.
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