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LIST OF ACRONYMS

NSLS	National Synchrotron Light Source
ACS	aqueous combustion synthesis
BET	Brunauer-Emmett-Teller
BSE	backscattered electron
DAQ	data acquisition unit
DRIFT	diffuse reflectance infrared spectroscopy
DTA	differential thermal analysis
EMF	electromotive force
K	equilibrium constant
KBr	potassium bromide
LFO	lanthanum ferrite, LaFeO_3
LMO	lanthanum manganite, $\text{LaMnO}_{3+\delta}$
MS	mass spectrometer
R	universal gas constant
RE	reference electrode
RTD	resistance temperature detector
SE	sensing electrode
SEM	scanning electron microscope
SHS	self-propagating high-temperature synthesis
T	temperature
TPB	triple phase boundary
TGA	thermogravimetric analysis
TPD	temperature programmed desorption
TPR	temperature programmed reaction
UHC	unburned hydrocarbons
VCS	volume combustion synthesis
XRD	X-ray diffraction
YSZ	yttria stabilized zirconia

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1. EXECUTIVE SUMMARY

Remarkable progress in nanotechnology has led to the development of new classes of materials with unprecedented control of structure, composition, defects, and resulting properties. A range of multifunctional ceramics, potentially applicable to high-temperature sensors, have been produced using templated synthesis and self or directed assembly. This bottom-up approach has also enabled production of hierarchical architectures not possible with traditional ceramic processing methods.

This project developed a robust, tunable, hierarchical nanoceramics materials platform for industrial process sensors in harsh-environments. Control of material structure at multiple length scales from nano to macro increased the sensing response of the materials to combustion gases. These materials operated at relatively high temperatures, enabling detection close to the source of combustion. It is anticipated that these materials can form the basis for a new class of sensors enabling widespread use of efficient combustion processes with closed loop feedback control in the energy-intensive industries.

Process heating is the largest fuel end-use in U.S. industry. Improved efficiency in combustion systems for industrial heat and power will increase economic competitiveness by reducing both national energy consumption and costs for materials widely used in consumer goods. An array of nano-ceramic gas sensors for real-time burner balancing could potentially increase combustion efficiency by 0.5% to 2.0%, which can result in an annual savings of 24 trillion Btu if widely implemented across industrial process heating systems.

The first phase of the project focused on materials selection and process development, leading to hierarchical nanoceramics that were evaluated for sensing performance. The second phase focused on optimizing the materials processes and microstructures, followed by validation of performance of a prototype sensor in a laboratory combustion environment.

The objectives of this project were achieved by: (1) synthesizing and optimizing hierarchical nanostructures; (2) synthesizing and optimizing sensing nanomaterials; (3) integrating sensing functionality into hierarchical nanostructures; (4) demonstrating material performance in a sensing element; and (5) validating material performance in a simulated service environment.

During the course of the project the following milestones were achieved:

- Hierarchical porous electrode microstructures were synthesized.
- A process was developed for synthesizing sensing nanomaterials
- Catalytic nanomaterials capable of operating in harsh environments were identified and synthesized.
- A process for functionalizing hierarchical structures was developed.
- The materials performance was validated in a simulated service environment

The project team, consisting of GE Global Research, Brookhaven National Laboratory, the University of Florida and the University of Maryland, formed a cross-disciplinary team with diverse expertise in nanosynthesis, nanomaterial characterization, electrocatalysis, and sensors. GE Global Research developed synthesis methods for developing hierarchical electrodes and sensing nanomaterials, incorporated them in sensor prototypes and evaluated performance in laboratory and combustion gas test rigs. Brookhaven National Laboratory developed advanced characterization tools and methods for characterizing the structure and composition of materials at the nanoscale. The University of Florida and the University of Maryland brought understanding

of sensing mechanisms and advanced characterization of combustion gas interactions with nanomaterials.

The project developed hierarchical nanoceramic electrodes for mixed potential zirconia gas sensors with increased surface area and demonstrated tailored electrocatalytic activity operable at relatively high temperatures (in the range of 400-800 °C), enabling detection of products of combustion such as NO_x close to the source of combustion. Methods were developed for synthesis of hierarchical nanostructures with high, stable surface area, integrated catalytic functionality within the structures for gas sensing, and demonstrated materials performance in harsh lab and combustion gas environments, containing gaseous products of combustion, such as CO, NO, NO₂, O₂, CO₂, H₂O and N₂.

This project demonstrated feasibility of a combustion gas sensor starting with applied research (TRL 2) through technology development in a laboratory environment and laboratory testing of a semi-integrated system (TRL 5) with prototype sensors. With feasibility having been demonstrated on the project, the technology is well-placed to serve a variety of markets as the technology maturity level develops.

2. INTRODUCTION

The key objective of this project was to develop a robust, tunable materials platform for high-temperature, gas-sensing applications. GE Global Research partnered with Brookhaven National Lab for high flux synchrotron x-ray diffraction capabilities and for sensor electrocatalytic characterization at the University of Florida and the University of Maryland.

The project had two phases.

- Phase 1A—Develop hierarchical nanoceramic architectures (Task 1) and identify suitable catalytic nanomaterials (Task 2)
- Phase 1B—Integrate catalytic functionality into hierarchical nanostructured architecture (Task 3) and develop and test sensor element (Task 4)
- Phase 2—Optimize sensing elements and verify performance in a combustion rig (Task 5)

The materials selection and process development was conducted in the first phase, leading to hierarchical nanoceramics that were evaluated for sensing performance. The second phase optimized the materials processes and microstructures, leading to a validation of performance in a prototype sensor in a combustion environment.

Control of material structure at multiple length scales from nano to macro was predicted to enhance sensing response of the materials to combustion gases while retaining selectivity. The sensing materials were operable at relatively high temperatures (in the range of 400-800 °C), enabling detection of products of combustion such as NO_x close to the source of combustion. The materials can form the basis for a new class of sensors enabling widespread use of efficient combustion processes, with closed-loop feedback control, in energy-intensive manufacturing and process industries. It was estimated that this project could lead to a savings of 24 trillion Btu annually with successful technology introduction, and it would also enhance U.S. competitiveness and lead to significant reductions in environmental emissions.

3. BACKGROUND

The goal of the project was to develop a tunable, robust materials platform, based on the unique properties of nanostructured materials. The materials would be used for new combustion gas sensors for industrial process environments with enhanced sensing response due to the increased surface area, enhanced selectivity due to the control of catalytic functionalization, and superior performance based on their unique multi-scale architecture. The sensors would, in turn, allow efficient and precise closed-loop feedback-control of industrial combustion processes.

Process heating equipment based on the combustion of fossil fuels is used ubiquitously throughout U.S. manufacturing and processing industries. The petroleum and chemical industries use combustion systems to heat liquid material streams in chemical reactors. The steel, aluminum, metal casting, and glass industries rely on fossil-fuel-fired furnaces for melting and reheating materials. In all industries, process heating accounts for about 5.2 quads of energy consumption or about 17% of industrial energy use [Capital Surini Group, 2001].

Combustion burners in process heaters are typically controlled using adjustments in the air/fuel ratio without real-time, online diagnostics. Multiple burner units, such as those used in steel reheat furnaces, rarely have sensors capable of measuring performance of individual burners. As a result, burner tuning and balancing is difficult to perform during operation. Burners are often run with excess air, which reduces energy efficiency, and the variation in burner performance can lead to operating the ensemble of burners at the settings of the lowest performing burner. Furthermore, product quality in many industries is highly dependent on the control of thermal processing. There is a lack of cost-effective and reliable sensors and control systems to measure and maintain process heat inputs to industrial processes. Several key barriers identified in the Roadmap for Process Heating Technology include the inability to optimize process air-fuel ratios to reduce emissions, few low-cost sensors that are rugged and accurate, and the lack of smart controls [Capital Surini Group, 2001].

Online combustion diagnostics of individual burners would provide the input needed for real-time feedback control. The gaseous combustion environment is a very sensitive gauge of the health of the combustion process. Measurement of combustion gas levels, such as NO_x , at the point of combustion would provide a critical set of feedback data for active control algorithms to increase efficiency, reduce emissions, and improve product quality.

There is a lack of reliable, low-cost gas sensors for measuring the levels of gaseous products of combustion, with the required levels of sensitivity and selectivity, in the harsh environment near fuel burners. Zirconia-based electrochemical gas sensors have had technological and commercial success in measuring O_2 levels in automotive exhaust [Schwank, 1999], and they serve as a demonstrated technology platform for combustion gas monitoring, if the zirconia-based approach can be extended to gases other than O_2 . The key gap is that electrode materials sensitive to NO_x and other products of combustion are required with the sensing response and stability for industrial applications.

Extending zirconia sensor technology for quantitative measurement of multiple-combustion gas concentrations has been pursued in the past [Gopel, 2000]. Of the various zirconia sensor designs, the mixed potential sensor offers advantages of simple construction for multigas sensing, low-cost packaging, and rapid response time. These sensors use pairs of electrode materials with differential response to the sensed gas, for example CO [Garzon, 2000], [Miura, 1996a], NO_x [Miura, 1998b], CO_2 [Imanaka, 2000], H_2 [Garzon, 2000], and hydrocarbons (HCs) [Brosha,

2000]. The past work showed the potential for extending zirconia-based sensors for combustion gas sensing. However, new sensing materials and electrode structures were required to attain the requisite sensitivity, selectivity, and stability for robust, high-temperature combustion gas sensing.

This project developed hierarchical nanoceramic electrodes for mixed potential zirconia gas sensors with increased surface area and demonstrated tailored electrocatalytic activity for NO_2 . The project developed methods for synthesis of hierarchical nanostructures with high, stable surface area, integrated catalytic functionality within the structures for gas sensing, and demonstrated materials performance in harsh lab and combustion environments. The hierarchical nanoceramics provide a materials platform for selective zirconia sensors with enhanced sensing response for combustion optimization.

The sensors can be used as part of a combustion health monitoring system that would allow optimal burner operation over time. Estimates of the effectiveness of periodic burner balancing have shown that combustion efficiency can increase by at least 0.5% and as much as 2%, when the specific burner air/fuel ratio is maintained. The technology could be deployed in industries using combustion energy systems for materials processing, including petroleum, chemicals, steel, glass, metal casting, aluminum, and forest products industries. Even using a conservative estimate of 0.5% increase in efficiency, this will lead 24 trillion Btu annually with successful technology introduction.

4. RESULTS AND DISCUSSION

The project 1) developed hierarchical electrode structures, 2) integrated sensing functionality with the electrode structures that were integrated in a sensing test package, and 3) evaluated sensing performance in laboratory and combustion rigs. Each technology area is described in the sections below.

Section 4.1 describes the development of processing methods for engineering high-surface-area architectures of yttria-stabilized zirconia (YSZ). A combination of particle consolidation, templating and self-assembly were evaluated. Structures were produced with particle consolidation methods that met the surface area targets. Advanced characterization of the structure of the nanomaterials was done by Brookhaven National Laboratory.

The development of the integration of sensing and electrode structure is described in several parts in Section 4.2. The mechanistic understanding of sensor behavior is explored in Section 4.2.1. The interaction of materials with NO_x gas was studied at the University of Florida and the University of Maryland to determine the gas-phase catalytic activity as well as the adsorptive behavior as it would be applied to semiconducting electrode mechanisms. Section 4.2.1.3 discusses the logic for material selection for sensor screening experiments, where materials are expected to have the desired properties for high sensitivity sensing electrodes. These general scientific principles guided the specific material selection.

A number of metal oxide materials were screened for sensitivity and selectivity to NO_2 , NO and CO in Section 4.2.2. These materials were used as electrodes on test sensors evaluated in a gas stream by introducing preselected concentration of NO , NO_2 and CO into a flow of 3% O_2 and balance N_2 . Candidate materials for NO_2 detection were identified that had both good sensitivity to NO_2 and good selectivity with respect to the other constituents of the gas stream.

The optimized sensor materials with catalytic functionality developed in 4.2.2 (and tested in laboratory apparatus described in 4.3), were incorporated into a sensor package in Section 4.2.3. The package was designed to be tested in a simulated service environment, and served as the test vehicle for evaluation of the sensor performance at GE Research.

Section 4.3 describes a laboratory combustion-simulative environment in which sensors were tested for sensitivity and selectivity with interference gases and water. Prototype repeatability is discussed, and sensitivity to changing gas conditions (e.g., gas flow rate). In addition, the sensitivity and response time of hierarchical sensor architectures tested in a laboratory environment is discussed. Finally, the hierarchical prototype sensors were put in-line in combustion emissions gas testing, and the results are reported.

4.1 Hierarchical Nanoceramic Sensor Electrodes

4.1.1 Processing of Hierarchical Nanostructures

The objective of this task was to develop processing methods for engineering high-surface-area architectures of yttria-stabilized zirconia (YSZ). A combination of particle consolidation, templating and self-assembly were evaluated. Structures were produced with particle consolidation methods that met the surface area targets.

Three different YSZ powder were obtained from vendors, as listed in Table 4.1.1. The YSZ2-A1 and YSZ2-C1 powders were used in the as-received state. The YSZ2-B powder was further processed before use. Surface area was measured using the Brunauer-Emmett-Teller method (BET). Crystallite size was measured using X-ray diffraction (XRD), including measurements taken at the National Synchrotron Light Source at Brookhaven National Laboratory. Particle size characteristics were measured using a Horiba Laser Scattering Particle Size Distribution Analyzer LA-910. Volume specific surface area was calculated from the mass specific surface area and the porosity, determined using the Archimedes method [ASTM, 2006].

Table 4.1.1. Three powder types chosen for particle consolidation synthesis and their surface areas, crystallite size, and particle size characteristics.

YSZ Powder	Surface area (m ² /g)	Crystallite size (nm)	D ₁₀ (nm)	D ₅₀ (nm)	D ₉₀ (nm)
YSZ2-A1	13.3	42	107	127	226
YSZ2-B2	6.0	>150	344	560	1125
YSZ2-C1	148.4	7	119	180	312

Free-standing, electrode structures were synthesized using thick film paste processing. The effect of the thick film paste binder on the electrode structures is shown in Fig. 4.1.1, where the surface area and crystallite size of the electrodes structures is shown as a function of thermal treatment of 2 hours. The YSZ2-B electrode had the lowest surface area at 800 °C and the surface area decreased with increasing temperature. The YSZ2-A1 electrodes had intermediate surface area at 800°C and the surface area decreased more rapidly with temperature than the YSZ2-B electrodes such that the surface area of the two types of electrodes was similar at 1200°C. There was no effect of the binder formulation on the sintering kinetics of the YSZ2-A1 electrodes. The YSZ2-C1 electrodes had very high surface area at 800°C, greater than 5×10^8 m²/m³. However, the surface area decreased rapidly with temperature for two of the binder formulations. One binder system was developed which stabilized the high surface area up to 1000 °C. Similar trends were observed for the evolution of crystallite size in the electrodes.

Fig. 4.1.1. Surface area (left) and crystallite size (right) as a function of temperature for unimodal electrode structures of YSZ2-A1 powder (blue symbols), YSZ2-C1 powders (green symbols) and YSZ2-B powders. The YSZ2-A1 and YSZ2-C1 structures were produced with 3 different binder systems.

Bimodal electrode structures were produced with mixtures of varying volume fractions of YSZ2-C1 and YSZ2-B2 powders. The evolution of surface area and crystallite size with temperature is given in Fig. 4.1.2 for those electrodes. The surface area of the bimodal electrode structures was intermediate that of the two unimodal powders, as expected. Several electrode structures had surface areas greater than $1 \times 10^8 \text{ m}^2/\text{m}^3$. Very little effect was observed for the stabilization of surface area of bimodal electrode structures. However, the average crystallite size at the highest temperature was smaller for the bimodal electrodes than for the high surface area YSZ2-C1 unimodal electrodes. Scanning electron microscopy images of the fracture surfaces are given in Fig. 4.1.3 for the YSCZ2-B2 unimodal electrode and 3 bimodal electrodes.

A summary of the specific surface area results is given in Fig. 4.1.4 with a comparison with the state-of-the-art electrode surface areas that had been previously developed for similar electrode structures used in solid oxide fuel cells. Several of the YSZ architectures had greater than $1 \times 10^8 \text{ m}^2/\text{m}^3$ surface area.

Fig. 4.1.2. Surface area (left) and crystallite size (right) as a function of temperature for bimodal electrode structures (labeled C-11, C-4, C-10, and C-12) made from mixtures of YSZ2-B2 powder (orange squares), and YSZ2-C1 powder (dark green diamonds).

Fig. 4.1.3. Scanning electron microscope images of fracture surfaces of a) YSZ2-B2 unimodal electrode, b) C12 bimodal electrode, c) C10 bimodal electrode and d) C11 bimodal electrode. The amount of YSZ2-C1 powder in the bimodal electrodes increased in the order of $C12 < C10 < C11$.

Fig. 4.1.4. Specific surface area versus average crystallite size for a) baseline electrodes of three different compositions (diamonds) and b) hierarchical YSZ nanostructures developed on this project sintered at 800 °C (dark green squares) and at 1000 °C (light green squares). Eight of the YSZ nanostructures have greater than 10x the surface area of the best baseline electrodes.

4.1.2 Characterization of Nanostructures

Two new instrumental capabilities were developed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A new high speed linear array x-ray detector for time-resolved x-ray powder diffraction was constructed and commissioned, and a heater was designed for in-situ studies and accelerated aging tests. The new capabilities allowed higher temperature for accelerated aging tests of hierarchical nanostructures and faster measurement capabilities for measuring the products from the synthesis of the catalytic nanomaterials. Synchrotron x-ray diffraction at Brookhaven National Synchrotron Light Source was used to characterize the structure of the nanomaterials. The objective was to determine the reproducibility of hierarchical materials prepared as scaffold structures.

Figure 4.1.5 shows the crystallite sizes of composites made with YSZ-H L as determined by X-ray diffraction measurements made at the Brookhaven National Laboratory. Below 1000°C, both the LaFeO_3 (LFO) crystallite size and the YSZ crystallite size was less than 100 nm for a wide range of compositions. The data indicate that well-percolated, catalytic nanostructures were made. Figure 4.1.6 shows the crystallite sizes of composites made with YSZ-M. Both co-synthesized and post-synthesized composites are shown. For 800°C processing temperature, both phases were nanocrystalline across the entire compositional range shown.

Fig. 4.1.5 Dependence of crystallite sizes of LFO and YSZ in hierarchical composites as a function of the volume fraction of YSZ phase, a-left) YSZ-H with balance LFO-V and b-right) YSZ-H with balance LFO-G; 800°C (blue), 1000°C (green), 1200°C (red). Solid symbols represent LFO phase and filled symbols represent YSZ phase.

Fig. 4.1.6. Dependence of crystallite sizes of LFO and a medium surface area YSZ in hierarchical composites as a function of the volume fraction of YSZ phase after processing at 800°C. Solid symbols represent LFO phase and filled symbols represent YSZ phase.

Microtomography data of composite electrode structures were taken using the Transmission X-ray Microscope (TXM) at the BL 6-2 beamline at the Stanford Synchrotron Radiation Laboratory (SSRL). The microscope, based on zone-plate technology, operated around 8 keV, is able to achieve a ~40 nm spatial resolution. This technique has the potential for a visualization of porous structure in three-dimensional space. An example of a measurement on a Au-YSZ porous material is given in Fig. 4.1.7. The red features are Au particles and the green features are YSZ material. Shown in the figure are two views of the sample which can be rotated 360 degrees to provide a fully three-dimensional image.

Furthermore, the x-ray energy can be tuned to below and above the absorption edge of an element of interest, by which additional absorption contrast can be obtained that can help visualize the spatial distribution of a particular element. While at present the energy range is still limited, it is feasible to study the distribution of iron (absorption edge at 7.112 keV) in LaFeO_3 using the transmission X-ray microscopy technique.

Fig. 4.1.7. (left) image of Au-YSZ composite with color added to distinguish Au particles (red) from YSZ material (green) and (right) a view of the same 3-D data set rotated 180 degrees by the visualization software. The data can be visualized through a full 360 degrees.

4.2 Sensing Mechanisms and Design

The mechanistic understanding of sensor behavior is described in Section 4.2.1. The interaction of materials with NO_x gas was studied to determine the gas-phase catalytic activity as well as the adsorptive behavior as it would be applied to semiconducting electrode mechanisms. Section 4.2.1.3 discusses the logic for material selection for sensor screening experiments, where materials are expected to have the desired properties for high sensitivity sensing electrodes.

A number of metal oxide materials were screened for sensitivity and selectivity to NO_2 , NO and CO as presented in Section 4.2.2. The materials were screened for sensitivity and selectivity in a dry gas mixture with preselected concentrations of NO , NO_2 and CO gases in a base gas flow with a composition of 3% O_2 and balance N_2 . Candidate materials for NO_2 detection were identified that had both good sensitivity to NO_2 and good selectivity.

The development of a prototype sensor package is described in Section 4.2.3. The package can be tested in a simulated service environment, resulting in the evaluation of the sensor performance at GE Research.

4.2.1 Sensing Mechanisms

The mechanistic understanding of sensor behavior is crucial for material selection and design of highly sensitive and selective devices. The University of Florida and the University of Maryland have proposed the Differential Electrode Equilibria [Wachsman 2001] as a comprehensive approach to understanding the contributions of semiconducting, gas-phase catalysis, and mixed-potential mechanisms, explained in more detail in section 4.2.1.1. To fully understand the mechanism contribution to sensor response, several fundamental materials were studied. First, LaFeO_3 and LaMnO_3 nano-catalytic and semiconducting materials were fabricated using arigorous study on aqueous combustion synthesis and reported in sections 4.2.1.1.1 through 4.2.1.1.5. The interaction of these materials with NO_x gas was studied to determine the gas-phase catalytic activity as well as the adsorptive behavior as it would be applied to semiconducting electrode mechanisms. This work is described in section 4.2.1.1.6 through 4.2.1.1.10 and predicts semiconducting response for both materials at lower temperatures (with LaFeO_3 sensors more sensitive), consistent with Differential Electrode Equilibria. Next, sensors fabricated using LaFeO_3 and LaMnO_3 sensing electrodes, and the response to NO_x gas was analyzed.

Sections 4.2.1.1.11 through 4.2.1.1.15 highlight the work, resulting in a higher sensitivity for LaFeO_3 -based sensors at lower temperatures as predicted. In addition, the gas-phase catalysis explains reduction in sensitivity for both sensor materials as temperatures increase. The results of the LaFeO_3 and LaMnO_3 -based sensors demonstrated that semiconducting mechanisms are probable at lower temperatures and that gas-phase catalysis can affect electromotive force (EMF) contributing from mixed-potential mechanism (described in section 4.2.1.2). Therefore, a non-semiconducting material, Au , was utilized to study the interaction of gas-phase catalysis and mixed-potential response. Sections 4.2.1.2.1 through 4.2.1.2.6 discuss the reduction of EMF when exposed to CO gas for highly catalytic nanoparticle Au composite sensing electrodes, validating the detrimental effect of gas-phase catalysis on sensitivity. Finally, the fundamental experiments demonstrated the need for a non-semiconducting material, with low gas phase catalytic activity in the temperature range of interest. Section 4.2.1.3 discusses the logic for material selection for sensor screening experiments, where materials are expected to have the desired properties for high sensitivity sensing electrodes.

4.2.1.1 Differential Electrode Equilibria

Solid-state electrochemical devices using stabilized zirconia electrolytes have been recognized as strong candidates for high-temperature, harsh-environment sensor applications [Azad 1992, Göpel 2000] for NO_x [Miura SSI 1996, Miura JElectrochemSoc 1996, Di Bartolomeo JAmCeramSoc 2004] detection. Of these concepts, potentiometric devices offer simplified design by generating electromotive force (EMF) in response to test gas exposure.

The Nernst equation has adequately explained the EMF for oxygen sensors [Ramamoorthy 2003]. However, when a simultaneous reduction or oxidation of another gas is present with oxygen, the competitive electrochemical reactions causes a mixed-potential to develop at either electrode [Fleming 1977, Miura 2000, Fergus 2010]. The mixed-potential results in a deviation from the Nernst predicted EMF. Gas phase reactions over catalytic electrodes have also been considered to influence sensor EMF [Fleming 1977, Hibino 1999, Elumalai 2005, Elumalai 2009]. In addition, the semiconducting nature associated with the adsorption and desorption of gas species on select metal-oxide electrodes can alter the EMF [Wachsman 2001, Di Bartolomeo JAmCeramSoc 2004, Di Bartolomeo JElectroChemSoc 2004]. A comprehensive holistic approach to sensor phenomena is outlined in Differential Electrode Equilibria [Wachsman 2001]. The mechanism includes the electrochemical based mixed-potential theory and the interaction of gas-phase catalytic activity, but also considers the influence of semiconducting behavior. To examine such phenomena, two p-type semiconducting perovskites, LaFeO₃ and LaMnO₃, were utilized as sensing electrodes. Materials and sensors were fabricated and their surface adsorption behavior was examined in conjunction with sensor performance.

4.2.1.1.1 LaFeO₃ and LaMnO₃ Synthesis

Lanthanum-based perovskite oxide powders are of interest for a range of applications including catalysts [Zwinkels 1993], sensor electrodes [Tejucá 1993], and solid oxide fuel cell electrodes [Minh 1993, Minh 1995, Steele 2001]. Powders with small crystallite size and high surface area have benefits for uses that depend on gas phase interactions for their performance. Of the many synthesis routes for producing oxide nanopowders, combustion synthesis is compositionally flexible, fast, and results in high homogeneity.

The synthesis of ceramic powders by decomposing mixtures of metal salt precursors and chelating agents, such as citric acid, has been known for many years [Pechini 1967]. The combination of aqueous metal salts with fuels, such as urea [Kingsley 1988] and glycine [Chick 1990], results in highly exothermic, self-sustaining reactions when heated. This technique, aqueous combustion synthesis (ACS), has been widely used to make a variety of oxide powder compositions [Patil 1997, Patil 2002].

The characteristics of the ACS process are governed by the choice of oxidizer, typically an aqueous solution of cation precursors, the choice of fuel source and the application of heat. Metal nitrate salts have generally been used as the oxidizers in such reactions. Fuel choices have included urea [Kingsley 1988, Sousa 1999, Mimani 2001, Civera 2003, Basu 2004], citric acid [Basu 2004, Schafer 1997, Roy 1999, Varma 2003, Deshpande 2004], hydrazine [Varma 2003, Deshpande 2004, Ekambaram 1995], polyvinyl alcohol [Ma 2006], hexamethylenetetramine [Mimani 2001, Nagaveni 2004], oxalyldihydrazide [Mimani 2001, Nagaveni 2004, Aruna 1998] and others. Of specific interest to this study, ethylene glycol [Dasgupta 2001, Dasgupta 2002 MatSci&Eng, Dasgupta 2002 SSI, Chen 2006 MatLett, Chen 2006 MatSci&Eng] has recently been used as an ACS fuel, as well as in other novel powder synthesis techniques [Bonet 1999,

Uekawa 2002]. The most commonly used fuel for ACS is glycine [Mimani 2001, Varma 2003, Deshpande 2004, Nagaveni 2004, Purohit 2001 MRB, Purohit JNucMatls 2001, Peng 2002, Erri 2004, Mukasyan 2007], which has been used extensively to produce perovskite oxides [Chick 1990, Basu 2004, Yang 2000, Mukasyan 2001, Deshpande 2003, Wang 2006, Striker 2007, Nair 2008].

Three ACS characteristics make the process highly useful for nanopowder synthesis [Varma 2003]: 1) intimate molecular level reactant mixing; 2) quick, high temperature reactions (often resulting in as-combusted crystallinity); and 3) the evolution of gases during the exothermic reaction, resulting in highly voluminous powders. Characteristics of combustion reaction signatures, such as the rate of temperature increase ($dT dt^{-1}$) and the duration of combustion, are useful for categorizing the combustion type. Volume combustion synthesis (VCS) and self-propagating high-temperature synthesis (SHS) are two modes of combustion which produce different powder properties [Mukasyan 2001, Deshpande 2003, Varma 1998]. In the VCS mode, the combustion occurs uniformly with a high $dT dt^{-1}$ ($\sim 600^{\circ}\text{C s}^{-1}$) reaching a relatively high temperature for a short duration (~ 10 s). In the SHS mode, combustion occurs locally before the reaction further propagates. The SHS mode of combustion typically lasts longer and has a lower $dT dt^{-1}$ and maximum temperature compared with VCS. SHS combustion modes have generally been shown to yield higher surface area powders than VCS combustion mode [Mukasyan 2001, Deshpande 2003], especially when the peak VCS temperature approaches the material's melting point [Chick 1990]. In general, the VCS mode occurs when fuel:oxidizer ratios are stoichiometric, while the SHS combustion mode is favored under fuel rich conditions.

The characteristics of ACS oxide powders are typically adjusted by optimizing the fuel:oxidizer stoichiometry after selecting the fuel [Basu 2004, Ekambaram 1995] or oxidizer reactants [Deshpande 2004]. There has been limited work on the combinatorial effect of using different combustion fuels with different cationic oxidizers. For instance, it is not known how widely translatable the optimization of fuel choice for one product is for additional compositions. The aim of this study is to compare the effect of fuel and oxidizer combinations for two fuels with two closely related oxidizers, and to determine how the resulting combustion characteristics influence powder properties. LaFeO_3 and LaMnO_3 powders were synthesized using ACS, where only the B-site cation oxidizer reactants differed. For each composition, glycine and ethylene glycol were independently used as combustion fuels with the corresponding nitrate oxidizer reactants. The combustion characteristics and powder properties were subsequently investigated. It was observed that for these multi-cationic oxides, the mode of combustion and the resulting powder properties were not strictly dependent on the fuel choice.

4.2.1.1.2 Experimental Procedure

Approximately 20 grams (0.083 moles) of LaFeO_3 and LaMnO_3 perovskite powders were fabricated using combustion synthesis. Metal nitrates (Johnson Matthey, Ward Hill, MA) were dissolved in water to form 1 M aqueous solutions, then mixed with either glycine (Johnson Matthey, Ward Hill, Ma) or ethylene glycol (Aldrich Chemical Co., Milwaukee, WI) fuel. Table 4.2.1 lists the reactants and desired oxide products for the four combustion systems of interest. The combustion reactants were mixed in stoichiometric fuel:oxidizer ratios, where the equivalence ratio, ϕ , is unity according to propellant chemistry [Jain 1981]. For example,

assuming that N_2 , CO_2 , and H_2O are the only gaseous products, reactions containing ethylene glycol fuel (which are similar to those with glycine) can be represented as follows:

where the oxidation of Mn^{2+} occurs during combustion [Aruna 1997].

Table 4.2.1. The reactants and products of the four combustion synthesis systems of interest.

Sample ID	Oxidizers	Fuel	Oxide Product
LFO-GL	$La(NO_3)_3$, $Fe(NO_3)_3$	Glycine	$LaFeO_3$
LFO-EG	$La(NO_3)_3$, $Fe(NO_3)_3$	Ethylene Glycol	$LaFeO_3$
LMO-GL	$La(NO_3)_3$, $Mn(NO_3)_2$	Glycine	$LaMnO_3$
LMO-EG	$La(NO_3)_3$, $Mn(NO_3)_2$	Ethylene Glycol	$LaMnO_3$

Prior to combustion, free and partially bound water was evaporated and reactants formed a gel-like consistency. Care was taken to ensure that the reactants of each system were uniform solutions of nitrates, fuel and molecularly bound water at the time of the combustion. The reactants were then heated on a hot plate under ambient conditions at $10^\circ C \text{ min}^{-1}$ in a 3.1 L, 15 cm diameter, stainless steel beaker with an attached 18 cm vertical stainless steel mesh chimney. Type K thermocouples (127 μm , Omega Engineering, Inc., Stamford, CT) were placed on the center surface of the reactants to determine combustion temperature (Agilent 34970A, Agilent Technologies, Inc., Santa Clara, CA) at 5 measurements s^{-1} . Perovskite powders were either formed during combustion, or from subsequent calcinations at 400° , 600° , 800° and $1000^\circ C$. Each product was fabricated at least 3 times. Combustion observations were indistinguishable, and powder properties were found to be acceptably repeatable.

Binary system experiments were designed to examine the separate oxidizer-fuel exothermic reactions. Namely, the combustion of individual nitrate-glycine combinations (La-GL, Fe-GL, Mn-GL) and nitrate-ethylene glycol combinations (La-EG, Fe-EG, Mn-EG) were analyzed. The same molar amount of fuel was used as the previous perovskite combustion syntheses with a stoichiometric amount of nitrate oxidizer.

Thermodynamic properties were used to estimate the adiabatic flame temperatures during combustion. The ΔH_f° and C_p values for the anhydrous reactants and products were obtained from various sources [Chen 2006, Zhou 2008, CRC 1997, Parida 1998, SGTE 2006].

The oxidizer-fuel combustion reactions, as well as individual reactant decompositions, were characterized using a differential thermal analysis (DTA) and thermogravimetric analysis (TGA) instrument (STA 409C, Netzsch, Inc., Selb, Germany). The measurements were made up to

800°C using a heating rate of 10°C min⁻¹. Samples were dried at room temperature prior to measurements to avoid reactions that occur between the nitrates and ethylene glycol during prolonged times at elevated temperatures [Uekawa 2002].

Powder crystal structures were determined at room temperature by X-ray powder diffraction (XRD) with Cu K α radiation (D8 Advance, Bruker, Germany). The Williamson-Hall methodology [Williamson 1953] was used to estimate crystallite size (D_{XRD}) from the XRD patterns. Specific surface areas were measured using the Brunauer-Emmett-Teller (BET) method with a surface area and porosity analyzer (ASAP 2020, Micromeritics Instrument Corporation, Norcross, GA). The surface area was used to approximate the average particle size diameter (D_{BET}) assuming dense, spherical particles. The ratio of D_{BET} to D_{XRD} provided an estimate for the degree of particle agglomeration. Finally, a field-emission (Hitachi S-4500, Hitachi High Technologies America, Inc., Pleasanton, CA) scanning electron microscope (SEM) was used to qualitatively analyze the particle size and morphology of the heat treated powders.

4.2.1.1.3 Synthesis Results

Lanthanum ferrite powders were synthesized using both glycine nitrate (LFO-GL) and ethylene glycol (LFO-EG) fuel. Phase purity, crystallite size, and surface area are shown in Table 4.2.2, determined using XRD and BET measurements of the as-combusted and calcined powders. During repeat experiments, crystallite sizes and surface areas were typically within 20%, with the values for similar products sequentially preserved. Figure 4.2.1 shows the XRD patterns of the powders after heat treatment at 800°C. After combustion, LFO-GL was determined to be a single phase LaFeO₃ orthorhombic perovskite, with space group Pbnm. Upon additional heating to 1000°C, the crystal structure of the perovskite remained the same. By comparison, the as-combusted LFO-EG powder was mostly amorphous, with very small amounts of crystalline perovskite. After heat treatment at 600°C, LFO-EG formed an orthorhombic perovskite with a space group of Pbnm, similar to LFO-GL. A small amount of La₂O₃ was observed in the heat treated powder, which diminished upon further heating to 1000°C. Nanocrystalline LaFeO₃ powders were obtained using both fuel types, with the ethylene glycol fuel producing powders with smaller crystallite sizes and higher surface areas.

Lanthanum manganite powders were also synthesized using both glycine (LMO-GL) and ethylene glycol (LMO-EG) fuels. The powder properties are shown in Table 4.2.2, and the XRD patterns after 800°C heat treatments are included in Figure 4.2.2. The as-combusted LMO-GL powder was a cubic perovskite, Pm $\bar{3}$ m. Upon heating to 800°C, the crystal structure changed to rhombohedral, R $\bar{3}$ c, with an estimated D_{XRD} of 33 nm. By comparison, the LMO-EG powder had an orthorhombic crystal structure, Pnma, after combustion. Heat treatments also resulted in a rhombohedral structure. Both fuels produced nanocrystalline LaMnO₃ perovskite powders, however in this case, the smaller crystallite size and higher surface area powder was synthesized using the glycine fuel.

The morphologies of the 800°C heat treated powders are shown in Figure 4.2.3. All powders had crystallite sizes consistent with those measured using XRD. The LaFeO₃ powders generally consisted of soft agglomerates with degrees of particle agglomeration, the ratio of D_{BET} to D_{XRD} , of 2.4 and 1.9 for powders fabricated using glycine fuel and ethylene glycol, respectively. The LaMnO₃ powders sintered more significantly during heat treatment, resulting in particles of

approximately 20 μm diameter and degree of agglomeration values of 3.0 and 5.5 for powders fabricated using glycine and ethylene glycol fuel, respectively. The 800°C calcined LaMnO_3 would require significant powder processing prior to utilization in ceramic forming applications. However, it is expected that all of the as-combusted powders would exhibit sintering characteristics suitable for densification, with the higher surface area LFO-EG and LMO-GL being most favorable using traditional ceramic processing techniques.

Table 4.2.2. The crystal structure, estimated crystallite sizes and surface areas for the as-combusted and heat treated powders.

Sample ID	Temperature (°C)	Space Group	Crystallite Size, D_{XRD} (nm)	Surface Area ($\text{m}^2 \text{g}^{-1}$)
LFO-GL	After Combustion	Pbnm	52	5.5
	400	Pbnm	49	8.8
	600	Pbnm	48	8.7
	800	Pbnm	51	7.4
	1000	Pbnm	79	3.2
LFO-EG	After Combustion	Amorphous	NA	16
	400	Amorphous	NA	18
	600	Pbnm	21	23
	800	Pbnm	44	11
	1000	Pbnm	150	3.0
LMO-GL	After Combustion	$\text{Pm}\bar{3}\text{m}$	33	22
	400	$\text{Pm}\bar{3}\text{m}$	38	20
	600	$\text{Pm}\bar{3}\text{m}$	47	23
	800	$\text{R}\bar{3}\text{c}$	33	9.1
	1000	$\text{R}\bar{3}\text{c}$	130	2.6
LMO-EG	After Combustion	Pnma	100	3.8
	400	Pnma	82	2.6
	600	$\text{R}\bar{3}\text{c}$	87	2.9
	800	$\text{R}\bar{3}\text{c}$	76	2.2
	1000	$\text{R}\bar{3}\text{c}$	130	1.5

Fig. 4.2.1. XRD patterns for (a) LFO-GL and (b) LFO-EG after combustion and an 800°C heat treatment. All peaks correspond to an orthorhombic, Pbnm, perovskite, except for a peak at around 30° 2θ, representing a small amount of La₂O₃.

Fig. 4.2.2. XRD patterns for (a) LMO-GL and (b) LMO-EG after combustion and an 800°C heat treatment. All peaks correspond to a rhombohedral, $R\bar{3}c$, perovskite.

The combustion temperature during the ACS process has a significant effect on the powder crystallite size [Chen 2006, Zhou 2008, Purohit 2006]. Combustion temperature profiles are shown as a function of time in Figure 4.2.4. The maximum measured combustion temperature (T_m), measured rate of combustion temperature increase (dT/dt), and the calculated adiabatic flame temperature (T_{ad}) are listed in Table 4.2.3. Although glycine fuel yielded the highest T_m for

LaFeO₃ powders, the ethylene glycol combustion had a slightly higher T_m for the LaMnO₃ powders. Higher $dT dt^{-1}$ values were observed for reactions that were more explosive. For instance, LMO-EG uniformly combusted, leading to an intense flame and some movement of high kinetic energy particles from the reaction zone. Subsequently, the powder was more voluminous. The lower energy combustion (LFO-EG) churned and smoldered non-uniformly, leading to a higher bulk density powder. The reactions ranked from most rapid (explosive) to least rapid (smoldering) in the order of: LMO-EG ($910^{\circ}\text{C s}^{-1}$) > LFO-GL ($680^{\circ}\text{C s}^{-1}$) > LMO-GL ($540^{\circ}\text{C s}^{-1}$) > LFO-EG ($140^{\circ}\text{C s}^{-1}$). LMO-EG, LFO-GL and LMO-GL reactions lasted approximately 10 s, where combustion temperatures decayed to about 75% of the maximum measured temperature and flames were no longer visible. Combined with the corresponding gas evolution, the particles quench rather quickly from their maximum combustion temperature. In contrast, the LFO-EG reaction and congruent gas evolution lasted for approximately 120 s. For both materials, higher measured combustion temperatures and faster reactions coincided with a larger crystallite size. This suggests that the reaction thermodynamics (and not kinetics) lead to pronounced grain growth and reduced specific surface area.

Fig. 4.2.3. SEM images of (a) LFO-GL, (b) LFO-EG, (c) LMO-GL and (d) LMO-EG after an 800°C heat treatment.

The calculated adiabatic flame temperatures (T_{ad}) are higher than those measured because of heat losses in the measurement system, similar to past studies [Chen Mat.Lett. 2006]. The calculations predict higher T_m values when ethylene glycol fuel is used rather than glycine. As a result, both LaMnO₃ and LaFeO₃ powders fabricated using ethylene glycol are expected to have coarsened

more than their glycine counterparts, resulting in lower surface areas. However, as previously shown, these qualities were not observed for the LaFeO_3 powders.

Fig. 4.2.4. Combustion temperatures plotted against time for (a) LaFeO_3 and (b) LaMnO_3 powders using glycine and ethylene glycol as combustion fuels. The absolute time of the plots has been offset for comparison purposes.

Table 4.2.3. The measured thermal characteristics of combustion, T_m and dT/dt , as well as the adiabatic flame temperatures, T_{ad} , calculated from thermodynamic data.

Sample ID	T_m (°C)	dT/dt (°C s ⁻¹)	T_{ad} (°C)
LFO-GL	640	680	2310
LFO-EG	470	140	2530
LMO-GL	600	540	2360
LMO-EG	620	910	2600

The previously discussed crystal structures can be rationalized by considering the measured combustion characteristics. The LFO-GL system had the highest observed T_m resulting in as-combusted crystallinity with the expected space group [Vazquez 1998, Li 2007]. LFO-EG had the lowest measured T_m and, likewise, was the only amorphous powder.

LMO-EG combustion possessed the second highest T_m and the highest rate of temperature increase. The orthorhombic structure after combustion is typical of LaMnO_3 heat-treated above 900°C [Huang 1997, Horyn 2003]. LMO-GL, however, had a lower T_m than LMO-EG (and lower dT/dt). The crystal structure observed after combustion was cubic, which can be observed for LaMnO_3 annealed between 330° and 530°C [Norby 1995], typically when the perovskite is highly oxidized [Aruna 1997, Mahendiran 1996]. The crystal structures observed in this study and the corresponding literature observations suggest that the LMO-EG reached a higher synthesis temperature than the LMO-GL process, which is consistent with the measured combustion characteristics.

The thermal evolution of the oxidizer-fuel systems, measured using DTA, is shown in Figure 4.2.5. Combustion initiation temperatures (T_{in}) were estimated using the onset of the first exothermic peaks on the DTA curves. Both LaFeO_3 samples had higher T_{in} than the LaMnO_3 samples. The TGA exhibited corresponding sample weight loss at the T_{in} values. Assuming anhydrous oxidizers and only perovskites products, the molar weight loss was predicted for each system and compared to the measured values. The glycine fuel systems, LFO-GL and LMO-GL, had 66 and 79% observed weight loss, respectively (compared to 70 and 66% predicted). The weight loss observed for LFO-EG and LMO-EG was 58 and 63%, respectively (compared to the predicted 68 and 63%).

Fig. 4.2.5. DTA plots for LFO-GL, LFO-EG, LMO-GL and LMO-EG.

Further DTA analysis was conducted on the binary reaction systems to more closely examine the individual oxidizer-fuel interactions, similar to past studies [Deshpande 2003]. For simple combustion systems, such as iron oxide [Erri 2004], the fuel interacts with only one oxidizing reactant. However, when multiple oxidizing reactants are involved in the combustion synthesis, it

is important to investigate the T_{in} for each binary reaction. Lanthanum, manganese and iron nitrate were each individually reacted with the two fuels. The DTA results are summarized in Table 4.2.4, showing the temperatures of thermally sequential reactions. In addition to the exothermic perovskite and binary combustion reactions, the endothermic chemical decomposition temperatures of the isolated reactants are included.

Table 4.2.4. A summary of the reaction temperatures for each synthesis system, including the constituent reactions, observed using DTA analysis.

System	DTA Reaction	Reaction Type	Temperature (°C)
LFO-GL components:	Fe nitrate decomposition	Endothermic	155
	Fe nitrate-GL combustion	Exothermic	155
	LFO-GL combustion	Exothermic	185
	La nitrate-GL combustion	Exothermic	195
	GL decomposition	Endothermic	250
	La nitrate decomposition	Endothermic	410
LFO-EG components:	LFO-EG combustion	Exothermic	150
	Fe nitrate decomposition	Endothermic	155
	La nitrate-EG combustion	Exothermic	155
	EG decomposition	Endothermic	220
	Fe nitrate-EG combustion	Exothermic	250
	La nitrate decomposition	Endothermic	410
LMO-GL components:	Mn nitrate-GL combustion	Exothermic	150
	LMO-GL combustion	Exothermic	150
	La nitrate-GL combustion	Exothermic	195
	Mn nitrate decomposition	Endothermic	220
	GL decomposition	Endothermic	250
	La nitrate decomposition	Endothermic	410
LMO-EG components:	Mn nitrate-EG combustion	Exothermic	145
	LMO-EG combustion	Exothermic	145
	La nitrate-EG combustion	Exothermic	155
	EG decomposition	Endothermic	220
	Mn nitrate decomposition	Endothermic	220
	La nitrate decomposition	Endothermic	410

The LMO-EG system exhibited the most uniformity in the reaction temperatures. All three of the oxidizer-fuel combinations, Mn-EG, La-EG, and LMO-EG, had very similar T_{in} , within a range of 10°C (with the Mn-EG being the lowest). The decomposition of all of the reactants occurred at much higher temperatures, with the ethylene glycol decomposing at 220°C. Therefore, it can be hypothesized that during LMO-EG combustion, the manganese nitrate first reacts with ethylene glycol, followed almost simultaneously by the lanthanum nitrate combustion with ethylene glycol, as seen by a comparison of the ethylene glycol DTA curves shown in Figures 4.2.5 and 4.2.6.

Fig. 4.2.6. DTA plots for the La-EG, Fe-EG, and Mn-EG binary systems.

The three oxidizer-fuel combinations in the LMO-GL system, La-GL, Mn-GL, and LMO-GL, reacted within a 45°C range, all below reactant decomposition temperatures. The LMO-GL system combusted at 150°C, similar to the Mn-GL binary reaction. The La-GL T_{in} occurred 45°C higher, at 195 °C. For the LMO-GL combustion, then, the reaction between the manganese nitrate and glycine fuel initiates synthesis.

The characteristics of the LFO-GL system closely resemble past studies on iron nitrate-glycine combustion [Varma 2003, Erri 2004]. The T_{in} of the Fe-GL binary system was 155°C, corresponding to the decomposition of iron nitrate and subsequent evolution of nitric acid [Wieczorek 1999]. The La-GL T_{in} was higher, around 195°C (40°C higher than the Fe-GL reaction). Combustion of all three fuel-oxidizer combinations, La-GL, Fe-GL and LFO-GL, occurred within a 40°C temperature range and were well below the decomposition temperature of glycine. Although falling in between binary reactions, the LFO-GL T_{in} fell closer to the higher binary system reaction (La-GL) temperature, unlike the other combustion systems.

The binary reactions for the LFO-EG system were significantly different from any of the other three systems. The LFO-EG T_{in} occurred around 150°C, corresponding to the La-EG T_{in} (155°C). The Fe-EG T_{in} , however, occurred at 250°C, 95°C higher than the La-EG reaction (and higher than the observed decomposition of ethylene glycol when isolated). A comparison of the LFO-EG

DTA curve in Figure 4.2.5 with the binary reaction curves in Figure 4.2.6 suggests that the lanthanum ferrite powder is produced by two separate exothermic reactions, one at the reaction temperature for La-EG and a broader higher temperature reaction near the reaction temperature for Fe-EG.

4.2.1.1.4 Synthesis Discussion

Thermodynamic analysis showed that the ethylene glycol fuel is expected to produce higher maximum combustion temperatures and therefore lower surface areas for both oxidizer species. In the current study, it was observed that using ethylene glycol did yield lower surface area and higher crystallite sizes for LaMnO_3 powders, as expected. In contrast, ethylene glycol fuel produced higher surface area LaFeO_3 powder, contrary to thermodynamic predictions.

The volume combustion synthesis (VCS) mode is thought to occur for an equivalence ratio near 1, between approximately $0.7 < \phi < 1.2$ [Mukaysan 2001, Deshpande 2003]. Those guidelines have been useful in predicting the combustion mode for single component oxide systems. The fuel-to-oxidizer ratios for the perovskite systems in this study were stoichiometrically mixed ($\phi=1$), but only three of the four reactions combusted in a mode similar to VCS. Both LaMnO_3 powders and the LaFeO_3 powder synthesized using glycine had maximum measured temperatures higher than 600°C and rate of temperature increases greater than 500°C s^{-1} (Figure 4.2.4), characteristics of a VCS combustion mode. Furthermore, their binary reactions occurred within a temperature range of 45°C , leading to near simultaneous combustion with corresponding TGA and DTA features (Figure 4.2.5). The combustion synthesis of those three powders behaved similar to a simple oxide system, such as iron oxide, where only one oxidizer reacts with the fuel. The result was a spontaneous reaction in a VCS mode, typical of an equivalence ratio near unity.

The lanthanum ferrite synthesized using ethylene glycol fuel did not show VCS combustion characteristics, despite an equivalence ratio of 1. That powder had a low rate of temperature increase (140°C s^{-1}), a long combustion time (~ 120 s), and a relatively low maximum measured combustion temperature (470°C), characteristics more typical of the self-propagating high-temperature synthesis (SHS) mode [Mukasyan 2001].

The binary reaction experiments showed that lanthanum nitrate reacted with ethylene glycol at roughly the same temperature that the lanthanum ferrite system combusted with ethylene glycol. The iron nitrate and ethylene glycol, however, reacted almost 100°C higher at $\sim 250^\circ\text{C}$. The temperature difference between the two binary reactants caused two distinct exothermic reactions, where the equivalence ratio for each reaction differed from stoichiometric propellant chemistry calculations.

The following reaction sequence is proposed. The lanthanum nitrate and ethylene glycol first react with an effective equivalence ratio of ~ 2 (fuel rich), consuming redox reactants. The fuel rich conditions result in a lower rate of temperature increase during combustion than for stoichiometric conditions. As the temperature reaches $\sim 250^\circ\text{C}$, the iron nitrate has largely decomposed into FeOOH [Wieczorek 1999] and the ethylene glycol has since been decomposed by the lanthanum nitrate-ethylene glycol exothermic reaction. The reaction that was observed during the iron nitrate and ethylene glycol binary experiment then occurs under highly fuel lean conditions. The exothermic reaction of lanthanum ferrite using ethylene glycol is therefore dominated by a La-EG fuel rich ($\phi > 1$) reaction where it is oxygen starved and can only proceed

by consuming ambient oxygen. Past work has demonstrated that this phenomenon leads to a SHS combustion reaction mode when $\phi > 1.2$ [Mukasyan 2001, Deshpande 2003], which was the combustion mode observed in the LFO-EG system.

The difference between the two exothermic binary reaction temperatures offers insight to the combustion characteristics, and therefore the powder properties. The difference in binary reaction temperatures, ΔT_{BR} , were determined by subtracting the lower binary combustion initiation temperature, T_{in} , from the higher for each perovskite system. For instance, the LFO-GL ΔT_{BR} is the difference between the La-GL T_{in} and the Fe-GL T_{in} , which is approximately 40°C. The ΔT_{BR} and the observed dT/dt for each perovskite system were found to be related empirically. As ΔT_{BR} increased, dT/dt decreased, as shown in Figure 4.2.7. The largest ΔT_{BR} value, that observed in the LFO-EG system, had SHS combustions mode characteristics. For multicomponent oxide powder synthesis, the relationship suggests that for ΔT_{BR} values of up to at least 50°C, stoichiometric reactants will still produce the VCS combustion conditions.

Fig. 4.2.7. The observed relationship between the difference in binary exothermic reaction temperatures, ΔT_{BR} , and the rate of temperature increase (■), dT/dt , and maximum measured temperature (●), T_m , for the four perovskite combustion systems.

4.2.1.1.5 Synthesis Conclusions

Aqueous combustion synthesis produced lanthanum manganite and lanthanum ferrite nanopowders with a high degree of crystallinity and chemical homogeneity after calcination. For stoichiometric amounts of fuel and oxidizers, where the volume combustion synthesis mode is typical, using glycine resulted in higher surface areas and lower crystallite sizes for lanthanum manganite powders compared with using ethylene glycol as the fuel. Ethylene glycol fuel produced a higher rate of combustion temperature increase and higher predicted maximum temperature, which resulted in lower powder surface areas. However, this trend was not observed for lanthanum ferrite powder synthesis. The choice of ethylene glycol fuel, not glycine, produced higher surface area lanthanum ferrite powder.

The perovskite powders of interest require two oxidizer reactant species, and therefore the binary reactions of each oxidizer-fuel combination were considered. When both oxidizer species react simultaneously with the fuel, the overall fuel:oxidizer ratio is relevant for predicting the combustion mode. However, when reaction temperatures diverge, the separate oxidizer-fuel reactions may combust with unintended fuel:oxidizer ratios.

DTA results confirmed a large difference between combustion initiation temperatures for lanthanum and iron nitrate pairs using ethylene glycol. The iron nitrate reacted at a relatively high temperature with ethylene glycol compared with lanthanum nitrate. The synthesis of LaFeO_3 using ethylene glycol is dominated by the initial reaction of lanthanum nitrate with ethylene glycol, and therefore the overall reaction may effectively behave as a fuel rich redox reaction. Fuel rich combustion conditions are known to produce self-propagating high temperature synthesis combustion mode characteristics, and those characteristics are consistent with the low rate of combustion temperature increase and high surface area powder observed when synthesizing LaFeO_3 using ethylene glycol fuel.

Large differences between the combustion temperatures of the binary fuel-oxidizer combinations, even when using overall stoichiometric fuel:oxidizer ratios, were more likely to produce combustion more similar to a self-propagating high temperature synthesis. Therefore, the overall fuel:oxidizer ratios are a good predictor of combustion behavior when using aqueous combustion synthesis to synthesize simple oxides. However, when synthesizing multi-cation oxides using multiple reactants, consideration of the binary reaction pairs is essential for understanding effective fuel:oxidizer conditions and predicting combustion behavior.

4.2.1.1.6 NO_x Adsorption Behavior on LaFeO₃ and LaMnO₃ (University of Florida and University of Maryland)

Temperature programmed desorption (TPD) and reaction (TPR) are two techniques used to investigate the gas adsorption and catalytic behavior of materials [Falconer 1983]. TPD is used to measure the adsorption/desorption behavior as well as irreversible reactions at the surface of catalysts [Yoo 2007 JElectrochemSoc, Yoo 2006, Huang 2000]. A sample is first saturated with surface adsorbates and then heated in an inert atmosphere from room temperature to determine decomposition temperatures and products. Adsorbed species have different bond strengths with the surface, with desorption at higher temperature indicating greater bond strength. Moreover, each observed desorption peak gives evidence of a different surface species and/or surface intermediate, as some adsorbates may rearrange to form other species, and the area under each desorption peak is proportional to the quantity of adsorbed species.

TPR can be used to investigate the kinetics of heterogeneous gas phase reactions on a given material in comparison with thermodynamic equilibrium calculations [Yoo 2007],[Yoo 2006], [Falconer 1983]. TPR differs from TPD in that the sample is under reactant gas flow as the sample is heated, and reactant and product gas concentrations are measured as a function of temperature. Though temperature programmed experiments provide transient kinetic information, the interpretation of such data is nontrivial and the system may exhibit convoluted results. Therefore, other experimental techniques such as infrared spectroscopy can be used to provide additional information about surface reactions.

Diffuse reflectance infrared spectroscopy (DRIFT) is a technique used to measure the bond vibrational frequencies of adsorbed surface species. Each species has a vibrational signature that

can be used for identification, and when used in conjunction, TPD, TPR, and DRIFT can provide information about surface reactions that is useful for mechanistic evaluation. Huang et al. [Huang 2000] and Van Assche et. al. [Van Assche 2008] used similar methods to conduct extensive mechanistic analysis of NO adsorption and decomposition on lanthanum oxide and lanthanum copper oxide respectively.

LaFeO₃ (LFO) and LaMnO_{3+δ} (LMO) were selected for TPD, TPR, and DRIFT analysis to compare materials with similar parent crystal structure (perovskite), but possessing different B-site cations. Iron has a valence charge of 3+ in LFO [Van Assche 2008] and manganese has valence charges of 3+ and 4+ in LMO [Bell 2000, Sakait 1996]. The different valence states of the B-site cation affect their catalytic NO_x reduction activity and thus should impact their sensor response. In a study by Wachsman et. al., it was shown from NO TPR experiments that LaBO₃ perovskites (B= Ni, Co, Fe, Mn, and Cr) with more reducible B-site cations, partially filled 3-d orbitals, were more active toward NO reduction, i.e. Ni>Co>Fe>Mn>Cr [Wachsman 2000]. Therefore, the combination of analysis techniques and the comparison of results between LFO and LMO in this investigation should allow for better mechanistic understanding of surface reactions and their impact on potentiometric sensor response.

4.2.1.1.7 NO_x Adsorption Experimental

LFO and LMO powders were prepared by aqueous combustion synthesis using ethylene glycol fuel [Striker 2010]. Lanthanum nitrate and iron nitrate solutions were mixed with ethylene glycol in a stoichiometric oxidizer to fuel ratio for LFO synthesis. Manganese nitrate was substituted for iron nitrate for the synthesis of LMO. Once solutions were adequately mixed, water was evaporated at 70°C until a viscous gel remained. Gels were placed on a hot plate and heated at 10°C/min until auto-ignition ensued, resulting in the production of homogeneous powders. Powders were calcined at 400°C followed by grinding and further calcination at both 600 and 800°C. Finally, powders were ball milled in ethanol for 24 hours, dried, and sieved. X-ray powder diffraction (XRD) using a CuK_α radiation source was used to confirm phase purity of both materials. The final specific surface areas were 12.8 and 4.6 m²/g for LFO and LMO respectively, measured by BET. Final stoichiometries were La(Fe³⁺_{0.99±0.01}Fe⁴⁺_{0.01±0.01})O_{3.01±0.01} and La(Mn³⁺_{0.63±0.01}Mn⁴⁺_{0.37±0.01})O_{3.19±0.01} using a redox titration technique similar to Porta et al. [Porta 2001] and Jaenicke et al. [Jaenicke 1992].

Details and schematics of the TPD experimental setup have been given previously [Yoo 2006, Kan 2009]. Adsorbing gas concentrations were 2000 ppm NO (NO), 2000 ppm NO in the presence of 20% O₂ (NO+O₂), 2000 ppm NO₂ (NO₂), and 2000 ppm NO₂ in the presence of 20% O₂ (NO₂+O₂). All gases were research grade and balanced by helium. Powder samples were normalized by surface area (~0.6 m²) and supported on a quartz frit in the middle of a continuous flow quartz reactor. Upstream of the sample the reactor had a 4 mm inner diameter, while downstream of the sample it had a 2 mm inner diameter to reduce gas residence time. A thermocouple in a quartz sheath was placed at the surface of the sample. The reactor was placed in the center of a custom made tube furnace capable of linear heating rates up to 30°C/min. Prior to each run the sample was pretreated at 700°C in a mixture of 4% oxygen balanced by helium flowing at 25 cm³/min. to ensure consistent lattice oxygen content and to remove any surface contaminants.

After the pretreatment, samples were cooled to 300°C at 30°C/min. under the same gas flow as the pretreatment. Once the sample reached 300°C, the adsorbing gas was flowed over the sample for 30 min., followed by cooling to 50°C at 5°C/min. under the same gas flow. Below 50°C, the gas was switched to helium and allowed to equilibrate for 16 hours. Once equilibrated, the sample was heated at 30°C/min. to 725°C in helium and the desorbed gas effluent was measured using an Extrel quadrupole mass spectrometer (MS). All gases were flown at the same rate of 25 cm³/min.

For TPR experiments, samples were pretreated in the same manner as the TPD experiments described in the previous section, except they were cooled to below 50°C at 30°C/min. without a 300°C adsorption step. The sample was kept under helium flow while reactant gases were mixed for 30 min. in a separate line. An automatic switch was initiated and the reacting gases were flowed over the sample. Once a steady state MS signal was reached, the sample was heated at 30°C/min. to 725°C while the gas effluent was monitored by the mass spectrometer. In the case of LFO, the samples continued to adsorb NO₂ for some time at room temperature. To prevent excessive adsorption, heating was initiated 12 min. after the switch. The reactant gas used was a mixture of 1000 ppm NO₂ and 20% O₂ balanced by helium.

For the DRIFT procedure, A 95% potassium bromide (KBr) and 5% metal-oxide mixture was mulled for 30 seconds. KBr was used as a medium for reflected IR signals since it absorbs little signal. The mulled samples were pretreated in the same manner as in TPD/TPR experiments. Once the sample was cooled to below 50°C, it was transferred to a sealed container and stored in a dry box until tested. DRIFT spectra were recorded using a Nicolet Magna 760 IR under dry nitrogen at room temperature. Dried KBr was used as a background to further accentuate the adsorbate species on the metal-oxide. Spectra were processed by subtracting H₂O and CO₂ characteristic peaks as both molecules could easily adsorb from atmosphere during transfer. OMNIC software was used to assign peak values for species identification.

4.2.1.1.8 NO_x Adsorption Results

TPD spectra of LFO NO and NO+O₂ adsorptions are shown in Figure 4.2.8. From the NO TPD, multiple corresponding NO and NO₂ non-Gaussian desorption peaks were observed, with the addition of O₂ peaks at higher temperatures, indicating decomposition of complex surface species. Since the formation of complex surface species depends on the concentration of two reactants (NO and O₂ or NO₂ and O₂) it is likely that the kinetic rate of desorption is second-order, though the order of the rate of desorption was not determined from these results. Assuming the reaction rate is second-order, the desorption peaks would be symmetric. A simplified approach to separate the individual species using a manual Gaussian peak fitting program in Excel was applied. Peak positions were selected based on points of change in the non-Gaussian curve and the heights and widths were adjusted until the sum of the heights of the fitted curves equaled the height of the experimental data at intervals of ~0.4 °C. Pearson's chi-square test was applied and the procedure was repeated until the fit of the curve matched visually and the calculated p-value was one, indicating a goodness of fit of 100%. Though Gaussian peaks are symmetric, second-order desorption does not stipulate Gaussian shaped peaks exist. However, this approach can be used to gain a general idea of the types of species that are decomposing and desorbing. As an example, the deconvolution of the NO desorption peaks from the NO TPD is shown in Figure 4.2.9. Since the powders being tested are polycrystalline materials, a variety of surface site terminations could exist, each with different energetics for bonding. Because of this, the peak widths may vary. This

is seen in the 300°C peak in the NO deconvolution. The larger width of the peak could mean it has very different energetics for binding of surface species than the other sites, or it could be an aberration of the simplified Gaussian fitting approach. The fitting process was applied to all desorption curves to determine peak temperatures and total species desorbed.

Fig. 4.2.8. LFO (a) NO TPD and (b) NO+O₂ TPD.

Each desorption peak corresponds to a different surface species, each with a unique activation energy for desorption. The presence of NO₂ desorption after NO adsorption is a result of surface reactions taking place between NO and solid-state surface oxygen since no oxygen was added to the system in the gas phase. When oxygen is added to the system, there is an increase in total species desorbed, particularly in the case of NO₂. The low temperature peaks that were seen in the NO TPD are no longer observed. It is clear that adsorbed oxygen plays a significant role in the formation of surface species that decompose into and desorb NO₂. Peaks and desorption amounts for NO and NO+O₂ TPDs are shown in Table 4.2.5. Desorption amounts for each peak were calculated by first converting the volumetric flow rate to a molar flow rate according to Eq. 1, and then using the MS signal intensity, time between measurements (time step), and the surface area of the powder according to Eq. 2.

$$FR = \frac{PV}{RT} \quad (\text{Eq. 1})$$

$$M_{\text{desorbed}} = \frac{\int_{t_i}^{t_c} FR * I_{\text{MS}} dt}{SA} \quad (\text{Eq. 2})$$

FR is the molar flow rate of gas (mol/min.) calculated from the ideal gas law where P is atmospheric pressure, V is the volumetric flow rate (0.025L/min.), R is the universal gas constant (0.082057 L·atm/k·mol), and T is room temperature (298 K). M_{desorbed} is the total amount of gas desorbed (mol/m²) from a peak between the time of initial onset (t_i) and the time desorption is complete (t_c), where I_{MS} is the MS intensity in ppm, SA is the surface area of the powder (0.59 m²), and the time step is ~1.2 s. In the table, it is seen that NO, NO₂, and O₂ peaks correspond to each other. This means that it is likely simultaneous desorption of decomposition products is occurring.

Fig. 4.2.9. Deconvoluted NO signal from the NO TPD over LFO.

Similar to the NO TPDs, mixed desorption products of NO and NO₂ are seen when NO₂ is adsorbed both alone and in the presence of oxygen (Figure 4.2.10). Similar peak temperatures are observed for both TPDs (Table 4.2.6). Increases in total desorption of both NO and NO₂ were observed when NO₂ was adsorbed in the presence of oxygen. In comparison to NO desorption, a larger increase in NO₂ was seen. O₂ peaks correspond to NO_x desorption peaks, indicating decomposition of complex surface species (i.e. nitrite and nitrate species can decompose into NO and O₂ and nitrate species can also decompose into NO₂ and O₂). Unlike the NO TPD, there are no desorption peaks below 200°C.

TPR results are compared with thermodynamic calculations in Figure 4.2.11. Thermodynamic calculations for NO₂ decomposition to NO and O₂ according to Eq. 3 were calculated using the Gibbs free energies of formation to determine the equilibrium constant (K) as a function of temperature according to Eq. 4 where ΔG° is the Gibbs free energy of the reaction, R is the universal gas constant, and T is temperature. The equilibrium constant is related to the partial pressures of NO (P_{NO}), O₂ (P_{O_2}) and NO₂ (P_{NO_2}) according to Eq. 5. The partial pressures

of NO₂ and NO are related to the initial partial pressure of NO₂ (P⁰_{NO2}) from the mass balance of nitrogen (Eq. 6). The partial pressure of O₂ is equal to the initial partial pressure of O₂ (P⁰_{O2}) plus the amount of O₂ generated during NO₂ decomposition in terms of the partial pressure of NO (Eq. 7). Eqs. 5-7 were solved simultaneously to determine the thermodynamic profiles for NO₂, NO, and O₂. For the calculations, the initial concentration of NO₂ was 1000 ppm and the initial concentration of O₂ was 20% (200,000 ppm). Since the high concentrations of O₂ would saturate the MS, the O₂ signal was not recorded and its thermodynamic profile is not shown here. Calculation were made using Matlab.

$$\Delta G^\circ = -RT \ln(K) \quad (\text{Eq.4})$$

$$K = \frac{P_{\text{NO}} P_{\text{O}_2}^{1/2}}{P_{\text{NO}_2}} \quad (\text{Eq.5})$$

$$P_{\text{NO}_2}^0 = P_{\text{NO}_2} + P_{\text{NO}} \quad (\text{Eq.6})$$

$$P_{\text{O}_2} = P_{\text{O}_2}^0 + \frac{1}{2} P_{\text{NO}} \quad (\text{Eq.7})$$

TPR results show that LFO adsorbs NO₂ up to ~200°C and then begins to desorb NO₂, as evidenced by the large peak at ~290°C. At 300°C, LFO begins to decompose NO₂ to NO, but the reaction is not complete within the temperature range as evidenced by the nonzero NO₂ concentration levels. Using the equilibrium constant and initial concentrations of NO₂ and O₂, the concentration of NO over the temperature range was calculated. Once the concentration of NO was known, since NO and NO₂ have a stoichiometric relationship because of the nitrogen atom, the concentration of NO₂ was subsequently calculated. The calculated curves are seen in Figure 4.2.11.

Table 4.2.5: (a) NO and (b) NO+O₂ deconvoluted desorption peaks and amounts of gas desorbed from LFO.

(a)						
NO		NO ₂		O ₂		
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	N:O Ratio
140	0.39	135	0.22			0.79
195	0.15	190	0.20			0.68
300	0.23	310	0.12			0.84
420	1.40	390	0.42	415	1.16	0.39
480	0.62	460	0.17	478	0.42	0.44
(b)						
NO		NO ₂		O ₂		
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	N:O Ratio
312	0.52	291	1.31	308	0.31	0.49
		338	2.78	345	0.94	0.33
412	1.21			410	1.94	0.24
479	1.17			470	1.28	0.32

Fig. 4.2.10 LFO (a) NO₂ TPD and (b) NO₂+O₂ TPD.

Table 4.2.6: (a) NO₂ and (b) NO₂+O₂ deconvoluted desorption peaks and amounts of gas desorbed from LFO.

(a)						
NO		NO ₂		O ₂		N:O Ratio
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	
305	0.31	309	1.76	316	0.22	0.48
330	0.09	335	2.31	340	0.58	0.38
365	0.37	379	1.39			0.61
424	2.16			415	1.13	0.49
474	0.68			460	0.65	0.34
(b)						
NO		NO ₂		O ₂		N:O Ratio
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	
305	0.31	317	2.78	321	0.31	0.47
330	0.11	335	2.01	342	0.62	0.36
365	0.51	355	1.70			0.59
425	2.27			417	1.19	0.49
480	0.69			462	0.68	0.34

Figure 4.2.12 shows NO and NO+O₂ LMO TPDs. From the NO TPD, multiple NO and NO₂ desorption peaks are observed, with O₂ desorption peaks only corresponding to peaks above ~200°C. In the presence of oxygen, NO_x desorption increases, as well as the ratio of NO₂/NO desorption. As with LFO, NO+O₂ significantly affects the surface reactions taking place. In both NO and NO+O₂ TPDs, the loss of oxygen is observed, beginning at ~480°C. The evolution of oxygen at this temperature is referred to as β oxygen and is attributed to lattice oxygen release compensated by manganese reduction from 4+ to 3+ valence state [Bell 2000]. Peaks and desorption amounts for NO TPDs are shown in Table 4.2.7.

Total NO_x desorption from NO₂ and NO₂+O₂ adsorption is similar for LMO (Figure 4.2.13), with the NO₂ TPD showing slightly more desorption. Oxygen does not change the NO₂ adsorption behavior much for LMO. The only differences are seen in some of the O₂ to NO desorption ratios, which indicates different quantities of nitrite and nitrate species desorbed for each experiment (Table 4.2.8). Surprisingly the NO to NO₂ desorption ratio is greater for the NO₂ TPD (Figure 4.2.13) than the NO TPD (Figure 4.2.12), confirming that some surface intermediate species form.

Fig. 4.2.11. LFO NO₂ TPR with thermodynamic equilibrium calculations.

The NO₂ TPR over LMO (Figure 4.2.14) shows two small desorption peaks at ~80°C and ~300°C, close to the 105°C and 308°C peaks seen in the NO₂ TPD. NO₂ decomposition begins at ~300°C, and is not complete within the temperature range of the experiment. Thermodynamic equilibrium curves for NO₂ and NO are seen in Figure 4.2.14 as well. The LMO TPR more closely matches thermodynamic expectations than what was observed with LFO.

LFO DRIFT results are seen in Figure 4.2.15. When NO and NO₂ were adsorbed on LFO with and without O₂, it was noted that the location of DRIFT peaks (cm⁻¹) were very similar. Total adsorption increased in order of NO, NO+O₂, NO₂, and NO₂+O₂, consistent with TPDs. Peak frequencies were identified as seen in the figure.

LMO DRIFT spectra for NO, NO+O₂, NO₂ and NO₂+O₂ are seen in Figure 4.2.16. Like LFO, peaks were very similar. LMO showed a greater number of peaks for NO adsorption in the presence of oxygen than without. In addition, NO₂ gas adsorptions show greater total quantities of surface vibrational frequencies than NO. Fewer peaks were identified from LMO Drifts than LFO and in much lower quantities, though lower quantities can be attributed to LMO having a lower surface area than LFO. Identified peaks are labeled in Figure 4.2.16.

From TPD it is possible to gain a general understanding of the number of species desorbed and identify the general species type (ionic, covalent, nitrite, or nitrate) from N:O atom ratios by integrating the areas under the peaks identified from the simplified Gaussian model, but it is not possible to identify the specific form of the species. DRIFT results were used to identify possible species decomposing and desorbing from the surfaces of LFO and LMO. However, experiments were conducted at room temperature, so the species identified are representative of the initial species upon heating, but it is possible that the species rearrange to form different species prior to decomposition and desorption.

Fig. 4.2.12. LMO (a) NO TPD and (b) NO+O₂ TPD.

Table 4.2.7: (a) NO and (b) NO+O₂ deconvoluted desorption peaks and amounts of gas desorbed from LMO.

(a)						
NO		NO ₂		O ₂		N:O Ratio
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	
140	0.32	140	0.23			0.77
250	0.08					1.00
		323	0.69			0.50
374	0.53			366	0.83	0.25
(b)						
NO		NO ₂		O ₂		N:O Ratio
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	
102	0.01					1.00
115	0.08	120	0.05			0.86
170	0.08	170	0.80			0.54
		250	0.79			0.50
		316	0.94	315	0.39	0.30
370	0.65	345	0.05	372	1.17	0.22
426	0.86			458	0.66	0.40

Fig. 4.2.13. LMO (a) NO₂ TPD and (b) NO₂+O₂ TPD.

Table 4.2.8: (a) NO₂ and (b) NO₂+O₂ deconvoluted desorption peaks and amounts of gas desorbed from LMO.

(a)

NO		NO ₂		O ₂		N:O Ratio
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	
105	0.07	110	0.13			0.67
175	0.35	185	1.16			0.59
		235	0.12			0.50
270	0.59					0.51
		308	1.53			0.50
372	1.28			375	1.71	0.27
440	0.62			460	0.77	0.29

(b)

NO		NO ₂		O ₂		N:O Ratio
Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	Peak (°C)	Desorbed (μmole/m ²)	
110	0.08	110	0.20			0.65
180	0.05	195	0.93			0.53
		255	0.13			0.50
290	0.09	310	1.39			0.53
373	1.46			370	1.33	0.35
442	0.85			445	0.62	0.41

Interpretation of NO_x complex formation using DRIFT can be very subjective due to the sensitive nature of NO and multi-valent cation interactions. NO contains an electron in the π^*_{2px} antibonding molecular orbital, and depending on the condition of that orbital (whether an electron is donated or accepted), the vibrational frequencies can change significantly. Nonetheless, there has been enough data reported for NO and NO₂ adsorption and surface formation on different metal-oxide cations that reasonable interpretations can be made, especially when combined with other techniques such as TPD/TPR. A NO_x correlation chart from Hadjiivanov et al.'s review was used for species identification in this study [Hadjiivanov 2000].

Identified surface species at room temperature are seen in Table 4.2.5. Species with a ratio of N:O of 1.00 are ionic NO^+ and NO^- , and covalent NO . Species with a ratio of N:O of 0.50 are ionic NO_2^+ , covalent NO_2 , and nitrite species with nitro or monodentate nitrito configurations. Finally, the only species with an N:O ratio of 0.33 is transitional nitrate NO_3^- .

Fig. 4.2.14. LMO NO_2 TPR with thermodynamic equilibrium calculations.

Fig. 4.2.15. DRIFT spectra for NO , $\text{NO}+\text{O}_2$, NO_2 , and NO_2+O_2 adsorption on LFO.

Fig. 4.2.16. DRIFT spectra for NO, NO+O₂, NO₂, and NO₂+O₂ adsorption on LMO.

Table 4.2.9: Identified NO_x surface species from DRIFT spectra of NO, NO+O₂, NO₂, and NO₂+O₂ adsorbed on LFO and LMO (italicized).

NO _x Species	Bond Type	Vibrational Modes	Frequency Range ³⁰ (cm ⁻¹)	NO	NO+O ₂	NO ₂	NO ₂ +O ₂	N:O Ratio
NO ⁺	Ionic	v(N=O)	2120-2400	2400	2424 2397	2400 2398	2412 2399	1.00
NO ₂ ⁺	Ionic	v _{as} (NO ₂)	2370-2400	2400	2424 2397	2400 2398	2412 2399	0.50
NO	Covalent	v(N=O)	1710-1970	1764	1768 1770	1764 1763	1766 1763	1.00
NO ₂	Covalent	v _{as} (NO ₂)	1600-1690	1630	1626	1630	1628	0.50
Nitro	$\text{M} - \text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$	v _{as} (NO ₂)	1380-1655	1468 1582	1471 1598, 1485	1478 1486	1470 1477	0.50
		v _s (NO ₂)	1255-1365	1320 1271, 1350	1272, 1326 1270	1325 1257	1270, 1326 1326	
Monodentate Nitrito	$\text{M} - \text{O} - \text{N} = \text{O}$	v(N=O)	1355-1480	1468	1471	1478	1477	0.50
		v(N-O)	1075-1365	1320	1272, 1326	1325	1270, 1326 1326	
NO ₃ ⁻	Transitional	v _{as} (NO ₃)	1355-1410	1391 1386	1383 1385	1393 1401	1392 1398	0.33
NO ⁻	Ionic	v(N-O)	1035-1490	1041	1044	1041 1041	1040 1040	1.00

4.2.1.1.9 NO_x Adsorption Discussion

To determine the type of species desorbed from TPDs, nitrogen and oxygen atoms were counted. When NO or NO_2 desorb without corresponding O_2 peaks, the ratio of N moles to O moles is 1 and 0.5 respectively. In the case where O_2 peaks correspond to NO and NO_2 desorption peaks, nitrite or nitrate species decomposed upon desorption, and the same procedure was used to identify which species desorbed. A nitrite decomposition results in a ratio of N:O of 0.5 and for a nitrate decomposition, the ratio is 0.33. In the cases where the ratio is not equal to these values, it is possible that multiple species decomposed and desorbed or part of the decomposition was retained by the surface. These ratios can be found in Tables 4.2.5-8 and possible corresponding species can be found in Table 4.2.9.

It is possible that the ratios can be driven down by oxygen desorption from LFO that takes place at 150-370°C and 390-480°C and on LMO at 300-450°C (α oxygen) and above 450°C, where β lattice oxygen desorbs [Teraoka 1984]. These temperature ranges were determined by O_2 TPDs. O_2 desorption from O_2 TPDs was less than 20% of O_2 desorption in the case of NO and NO_2 TPDs. It is unlikely that as much O_2 adsorbed on the surface during NO and NO_2 TPDs as would have in O_2 TPDs, so it is assumed that most of the oxygen desorption is from decomposed species.

From the NO TPD of LFO (Figure 4.2.8 (a)), the first three temperatures (140, 195, and 300°C) have small amounts of desorbed NO and NO_2 relative to the two high temperature peaks, and no corresponding O_2 desorption (Table 4.2.5), therefore they are considered to be from ionic/covalent surface species. From the 140°C peak, a 0.7 N:O ratio is seen and is thus a combination of NO and NO_2 species. The 195°C and 300°C peaks also exhibit mixed ratios of 0.68 and 0.84 with the latter being comprised of more NO than the former.

At 420 and 480°C, O_2 desorption peaks correspond with NO and NO_2 desorption peaks indicating decomposition of complex adsorbed species. From the 420°C peak, a ratio of 0.39 suggests primarily nitrate species desorb with some accompanying nitrite. From the 480°C peak, the opposite is true with a ratio of 0.44 suggesting primarily nitrite species are desorbed. Therefore when NO is adsorbed on LFO, nitrite species are more stable than nitrate.

When oxygen was added (Figure 4.2.8(b)), the ionic/covalent species disappear and the first desorption peak at 312°C has a ratio of 0.49. This peak is thus decomposition of a nitrite species. The three peaks that follow at 338, 412, and 479°C all have N:O ratios of 0.33, 0.24, and 0.32, consistent with nitrate species. Since it is impossible to have a species decompose into a ratio lower than 0.33, the 0.24 ratio is an example where the ratio could have been driven down by oxygen desorption. Given the low ratio, it is still conclusive that nitrate species decomposed and desorbed. It is seen that the addition of oxygen encourages the formation of nitrate species in the case of NO adsorption on LFO.

The first desorption peak in the NO_2 TPD (Figure 4.2.10(a)) is at 305°C where a ratio consistent with nitrite species exists (Table 4.2.6). As temperature increases, there is a transition to nitrate species that desorb for the pure NO_2 adsorption case at 330°C, followed by another nitrite peak at 424°C, and yet another nitrate peak at 474°C. In addition, ionic/covalent species desorb at 365°C since no corresponding O_2 desorption is seen. The ratio of 0.61 suggests more NO_2 than NO desorption.

When oxygen is added (Figure 4.2.10(b)), unlike the NO TPDs, the species do not change. All peaks exhibit the same type of ratios. For NO+O₂, NO₂, and NO₂+O₂, nitrate species are most stable.

LMO TPDs (Figure 4.2.12) all exhibit low temperature peaks with no corresponding O₂ desorption peaks indicating ionic/covalent species desorption (Table 4.2.7). In addition, hardly any nitrite species are desorbed (N:O equal to ~0.5 when NO/NO₂ and O₂ desorption occurs) with nitrate species having the highest stability on the surfaces. When oxygen was added to the NO TPD, an additional nitrate peak was seen at 426°C, making it more stable.

The addition of oxygen has little effect on the species formed in the case of NO₂ adsorption (Figure 4.2.13). All peaks are the same except the 235 and 270°C peaks from the NO₂ TPD combine to form one peak at 250°C when oxygen was added (Table 4.2.8). In all experiments, nitrate species were the most stable on LMO.

DRIFT was used to correlate the desorption peaks from TPD with specific species, however, since DRIFT results were from room temperature measurements, it is possible surface species rearranged prior to decomposition and desorption. From the NO TPD (Figure 4.2.8(a)), it is seen that the largest amount of species desorbed occurred at 420°C. At this desorption temperature, the N:O ratio is 0.39 (Table 4.2.5(a)). This ratio means the decomposing and desorbing species is a mixture of nitrate and nitrite species with nitrate being the majority. The only nitrate species detected from DRIFT (Table 4.2.9) was free-like transitional nitrate at a frequency of 1391 cm⁻¹. Two nitrite species were detected, but were unable to be distinguished due to overlap of peak frequencies. Therefore, the remaining nitrite portion is either nitro, monodentate nitrito, or a mixture of the two. The next largest peak from the NO TPD is at 480°C (Figure 4.2.8(a)) and has a N:O ratio of 0.44 (Table 4.2.5(a)). This ratio still indicates a mixture of nitrate and nitrite, but in this case, the nitrite species is the majority. Since no other nitrate or nitrite species were detected (Table 4.2.9), it is assumed that the same type of species are desorbing as in the case of the previous peak, just in different quantities. The peaks at lower temperatures were composed of mixtures of NO (NO⁻, NO⁺, NO) and NO₂ (NO₂⁺ and NO₂) species.

In the NO+O₂ case (Figure 4.2.8 (b)), there were two more peaks below 420°C in which a nitrite or nitrate decomposed. In this case, free-like transitional nitrate species were identified (Table 4.2.9) desorbing at 338, 412, and 479°C in order of most to least species desorbed (Table 4.2.5(b)). The peak at 312°C is purely a nitrite decomposition comprised of either nitro, monodentate nitrito, or a combination of those species. All ionic/covalent species formed more stable nitrite and nitrate species with added oxygen, as none were detected by DRIFT (Table 4.2.9).

NO₂ adsorption on LFO (Figure 4.2.10 (a)) resulted in larger quantities of nitrite and nitrate formation (Table 4.2.6(a)) than NO adsorption (Table 4.2.5(a)). No ionic species were formed at low temperature, but mixed ionic desorption was seen at 365°C. With a N:O ratio of 0.61, desorption is primarily NO₂ by nature and is likely to be ionic (NO₂⁺) since the peak at 2400 cm⁻¹ (Figure 4.2.16) is much greater for NO₂ than NO adsorption.

With the addition of oxygen (Figure 4.2.10 (b)), nitrite and nitrate formation once again increases (Table 4.2.6(a)). The same species are formed, but are formed more readily when more oxygen is present either with the adsorption of NO₂ instead of NO, or if O₂ is present in the gas stream.

NO adsorption on LMO (Figure 4.2.12 (a)) resulted in more straight forward N:O ratios for ionic/covalent species desorbing at low temperatures (Table 4.2.7(a)). The N:O ratio for the 140°C peak shows a mixed desorption, but the peaks at 250 and 323°C show pure NO and NO₂ desorption respectively. However, the DRIFT spectra (Figure 10) showed no measurable amounts of ionic/covalent species (Table 4.2.9) at room temperature. It is possible for these peaks that a nitrite or nitrate species decomposed and desorbed as NO or NO₂ while O₂ constituents remained on the surface. In the case of the peak at 323°C, it is possible that the nitrite desorbed without decomposing at all. DRIFT detected a nitrite species in the nitro form (Table 4.2.9), which could be associated with the desorption peak at 323°C. The peak at 374°C is more straightforward. The ratio of N:O is a nitrate ratio with some O₂ desorption. The only identified nitrate species is the same as LFO: free-like transitional NO₃⁻.

When oxygen was added (Figure 4.2.12 (b)), more ionic species desorbed (Table 4.2.7(b)), and in this case DRIFT spectra revealed ionic species on the surface of LMO at room temperature (Table 4.2.9). Most of the species were in the form of NO₂ and the only NO₂ species identified were of the form NO₂⁺. The three highest temperature peaks have ratios exhibiting nitrate decomposition and desorption with the highest at 426°C desorbing some nitro species in addition.

Unlike LFO, adsorption of NO₂ resulted in an increase in ionic species formation and desorption at lower temperatures (Figure 4.2.13 (a)). The NO₂ desorptions at 308 and 175°C are all or almost all NO₂ (Table 4.2.8(a)) and can be identified from peak heights with the 308°C peak being covalent NO₂ and the 185°C peak being ionic NO₂⁺ (Table 4.2.9). The peak at 270°C is also easily identified since it is all NO. The largest NO desorption is covalent NO. At high temperatures, nitrate desorption increases relative to NO adsorption and no nitrite desorption is seen.

The addition of oxygen to NO₂ increased nitrate formation and caused the formation of some nitrite species at higher temperatures (Table 4.2.8 (b)). In the case of the nitrite formation, it is possible from the DRIFT spectra that these species could be monodentate nitrito instead of nitro, but they cannot be distinguished due to overlap of peak frequencies (Table 4.2.9). Covalent NO₂ and ionic NO₂⁺ still form, but slightly less than with only NO₂ adsorption.

Overall, LMO is less active for nitrite and nitrate formation and NO_x species adsorption than LFO. Where NO₂ and O₂ streams facilitated the conversion of ionic and covalent species to more stable higher temperature species on LFO, there was not a significant impact on LMO.

Though the TPD desorption ratios and DRIFT spectra match reasonably well for desorbing nitrite and nitrate species, it is likely that surface species are rearranging and forming intermediates before decomposing and desorbing at varying temperatures as the sample is heated. Evidence for such behavior can be seen in the TPRs in Figures 4.2.11 and 4.2.14 where NO₂ is converted to NO as the sample is heated in a constant gas stream according to Eq. 3.

The reverse reaction of Eq. 3 is thermodynamically favorable at low temperature and the forward reaction is favorable at high temperature. This is determined by calculating the Gibbs free energy of the overall reaction (ΔG°), where ΔG°_i is the Gibbs free energy of formation for a particular species (Eq. 8). The calculation gives positive values at low temperature and negative values at high temperatures, indicating a transition toward favorable NO₂ decomposition as the temperature is increased.

$$\Delta G^\circ = \Delta G_{\text{NO}}^\circ + \frac{1}{2} \Delta G_{\text{O}_2}^\circ - \Delta G_{\text{NO}_2}^\circ \quad (\text{Eq. 8})$$

In the case of LFO and LMO, conversion begins at $\sim 300^\circ\text{C}$, $\sim 100^\circ\text{C}$ higher than thermodynamic calculations suggest. It was previously shown from TPD and DRIFT that nitrite and nitrate species form on the surface of LMO and LFO when NO or NO_2 is adsorbed from 300°C to room temperature. Formed nitrite and nitrate species will decompose below the decomposition temperature of NO_2 with nitrite species having less stability than nitrate [Stern 1972]. In fact this is what is seen in the TPRs where both LFO (Figure 4.2.11) and LMO (Figure 4.2.11) start to decompose nitrite species at $\sim 100^\circ\text{C}$. Further decomposition of nitrate species occur at different temperatures for the two materials. According to Yuvaraj et. al. [Yuvaraj 2003], the stable anhydrous nitrates for iron and manganese, $\text{Fe}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_2$, have decomposition temperatures of $\sim 160^\circ\text{C}$ on LFO and $\sim 200^\circ\text{C}$ on LMO. Therefore nitrate species are more stable on LMO than LFO. This is seen from TPR results since LMO begins decomposing nitrate species at $\sim 200^\circ\text{C}$ and LFO below $\sim 200^\circ\text{C}$, overlapping with nitrite decomposition.

Furthermore, LFO was observed to exceed the NO_2 to NO conversion predicted by thermodynamics, while LMO lags conversion. This is due to nitrite/nitrate formation and stability differences on LFO and LMO rather than the metal-oxides being more or less active toward decomposition of NO_2 .

TPR results also show LFO to have higher adsorption capacity than LMO, consistent with TPD results seen from the amounts of decomposed surface species following low temperature adsorption. LFO has large quantities of overlapping nitrite and nitrate desorption, but LMO only desorbs small quantities of nitrite and nitrate species with onset separated by $\sim 100^\circ\text{C}$.

According to Mixed Potential Theory [Miura 1996 SSI, Miura 1998], the potential difference between a sensing electrode and a reference electrode in a potentiometric sensor is attributed to the redox reactions taking place on both electrodes according to Eqs. 9 and 10.

When the sensing electrode is exposed to the reacting gas (NO or NO_2) and the reference electrode is exposed to air, both reactions (either forward reactions of Eqs. 9 and 10 for NO_2 exposure or reverse reactions for NO exposure) occur at the sensing electrode. When NO_2 , an oxidizing gas, is exposed to the sensing electrode, oxygen is produced at the electrode and increases the potential relative to the air reference. Likewise, when NO, a reducing gas, is exposed to the sensing electrode, oxygen is consumed and the potential at the sensing electrode decreases relative to the reference electrode. Therefore a positive response will be observed for NO_2 exposure and a negative response for NO exposure. This was demonstrated by Miura et. al. [Miura 1996 SSI] for a CdMn_2O_4 spinel metal-oxide sensing electrode with a platinum air reference. Additionally, Brosha et. al. [Brosha 2002] showed this same behavior when LMO was exposed to CO, a reducing gas like NO, relative to a platinum air reference, though their lead configuration was opposite which generated a positive response.

However, the actual sensing mechanism is very complicated and involves many contributions. For example, it was shown that for the configuration where the sensing (LaFeO_3 or WO_3) and platinum reference electrodes were placed on opposite sides of the electrolyte and both electrodes

were exposed to the same gas environment, LaFeO₃, a p-type semiconductor, and WO₃, an n-type semiconductor, both exhibited positive responses when exposed to NO₂ and negative responses when exposed to NO [Di Bartolomeo 2004, Di Bartolomeo 2000]. Since both electrodes were exposed to the same gases, both reactions (Eqs. 9 and 10 for NO₂ exposure or NO exposure) occurred on both electrodes, but the rates of reactions were different.

In another configuration where LaFeO₃, the sensing electrode, and platinum, the reference electrode, were placed on the same side of the electrolyte as close fingers and both electrodes were exposed to the same gas environment, LFO exhibited opposite behavior to that of the configuration where electrodes were on opposite sides of the electrolyte giving a negative potential response to NO₂ and a positive potential response when exposed to CO [Di Bartolomeo 2004 JEuropCerSoc, Di Bartolomeo 2004 SSI, Di Bartolomeo JElectroChemSoc 2004]. In the same configuration, WO₃ produced opposite potential responses to LaFeO₃ exhibiting positive response when exposed to NO₂ and a negative response to CO. It was shown that in the close finger configuration, the different semiconductor types, behaved differently in the same gas environment. This behavior is not consistent with, and cannot be explained by Mixed Potential Theory redox reactions alone, but must include other contributions to sensor response, such as geometrical configuration [Macam 2010], electrode microstructure [White 2008], heterogeneous catalysis [Yoo JElectroChemSoc H217-H221 2006, Yoo Sens&ActsB 2007 915-921, Yoo JElectrochemSoc 2007, Yoo JElectroChemSoc 2006 H115-H121, Yoo Sens&ActsB 2007 644-652], adsorption of charged surface species [Yoo JElectroChemSoc 2007, van Assche 2008 SSI, Yoo JElectroChemSoc 2006 H115-H121], and shifts in Fermi energy [Nowotny 2005].

In evaluating the sensing mechanism for LFO and LMO, possible paths for formation of nitrite and nitrate species must be considered. Eqs. 11-16 comprise possible formation pathways [van Assche 2008 JElectroChemSoc, van Assche 2008 SSI]. When NO is adsorbed without any oxygen present, nitrite and nitrate species are formed with lattice oxygen according to Eqs. 11 and 13. When oxygen is present, additional paths may exist according to Eqs. 12 and 14.

Likewise for NO₂ gas adsorption, Eq. 15 is the likely formation pathway of nitrate species without gas phase oxygen present and Eq. 16 is another possibility when gas phase oxygen is present.

When NO was adsorbed on LFO and LMO in TPD and DRIFT experiments, transitional nitrate species predominately formed, probably according to Eqs. 11 and 13, using lattice oxygen to form complex species since adsorbed oxygen was unavailable. When this happens, electrons are injected into the electrode as the charged nitrates are formed. This results in a change in the Fermi energy at the electrode where the nitrates are formed.

Since nitrate formation increased when NO was adsorbed in the presence of oxygen, it is likely that formation of complex species proceed according to Eqs. 12 and 14, in which adsorbed oxygen from the gas phase is used to form nitrate species, as well as Eqs. 11 and 13, in which lattice oxygen alone is used to form nitrate species. This would cause the injection of holes in the case of nitrate formation with adsorbed oxygen in concert with injection of electrons in the case of nitrate formation with lattice oxygen resulting in a change in the Fermi level.

In the NO₂ case, nitrite species were predominately formed and the adsorption levels and types of species did not change with or without oxygen. Eqs. 11-16 cannot explain this type of species formation from NO₂ adsorption unless NO₂ decomposes to NO and O₂ prior to formation of nitrite species. This is likely to happen at higher temperatures (~600°C or higher), but different reactions are likely to occur at lower temperatures. Another scenario is adsorbed NO₂ directly draws electrons from the lattice according to Eq. 17.

This would cause the injection of holes in the sensing electrode and a different response than the NO case where electrons are injected. This behavior can partially explain the opposite responses seen from NO and NO₂ gas exposure on LaFeO₃. It is also possible that more complicated surface reactions are occurring simultaneously that are unable to be identified from these results. It is not possible to explain the overall changes of sign of sensor response seen in the different geometrical configurations, but it is conclusive that the formation of these charged species, which when formed change the Fermi energy of the electrode, are contributing to the changes in sensor response.

With the previous discussion in mind, it is obvious the overall response mechanism varies depending on the operating temperature. At temperatures above ~600°C, response is controlled by the catalytic nature of the perovskites in accordance with Eq. 3 and shown in Figures 4.2.11 and 4.2.14. At temperatures below ~600°C, the sensor response will be dictated by contributions from semiconducting mechanisms, as well as electrochemical mechanisms, as proposed by Differential Electrode Equilibria. The semiconducting response of the perovskite electrodes is governed by the formation and decomposition of the complex nitrite and nitrate surface species. The lower the temperature, the more species exist on the surface, which causes the increase in response signal observed by Di Bartolomeo [Di Bartolomeo 2004 SSI, Di Bartolomeo JElectroChemSoc 2004, Di Bartolomeo JAmCerSoc 2004]. However lower operating temperatures also causes more stable surface species, which causes the increase in response time, also observed by Di Bartolomeo [Di Bartolomeo 2004 SSI, Di Bartolomeo JElectroChemSoc 2004, Di Bartolomeo JAmCerSoc 2004].

These results clearly show that there are multiple species and/or intermediates on the surface of the electrode under potentiometric sensor operating conditions (gas composition and temperature). Moreover, each of these species can contribute to the sensing mechanism, and therefore, sensor response includes contributions from catalytic oxidation/reduction, electrocatalytic oxidation/reduction, and changes in semiconducting behavior (Fermi level) associated with surface species adsorption/desorption. While the prevalent theory for non-Nernstian sensor response is “Mixed Potential”, it focuses on only the electrocatalytic reaction mechanism and thus misses these other mechanistic contributions, as explained by Differential Electrode Equilibria.

When comparing the expected sensor responses of NO and NO₂ for LFO and LMO, since LFO is more active for the formation of surface species and nitrate species are less stable on the surface compared to LMO, LFO is expected to have a larger semiconducting contribution and exhibit faster semiconducting transients for NO and NO₂ gas than LMO.

4.2.1.1.10 NO_x Adsorption Conclusions

From TPD, TPR, and DRIFT results, LFO and LMO show complex nitrite and nitrate surface formation when NO or NO₂ are adsorbed. TPDs were conducted to identify the general number of, and general type (ionic, covalent, nitrite, or nitrate) of desorbing species using a simplified Gaussian model. DRIFT results were used to identify NO_x adsorbates at room temperature, and were correlated to TPD peaks. TPR was used to probe catalytic and kinetic activities for the reduction of NO₂. LFO formed surface nitrite and nitrate species in greater quantities and surface species were less stable than those on LMO. LFO was also shown to be more active for NO_x surface conversion. NO_x sensor mechanisms on LFO and LMO are proposed to have semiconducting mechanism contributions related to the formation of surface species identified herein that will influence sensitivity and response time. Since Mixed Potential Theory does not account for semiconducting contributions, Differential Electrode Equilibria is proposed to explain the sensor performance of semiconducting oxides. Finally, it is clear that any NO_x sensor mechanism for these types of semiconducting oxides must include the formation of complex surface species, such as nitrites and nitrates, as intermediates and Mixed Potential Theory does not.

4.2.1.1.11 Potentiometric Response of LaFeO₃ and LaMnO₃ Sensor Electrodes to NO₂

The Nernst equation has adequately explained the electromotive force (EMF) for oxygen sensors [Ramamoorthy 2003]. However, when a simultaneous reduction or oxidation of another gas is present with oxygen, the competitive electrochemical reactions causes a mixed-potential to develop at either electrode [Fleming 1977, Miura 2000, Fergus 2010]. The mixed-potential results in a deviation from the Nernst predicted EMF. Gas phase reactions over catalytic electrodes have also been considered to influence sensor EMF [Fleming 1977, Hibino 1999, Elumalai 2005, Elumalai 2009]. In addition, the semiconducting nature associated with the adsorption and desorption of gas species on select metal-oxide electrodes can alter the EMF [Wachsman 2001, Di Bartolomeo JAmCeramSoc 2004, Di Bartolomeo JElectroChemSoc 2004]. A comprehensive approach that accounts for these mechanisms is called Differential Electrode Equilibria [Wachsman 2001].

Two p-type semiconducting metal-oxides that have been examined for their interaction with NO₂ are LaFeO₃ and LaMnO₃ [Armstrong in-press 2011]. LaFeO₃ exhibited greater capacity for nitrite and nitrate specie adsorption that were less stable than LaMnO₃. Therefore, it was expected that the sensitivity of a sensor using a LaFeO₃ sensing electrode (SE) sensor be higher. The purpose of this study is to compare the sensing electrode sensitivity of these materials to NO₂ each using a stabilized zirconia electrolyte and a Pt reference electrode.

4.2.1.1.12 LaFeO_3 and LaMnO_3 Sensor Experimental

Nanocrystalline lanthanum ferrite (LFO) and lanthanum manganite (LMO) perovskite powders were synthesized using aqueous combustion synthesis [Kingsley 1988, Patil 2002]. Metal nitrate precursors (Johnson Matthey, Ward Hill, MA) and ethylene glycol fuel (Aldrich Chemical Co., Milwaukee, WI) reactants were mixed in a stoichiometric fuel:oxidizer ratio. Powder synthesis and properties are detailed elsewhere [Striker 2010].

Solid-state planar sensors were fabricated using 150 μm thick, 9.5 mm diameter 8 mol% YSZ (8YSZ) substrates (Pi-Kem Ltd., Staffordshire, England). 1.5 mm diameter Pt reference electrodes (RE) were deposited on the substrate using a metallo-organic adhesion layer (BASF, 05X), followed by embedding a Pt 100 mesh gauze (Johnson Matthey, Ward Hill, MA) into a Pt slurry (Heraeus, CL11-5349). 6.4 mm diameter sensing electrodes (SE) were deposited on the opposite side using an α -terpineol based slurry of either lanthanum ferrite or lanthanum manganite with an embedded Pt 100 mesh gauze voltage lead. After drying, the reference and sensing electrodes were co-fired to 800 $^\circ\text{C}$ with a 2 h dwell. Figure 4.2.17 illustrates the cross sections of the two different types of sensors fabricated.

Fig. 4.2.17. Planar sensors consisting of (a) lanthanum ferrite and (b) lanthanum manganite sensing electrodes on 8YSZ substrates, each with a Pt reference electrode.

Two samples using LFO and three samples using LMO sensing electrodes were investigated using an air-reference configuration at GE Global Research. The SE and RE Pt gauze was spot welded to Pt voltage leads to provide electrical connection with a data acquisition (DAQ) unit (Solartron 1480 MultiStat). The positive terminal of the DAQ unit was connected to the perovskite SE, such that: (+) LFO or LMO / YSZ / Pt (-). The sensors were then sealed to enclose the perovskite SE in a 9.5 mm diameter alumina tube using a zirconia based cement (Ultra-TempTM 516, Aremco Products Inc., Valley Cottage, NY). A tube furnace (Applied Test Systems Inc.) was then used to heat the samples to 400 $^\circ\text{C}$ to cure and seal the cement. Electromotive forces (EMF) and sensor temperatures (using type K thermocouples) were collected using the DAQ unit. The SE was consecutively exposed to 500 $\text{cm}^3 \text{min}^{-1}$ of 0, 30, 0, 100, 0, 300, 0 ppm of NO_2 , with a 7% fixed O_2 concentration balanced with N_2 in 15 min segments. After an initial NO_2 exposure at 400 $^\circ\text{C}$ to ensure proper electrical contact and response, sensors were allowed to age for 24 h prior to temperature variation to determine thermal related sensitivity and response effects.

4.2.1.1.13 LaFeO₃ and LaMnO₃ Sensor Results

Sensor sensitivity was determined after 15 minutes dwell at each NO₂ concentration. Since low temperature measurements resulted in sluggish response, a known baseline was used to determine sensor EMF for all measurements. Baseline values were first obtained from the steady state voltage in 3 % O₂ balance N₂ prior to NO₂ exposure and after testing. A linear baseline function was then determined using the initial and end baseline values. Figure 4.2.18 (a) plots the raw EMF measured for a LaMnO₃ SE during exposure to NO₂ with the empirically determined linear baseline function. EMF at each NO₂ concentration was subsequently determined by subtracting baseline values, as established using the baseline function, from the absolute measured voltage. Figure 4.2.18 (b) illustrates the sensor sensitivity to NO₂ after baseline correction.

The sensitivity of 3 LaMnO₃ and 2 LaFeO₃ SE sensors to NO₂ were averaged at around 300, 400 and 500°C. Fig. 3 shows the average transient response of LaMnO₃ at 290°C and LaFeO₃ at 300°C. Standard deviation values are denoted with error bars at the end of each 15 minute NO₂ segment. The samples show slow kinetic response, as is expected for the low ionic conductivity of YSZ at temperatures below around 350°C [Miura 2000]. Although not at steady state, LaFeO₃ samples have higher EMF after 15 minutes at 300 ppm NO₂ concentration, approximately 0.150 V compared to 0.130 V for LaMnO₃ samples.

Fig. 4.2.18. (a) The 500 °C raw voltage response of a LaMnO₃ SE sensor to NO₂ exposure (red) with the empirically determined baseline function (blue). (b) The baseline adjusted EMF response with circles indicating the sensitivity values determined after 15 minutes of exposure to 30, 100 and 300 ppm NO₂.

The average sensitivity as a function of time at 400°C and 395°C for LaFeO₃ and LaMnO₃ SE sensors is plotted in Fig. 4. Although response times are clearly faster than the samples at measured at around 300°C, steady state conditions are still not reached as EMF for both sensing electrodes continued to increase after 15 minutes at each NO₂ concentration. LaFeO₃ samples again have a higher sensitivity compared to LaMnO₃ at 0.099 and 0.049 V, respectively. However, the sensitivity of both samples decreased significantly as the temperature was increased.

Fig. 4.2.19. The baseline adjusted EMF response of sensors using LaMnO₃ SE at 290°C and LaFeO₃ SE at 300°C. Error bars represent one standard deviation after 15 minutes of exposure to 30, 100 and 300 ppm NO₂.

Finally, the 500°C transient sensitivity is plotted in Figure 4.2.21. LaMnO₃ SE samples do seem to reach steady state, and exhibit higher sensitivities than the LaFeO₃ samples after 15 mins of testing at each NO₂ concentration, opposite the observations at lower temperatures. Sensitivity continued to decrease indirectly with temperature, resulting in 0.011 and 0.026 V for LaFeO₃ and LaMnO₃ SEs, respectively.

Fig. 4.2.20. The baseline adjusted EMF response of sensors using LaMnO₃ SE at 395°C and LaFeO₃ SE at 400°C. Error bars represent one standard deviation after 15 minutes of exposure to 30, 100 and 300 ppm NO₂.

Fig. 4.2.21. The baseline adjusted EMF response of sensors using LaMnO₃ and LaFeO₃ SEs at 500°C. Error bars represent one standard deviation after 15 minutes of exposure to 30, 100 and 300 ppm NO₂.

The EMF after 15 minutes exposure to 300 ppm NO₂ was determined using baseline adjustment for various temperatures. Figure 4.2.22 compares these values for LaFeO₃ and LaMnO₃ as a function of temperature. For both materials, EMF seems to plateau below around 350 °C, with LaFeO₃ having a higher average sensitivity than LaMnO₃. Upon increasing temperature the sensitivity of both materials decreases dramatically. The LaMnO₃ sensitivity decreases at a slightly lower temperature, where 50 % of the maximum EMF observed ($\frac{1}{2}EMF_{max}$) occurred at approximately 393 °C. Alternatively, the temperature at $\frac{1}{2}EMF_{max}$ for LaFeO₃ was approximately 413 °C. LaFeO₃ sensitivity became less than LaMnO₃ at about 450 °C, where it remained lower as both sensitivities approached zero.

Fig. 4.2.22. EMF of LaFeO₃ and LaMnO₃ sensing electrodes during exposure to 300 ppm of NO₂ at various temperatures. Error bars of the LaMnO₃ SE sensor EMF represent one standard deviation determined from three samples.

4.2.1.1.14 LaFeO₃ and LaMnO₃ Sensor Discussion

Sluggish transient response for both LaFeO₃ and LaMnO₃ SE materials prevented response time from being calculated with high certainty. Past LaFeO₃ SE studies also observed response times in the order of minutes, especially for recovery [Yoon 2001, Grilli 2001, Di Bartolomeo JAmCeramSoc 2004]. Without reaching steady state after 15 minutes, knowledge of the maximum EMF was absent. This was the case for all measurements except for LaMnO₃ sensors at temperatures in excess of 500 °C. The slow transient response should therefore be considered during the interpretation of the relative sensitivities between LaFeO₃ and LaMnO₃ SE materials. If the EMF of the samples after 15 minutes of exposure to 300 ppm NO₂ is indicative of the

material sensitivity, then LaFeO_3 has a higher sensitivity than LaMnO_3 at temperatures below about 450 °C.

Mixed-potential theory predicts a positive EMF when exposed to NO_2 test gas for the current configuration, similar to past studies [Miura 1996 SSI]. Differential Electrode Equilibria declares that along with electrochemical mechanisms such as mixed-potential, gas-phase catalytic activity and semiconducting EMF contributing mechanisms require consideration also. LaFeO_3 and LaMnO_3 are highly catalytic materials [Bell 2000, Armstrong 2011 in press]. In the previous study, LaFeO_3 exhibited the ability to convert NO_2 to NO at lower temperatures than LaMnO_3 [Armstrong 2011]. Although the onset of catalytic conversion was around 300 °C for both materials, the LaFeO_3 temperature for 50 % conversion ($T_{50\%}$) was about 390 °C with full conversion peaking around 540 °C. In contrast, the $T_{50\%}$ for LaMnO_3 was undefined because full conversion to NO had not been empirically obtained, rather NO concentration continued to increase beyond 700 °C.

Past sensor studies have shown the importance of gas-phase catalytic activity on sensor EMF [Fleming 1977, Hibino 1999, Elumalai 2005, Elumalai 2009, Striker 2011 Au sensors]. Namely, gas-phase conversion to equilibrium concentrations reduces the EMF caused by mixed-potential. If a mixed-potential mechanism is a significant contribution to the sensor EMF, then the sensitivity of both sensor samples would decrease markedly beginning at around 300 °C, which is observed in Figure 4.2.22. In addition, mixed-potential EMF contributions would remain larger at higher temperatures for LaMnO_3 since full gas-phase catalytic conversion was not reached in the temperature range of the TPR test. Figure 4.2.22 also shows higher sensitivity for LaMnO_3 SE at temperatures above 450 °C.

EMF typically has a logarithmic dependency on testing gas concentration except when mass transport limitations can cause a linear relationship [Garzon 2000]. Table 4.2.10 summarizes the R^2 values for linear and logarithmic dependencies of EMF on NO_2 concentration at three temperatures. For both SE materials, a logarithmic dependency became less adequate for predicting EMF as temperature increased. This observation supports the premise that gas phase catalytic conversion of NO_2 reduces the EMF as temperature increases, thereby inducing mass transport limitations caused by low concentrations of NO_2 [Garzon 2000]. Furthermore, LaFeO_3 is more adequately explained at all temperatures by a linear EMF dependency on NO_2 concentration. In contrast, the EMF dependency for LaMnO_3 SE seems to transition from being logarithmic in nature at low temperatures to linear at higher temperatures. As shown previously [Armstrong 2011 in press], LaFeO_3 had slightly higher catalytic activity suggesting a tendency for more linear EMF dependency at lower temperatures than LaMnO_3 .

Table 4.2.10. The coefficient of determination (R^2) for the linear and logarithmic regression of EMF dependency on NO_2 concentration and three temperatures for both LaFeO_3 and LaMnO_3 sensing electrodes.

Temperature [°C]	LaFeO_3 SE		LaMnO_3 SE	
	Linear R^2	Logarithmic R^2	Linear R^2	Logarithmic R^2
300	0.998	0.943	0.953	0.994
400	0.999	0.932	0.971	0.984
500	0.998	0.889	0.990	0.962

The influence of semiconducting mechanisms on EMF cannot be deconvoluted from mixed-potential contributions without further empirical investigation. However, the semiconducting behavior can be examined more closely using the prior investigation of surface adsorption of nitrite and nitrate species on LaFeO_3 and LaMnO_3 [Armstrong 2011 in-press], both fabricated in similar fashion [Striker 2010]. Nitrite species, of NO_2 or NO_2^- (nitro and nitrito) form, and nitrate ions (NO_3^-) were shown to adsorb on both materials using diffuse reflectance infrared spectroscopy (DRIFT) at room temperature. The adsorption of NO_2 on a p-type semiconductor SE to form the ionic species would yield a positive sensor charge (using the experimental configuration described previously) according to:

Temperature programmed reactions (TPRs) were then used to determine the desorption temperature and ratio of nitrogen and oxygen species [Armstrong 2011 in-press]. Figure 4.2.23 summarizes the total moles of nitrogen, standardized to area, adsorbed on the surface of the materials as a function of temperature. LaFeO_3 approximately twice the nitrogen containing species adsorbed than LaMnO_3 . Using the nitrogen and oxygen ratios at each desorption peak, the amount of nitrite (N:O ratio of 0.5) and nitrate (N:O ratio of 0.33) species were estimated for each temperature and plotted in Figure 4.2.24. LaFeO_3 has a larger amount of adsorbed species for both nitrite and nitrate species as well. According to Eq. 18 and 19, a positive charge would be imparted from the ionic nitrite and the nitrate species adsorbed. The LaFeO_3 SE would therefore be expected to have a larger positive semiconducting contribution to EMF than the LaMnO_3 SE. Semiconducting effects should be easier to observe since adsorbed species are more pronounced at lower temperatures below around 400 °C. Although mixed-potential contributions are also present, empirical data shows higher EMF response for LaFeO_3 at lower temperatures, consistent with the expected semiconducting influence.

Fig. 4.2.23. Total moles of nitrogen adsorbed on LaFeO₃ and LaMnO₃ as a function of temperature.

Fig. 4.2.24. Amount of adsorbed species on LaFeO₃ and LaMnO₃ as a function of temperature.

4.2.1.1.15 LaFeO₃ and LaMnO₃ Sensor Conclusions

Sensors using LaFeO₃ and LaMnO₃ sensing electrodes were fabricated using Pt air reference electrodes. LaFeO₃ based sensors had a higher positive EMF signal when exposed to NO₂ than LaMnO₃ sensors below 450 °C. EMF response of both sensors reduced rapidly beyond 350 °C which is likely attributed to the increased gas-phase catalytic conversion of NO₂ to NO which reduces mixed-potential mechanistic EMF contributions. Semiconducting effects on the p-type perovskite sensing electrodes are considered to increase the EMF through adsorption of ionic nitrite and nitrate species. Since past studies have shown that LaFeO₃ has a higher capacity for nitrite and nitrate adsorption, it is expected that sensors of the same SE material would have a larger positive semiconducting contribution to EMF compared to LaMnO₃ based sensors. Without knowledge of the extent of mixed-potential contributions to EMF, empirical sensor data is at least consistent with the anticipated effect of semiconducting behavior in the presence of NO₂. Namely, LaFeO₃ based sensors had a higher EMF than those using LaMnO₃ sensing electrodes at temperatures known to have significant NO₂ generated surface adsorbents.

4.2.1.2 Mixed-Potential Theory

Electrochemical reactions can occur at the electrolyte and electrode interface to incur an EMF. One such reaction occurs when CO consumes oxygen ions from the electrolyte structure resulting in the production of CO₂:

Similarly, electron transfer can occur in the presence of NO or NO₂:

According to mixed potential theory [Fleming 1977, Miura 2000, Fergus 2010], Eq. 20 and the forward reaction of Eq. 21 require the simultaneous and competitive reduction of oxygen to proceed:

Oppositely, the reverse reaction of Eq. 21 requires the oxidation of oxygen (reverse reaction in Eq. 22). When steady state is achieved between the electrons produced during oxidation and consumed during reduction, a mixed-potential is established at the electrode.

4.2.1.2.1 Nanostructured Au-YSZ composite electrodes for potentiometric sensor response

Gold sensing electrodes have been studied for their potentiometric response to hydrocarbons [Hibino 1998, Mukundan 1999] and CO [Williams 1982, Mukundan 1999, Mizusaki 1999] resulting from higher oxygen reduction overpotential [Garzon 2000], and therefore different mixed potential, than Pt reference electrodes. Altering CO concentration causes a change in overpotential at the Au electrode, corresponding to a change in voltage between the electrodes [Fergus 2007]. Although work has studied the sensing behavior effect of varying Au particle size, post-calcination electrode structures maintained larger than 1 µm particles despite using fine starting powders [Hibino 1999]. Results showed an increased sensitivity to propene when reducing particle size.

Further decrease of particle size into the nano-regime (less than 100 nm) has been understood to considerably change the catalytic nature of gold [Haruta 1997, Min 2007]. Since gas-phase catalytic conversion of test gas occurs competitively with mixed potential reactions in non-nernstian sensors [Fleming 1977, Hibino 1999], it is believed that nanoparticle, highly catalytic, gold should decrease sensitivity. Therefore it is of interest to develop nanostructured gold electrodes for use in potentiometric sensors. Methods were developed to reduce thermal grain growth during calcination by using composite Au-YSZ structures, and the catalytic activity and sensor response was explored. Finally, sensor characteristics were interpreted using the gas-phase catalytic characteristics of the gold sensing electrodes.

4.2.1.2.2 Experimental

Solid-state planar sensors were fabricated using two different types of Au sensing electrodes on 150 μm thick, 9.5 mm diameter 8 mol% YSZ (8YSZ) substrates (Pi-Kem Ltd.). Coarse Au electrodes, approximately 1.5 mm in diameter, consisted of a Au 100 mesh gauze woven from 64 μm diameter wire (Alfa Aesar), embedded in a porous thick film prepared from a 8YSZ (Tosoh Corporation, TZ-8Y) slurry. Nanostructured Au electrodes were fabricated by embedding Au 100 mesh gauze in a mixture of Au metallo-organic solution (BASF, A1119) with 8YSZ slurry, targeting a final Au:YSZ solids ratio of 1:5, respectively.

Pt reference electrodes, also 1.5 mm in diameter, were deposited on the opposite side of the substrate using a metallo-organic adhesion layer (BASF, 05X), followed by embedding a Pt 100 mesh gauze (Alfa Aesar) into a Pt slurry (Heraeus, CL11-5349). After drying, the reference and sensing electrodes were co-fired to 900 $^{\circ}\text{C}$ and held for 2 h. Figure 4.2.25 illustrates the cross sections of the two different types of sensors fabricated.

Fig. 4.2.25. Planar sensors consisting of (a) coarse Au and (b) nanostructured Au sensing electrodes on 8YSZ substrates, each with a Pt reference electrode.

Backscattered electron (BSE) images of the electrode cross-sections were obtained using a scanning electron microscope (SEM; Carl Zeiss SMT, Supra 55VP). 50 kX images, with a 2 nm resolution, were analyzed by adjusting grey level ranges to ensure accurate binary phase elucidation using image analysis software (Clemex Inc., Vision). The average particle size, interparticle mean free path, and volume fraction of the 8YSZ and Au phases in the nanostructured electrode were determined. The percentage of contiguous Au-8YSZ interfaces and total Au and 8YSZ particles in contact were also determined.

Four samples consisting of coarse Au sensing electrodes, and two consisting of nanostructured Au sensing electrodes, were investigated in an alumina tube heated with a high temperature furnace (CM Furnaces Inc.) to determine the average electromotive force (EMF) during exposure to test gases. The sensor temperatures were maintained at 500 °C using feedback from type K thermocouples. Sensing and reference electrodes were exposed to the same 500 cm³/min test gas, where CO, NO₂ and NO were consecutively varied in segments of 0, 10, 30, 100, 300, 100, 30, 10 ppm in the presence of 3% O₂ balanced with N₂. Each segment in the testing protocol lasted for 15 minutes. Pt wire was spot welded to each electrode gauze, and electrical EMF was monitored using a data acquisition unit (Agilent Technologies, 34970A) configured with the positive terminal connected to the Au electrodes, such that: (+) Au/YSZ/Pt (-).

The catalytic nature of the sensing electrode structures (coarse and nanostructured) were analyzed using temperature programmed reactions (TPRs) for NO₂ and CO in the presence of O₂. Methods were similar to those described elsewhere [Armstrong 2010]. Electrode structures were pretreated at 700 °C, followed by cooling to below 50 °C, in 25 cm³/min of 4% O₂, balance He. The lines and samples were then purged using He for 30 min. At a flow of 25 cm³/min, reactant concentrations consisted of 2000 ppm CO and 8000 ppm O₂ for CO TPR, and 2000 ppm NO₂, 8000 ppm O₂ for NO₂ TPR. The samples were heated to 725 °C at 30 °C/min during which TPR products were analyzed using a quadrupole mass spectrometer (Extrel CMS, LLC.).

4.2.1.2.4 Results

A coarse Au sensing electrode SEM image is shown in Figure 4.2.26 and contains a cross-section of a microstructure with typical defects. Au gauze, woven from 64 µm diameter wire, is embedded in an 8YSZ sintered matrix, as illustrated by the Au wire in the image. Two varieties of cracks are observed in the 8YSZ porous structure: fine scaled cracks (less than 1 µm) around the wire, likely formed as a result of stresses associated with thermal expansion mismatch between Au and 8YSZ; and larger cracks (great than 5 µm) most likely due to shrinkage associated with sintering the highly active 8YSZ nanoparticles. In addition to porosity on the same scale as the 8YSZ particle size (less than 100 nm) large pores ranging in size of about 20 to 100 nm were observed at the porous-dense 8YSZ interface, likely formed during drying or organic burnout.

Fig. 4.2.26. BSE SEM cross-section image of the coarse Au electrode, showing a Au wire embedded in porous 8YSZ, both deposited on a dense 8YSZ substrate.

A cross-section of the nanostructured gold electrode is shown in Fig. 3 and image analysis results are summarized in Table 4.2.11. Consisting of 32 vol% of the solids, the Au particles have an average particle size of 62 nm, ranging from about 5 to 300 nm in size. Approximately 16% of the 2-D 8YSZ interfaces are contiguous with Au particles, and 30% of the 8YSZ particles are in contact with Au particles. In addition to defects similar to those observed in the coarse Au electrode, a second order of sub-micron porosity was observed consisting of pores between 200 and 500 nm in diameter.

Fig. 4.2.27. (a) A BSE SEM image of the nanostructured Au electrode and (b) the binary phase image constructed for Au (blue) and YSZ (green) using image analysis software.

Table 4.2.11. Image analysis results quantifying Au and 8YSZ microstructure for the nanostructured Au electrode.

Material	Volume Fraction	Average Size	Particle Mean Path	Free
8YSZ	17.6%	67.7 nm	282 nm	
Au	8.3%	61.6 nm	545 nm	

The average sensor response to CO, NO₂ and NO are plotted in Figure 4.2.28. All samples exhibited a negative EMF when exposed to CO and NO test gas, and a positive EMF when exposed to NO₂. Sensors with coarse Au sensing electrodes had larger absolute responses in all cases when compared to those with nanostructured Au electrodes. A slight hysteresis effect was observed for sensors consisting of coarse Au electrodes when exposed to NO₂ and NO, where absolute emf values remained higher than previous measurements when gas concentrations were reduced. This effect was also observed for the nanostructured Au sensors during NO sensitivity testing.

Fig. 4.2.28. Average transient sensor responses to consecutive exposure to 0, 10, 30, 100, 300, 100, 30 and 10 ppm of CO, NO₂, and NO for sensors with coarse Au and nanostructured Au sensing electrodes.

The EMF of the two sensor types are shown in Figures 29-31 and plot data points acquired and averaged after a 15 minute dwell at each testing gas segment. Standard deviations for the four tested sensors with coarse Au electrodes are illustrated, demonstrating good reproducibility with values less than 14, 6 and 2 mV when exposed to CO, NO₂ and NO gases, respectively. Higher sensitivity to each gas was observed for the coarse Au electrode sensors, which at 300 ppm of CO, NO₂ and NO yielded an average of -116, 37.8 and -7.5 mV, respectively. The nanostructured Au electrodes produced emf signals of -29.4, 17.1, and -4.0 mV for the same gases, all lower than the coarse Au electrodes. For both gases, highest sensitivity was observed when exposed to CO, followed by NO₂ and then NO gases.

Fig. 4.2.29. Average sensor responses when exposed to 0, 10, 30, 100, 300, 100, 30, 10 and 0 ppm of CO for sensors with coarse Au and nanostructured Au sensing electrodes. Error bars represent the standard deviation of four averaged sensors.

Fig. 4.2.30. Average sensor responses when exposed to 0, 10, 30, 100, 300, 100, 30, 10 and 0 ppm of NO₂ for sensors with coarse Au and nanostructured Au sensing electrodes. Error bars represent the standard deviation of four averaged sensors.

Fig. 4.2.31. Average sensor responses when exposed to 0, 10, 30, 100, 300, 100, 30, 10 and 0 ppm of NO for sensors with coarse Au and nanostructured Au sensing electrodes. Error bars represent the standard deviation of four averaged sensors.

The catalytic activity of the gold sensing electrodes for gas-phase reactions were determined using temperature programmed reactions (TPRs). Figure 4.2.32 illustrates the temperature dependence of thermodynamically favored CO₂ formation for the coarse and nanostructured Au, including the concentration of CO and O₂ reactants. Even at high temperatures, the coarse Au electrode did not exhibit any CO₂ conversion, whereas the nanostructured Au facilitated CO₂ formation at low temperatures with complete conversion by 250 °C. Figure 4.2.33(a) compares the temperature dependence of catalytic activity for the formation of CO₂ between the coarse and nanostructured Au electrode materials.

The same experiment was completed for the formation of NO from NO₂ and O₂. A similar difference was observed between the two electrode materials. Namely, the coarse Au electrode

did not begin converting NO_2 to NO until around 650°C while conversion of the nanostructured Au occurred at 400°C , a much lower temperature. A comparison of the two materials is made in Figure 4.2.33(b), showing the different temperature dependences for the catalytic formation of NO .

Fig. 4.2.32. Temperature programmed reaction for the gas-phase reaction of CO and O_2 to CO_2 as a function of temperature for the (a) coarse Au and (b) nanostructured Au electrode materials.

4.2.1.2.5 Discussion

The presence of reducing (or oxidizing) gases in addition to O_2 , especially CO , have been shown to change the polarization current for platinum electrodes [Can 1995], confirming mixed potential effects. However, since the Pt reference electrodes were similar for both nanostructured and coarse Au sensing electrode samples, the difference in results in the current study can be attributed solely to the Au sensing electrodes. The Au sensing electrodes are subjected to the mixed-potential mechanism aforementioned during exposure to the test gases (CO , NO_2 , or NO). In addition to the electrochemical processes described by mixed-potential theory, gas-phase reactions can occur simultaneously over catalytic electrodes during operation [Fleming 1977].

Using the Gibbs free energy of formation for the gases, the equilibrium constant and subsequent concentrations were determined as a function of temperature. These calculated values are also plotted in Figure 4.2.33, demonstrating that at sensor operating temperature (500°C) the following gas-phase reactions are thermodynamically favored to occur:

At 500°C, experimental results showed that Eq. 23 and 24 are kinetically favored in the presence of the nanostructured Au only, and not the coarse Au electrode.

Fig. 4.2.33. The temperature dependence on the catalytic activity for the formation of (a) CO₂ and (b) NO for both coarse and nanostructured Au electrode materials.

The gas-phase conversion of the testing gas towards equilibrium reduces the mixed-potential sensitivity by reducing the local triple point boundary concentration of O₂ [Fleming 1977, Hibino 1999] or by simply reducing the amount of test gas available for electrochemical reactions [Elumalai 2005, Elumalai 2009]. Therefore, in the current study, differences in gas-phase catalytic activity of the gold electrodes should effect the sensitivity. The highly catalytic nanostructured Au electrode material is predicted to have a lower sensitivity than coarse Au for CO and NO₂ test gas. The sensor results shown in Figures 4.2.30 and 4.2.31 support this prediction, coarse Au was almost 4 times as sensitive to CO gas, and 2.2 times as sensitive to NO₂, when compared to the nanostructure Au electrode.

4.2.1.2.5 Conclusions

Gold sensor electrodes were fabricated in two ways: first, a gold gauze was embedded in a porous YSZ matrix and identified as the coarse Au electrode; second, a metallo-organic gold solution

was mixed with YSZ to form a nanostructured Au electrode. The composite nature of the Au nanostructured electrode preserved average gold particle size of 62 nm even after electrode calcination. Sensing electrodes were made with either the coarse Au or nanostructured Au electrodes and exposed to CO, NO₂ or NO test gases with 3% O₂, balance N₂. Coarse Au electrodes had a substantially larger sensitivity to all test gases, more than twice the sensitivity of the nanostructured Au to CO and NO₂ exposure. The high gas-phase catalytic activity of the nanostructured Au electrode, as determined through temperature programmed reactions, is considered to reduce the mixed-potential sensitivity to the test gases. In comparison, the coarse Au sensing electrode was not catalytic to CO₂ and NO formation at 500 °C, the temperature of sensor operation.

4.2.1.3 Gas-surface Interactions Evaluated at Brookhaven National Laboratory

To further understand and validate the sensing mechanisms, an XAFS experiment was performed at Brookhaven National Laboratory under conditions similar to those actual sensors are used, at high temperatures and with the flow of gas mixture containing species such as NO₂. X-ray absorption fine structure (XAFS) is a synchrotron-based, element-specific x-ray technique for probing the interaction between possible catalytic sites and gas molecules to be sensed.

The XAFS experiments were performed at the X18B beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, with combined participation by the GE team and scientists Dr. Jun-Sik Lee and Dr. Jun Wang of the NSLS. A furnace specially designed for XAFS measurement, which was made available to us by the Chemistry Department at the BNL, was used. In addition to heating the sample to maximum 900°C, this furnace allows flowing gas during the measurement. This furnace was modified to accommodate lead wires connecting the two electrodes from the sensor so that the electrical sensing signals can be measured simultaneously as a gas mixture is introduced.

WO₃, Au and Pt were chosen for XAFS studies, due to the d-orbital configuration of the metal elements (d⁴, d⁹ and d¹⁰ respectively for W, Pt and Au), and the proper energy range of their L absorption edges. A gas mixture containing 0.1% NO₂/0.6% O₂/N₂ balance and 0.6% O₂/N₂ balance with controlled flow rate (20-25 cc/min) were switched on and off alternatively to study the effect of NO₂ on the d-orbital occupancy of W, Au and Pt. The sensing temperatures were in a range between 480-700°C, depending on the type of materials. A “white line” was observed in XAFS at the L2 and L3 edges, corresponding to a p → d transition when the d-orbitals are partially occupied. Since for Au the d-orbitals are completely filled, the white line intensity was zero. It was postulated that the interaction between a gas molecule and a d-orbital could change the intensity of the “white line”. If a gas molecule serves as an electron donating group, the d-orbital occupancy will be decreased and so will be the white line intensity, and vice versa when a gas molecule serves as an electron withdrawing group.

The actual sensors (with two electrodes connected to a digital voltmeter) and sintered powers on a yttria-stabilized zirconia disc were measured. The introduction of NO₂ appeared to have some, but very subtle, effect on the white line intensity at the W L2 and L3 edges in the experiment when a WO₃ sensor was measured, but such effect was not observed in a later experiment when sintered WO₃ powder was used. There was no observable effect on the white line intensity of Au and Pt by switching NO₂ containing gas on and off.

On one hand, these results seem to suggest that the d-orbitals of the metal sites are not actively involved in the sensing process. But on the other hand, one may argue that the metal sites that are involved in sensing are on the very top surface, and these sites only count for a small portion of the metal sites, active and inactive, that were probed by the x-rays. While a more surface-sensitive technique may be considered (such as electron-yield measurement), a sample environmental chamber with combined high-temperature and gas flow capability for electron yield measurement is not at present available.

4.2.1.4 Sensor Electrode Design Based on Mechanism Fundamentals

Differential Electrode Equilibria comprehensively includes electrode sensing mechanisms, including the widely accepted mixed-potential mechanism. The understanding of these mechanisms is crucial for designing a sensor capable of high NO and NO₂ sensitivity at high temperatures, between 400 and 800 °C. First, the use of semi-conducting electrodes was shown to only contribute to EMF at temperatures where gas adsorption was prominent. In the case of two widely studied perovskite materials, LaFeO₃ and LaMnO₃, the use of DRIFTS analysis coupled with experimental sensor data showed that these temperatures were below about 400 °C. In addition, the gas-phase catalytic activity of the perovskite materials proved to reduce the sensitivity of the sensors at lower temperatures than desired, beginning at around 300 °C. To decouple the mechanisms, a non-semiconducting electrode material, Au, was used to demonstrate the effect of gas-phase catalytic activity. The sensitivity of highly catalytic Au sensor electrodes was lower than non-catalytic Au when exposed to CO gas. High gas-phase catalytic activity was confirmed to convert the CO test gas to CO₂, resulting in gas-phase equilibrium and thereby reducing the sensitivity caused by mixed-potential mechanism. Based on these results, two design considerations were determined to be critical for sensing of NO_x gas at high temperatures: 1) materials with semiconducting behavior caused by gas adsorption at low temperatures (< 400 °C) do not contribute to sensor response in the temperature ranges of interest, and therefore should not be considered as potential electrodes; 2) materials with high gas-phase catalytic activity reduce the mixed-potential response, and should also be eliminated for sensing electrode consideration. Sensing electrode selection was then limited to non-semiconductive materials without significant gas-phase catalytic activity in the temperature range of interest.

4.2.2 Material Selection

A number of metal oxide materials were screened for sensitivity and selectivity to NO_2 , NO and CO . These materials were screened for sensitivity and selectivity in a dry gas stream by introducing preselected concentration of NO , NO_2 and CO into a flow of 3% O_2 and balance N_2 . The results of these tests are presented. Candidate materials for NO_2 detection were identified that had both good sensitivity to NO_2 and good selectivity.

4.2.2.1 Experimental Procedure

The testing setup used to screen the metal oxides is outlined in this section. Details of the equipment used in the setup are given in Appendix A. Metal oxides were screen printed on to a yttria stabilized zirconia (YSZ) substrate forming the sensing electrode (SE). The opposite side of the YSZ contained a platinum reference electrode (RE). Both electrodes were electrically connected via platinum mesh and wires to the data acquisition system.

Samples were mounted on hollow ceramic tubes with one side containing the reference electrode, open to air and cemented and sealed to the tube end with high temperature Aramco. The other side of the sensor contained the SE of the sample and was mounted so that it was exposed to the gas flow containing the test gases. The assembly was inserted into a furnace with a controllable temperature.

Gas flow through the furnace was controlled using mass flow controllers set via a LabView program. The voltage difference between the RE and the SE was recorded as a function of time every 10 seconds. Figure 4.2.34 shows the experimental set-up for the materials screening.

Fig. 4.2.34. Experimental set-up for materials screening metal oxide for sensitivity and selectivity to NO_2 , NO , and CO as function of temperature.

4.2.2.2 Results

The responses of the oxides to each gas with no interference gas present are displayed in the charts below. For a temperature of 700°C, the signal strengths with 300 ppm of NO₂ are given in Figure 4.2.35. The desired minimum sensitivity to 300 ppm of a gas is a signal level of 30 mV. Using this criterion, only NO₂ could be adequately detected at 700°C. No sample tested had adequate sensitivity to NO and CO. Signal strengths of less than 0.004 V can lead to difficulty in analyzing the data, especially if there is any background drift on the signal, or the characteristic response of the material is very large.

An equally important behavior to ascertain is the interference of other gases with the response of the sensor to each gas. This is expressed in terms of the knockdown ratio. This ratio is the response of the material to a test gas in the presence of one or more interference gases divided by the response of the material with only the test gas present. Ideally, this should be 1, which indicates perfect selectivity to the test gas. By using these two criteria (sensitivity at 700 °C and a knockdown ratio > 0.75) the best candidate materials for sensing NO₂ can be selected from the tested samples. These are underlined in red on the plots in Figures 4.2.36 and 4.2.37. The dashed red lines in the figures indicate the values for the two criteria as well.

At 600 °C, higher sensitivity was achieved for almost all samples and gases. Metal oxide samples were screened for use in high temperature NO₂, NO and CO gas sensors. Of the samples screened, five metal oxide materials were found to have the required sensitivity and selectivity for sensing NO₂ at temperatures of 600 °C and 700 °C.

Fig. 4.2.35. Potentiometric response of materials to 300 ppm of NO₂ at 700 °C.

Fig. 4.2.36. Knockdown ratio vs. sensitivity for screened samples for NO₂ sensitivity with NO present.

Fig. 4.2.37. Knockdown ratio vs. sensitivity for screened samples for NO₂ sensitivity with CO present.

4.2.3 Sensor Fabrication

The optimized sensor materials with catalytic functionality developed in 4.2.2 (and tested in laboratory apparatus described in 4.3), were incorporated into a sensor package. The package can be tested in a simulated service environment, resulting in the evaluation of the sensor performance at GE Research.

Previous development of co-synthesis techniques to fabricate structures of yttria-stabilized-zirconia with catalytic sensing materials provided fundamental know-how for forming hierarchical structures. The co-synthesis route, where both electrode materials and electrolyte materials are deposited and co-sintered, provides an adequate technique for the formation of composite structures. In addition, post-synthesis techniques, used previously on the project, offer a promising strategy for forming hierarchical structures. During post-synthesis, one or both materials are deposited onto an electrode scaffolding structure previously deposited and sintered. Both approaches were utilized to construct hierarchical electrodes for incorporation into sensors for testing. Four structures were fabricated, and the electrode structures are currently being tested in sensor devices for their NO_2 and NO sensitivity.

Sensors using the electrode materials have shown sensitivity to NO_2 , with various degrees of selectivity to NO_2 in the presence of NO as a function of temperature. Past efforts for heating the sensors to desired temperatures utilized tube furnaces for laboratory testing, as well as resistive platinum filaments for localized heating. Development of sensor-RTD (resistance temperature detector) integrated device have led to more miniaturized designs to minimize thermal stresses and testing artifacts related to temperature non-uniformity. The sensor element size was decreased to $\sim 2 \times 5$ mm to decrease the footprint on the RTD (7×5 mm). Figure 4.2.38 shows a schematic and a picture of the sensor-RTD integrated device. As described in previous reports, the RTD allows for sensor element operation of up to 900°C , with ambient temperatures as low as room temperature.

Fig. 4.2.38. A schematic of the cross section of the sensor integrated with a RTD (right) and a photograph of the integrated package (left)

An effort to develop a robust NO_x sensor prototype led to modifications in the RTD current collectors and voltage contacts. A wireless electrical feedthrough design was necessary to reduce failure mechanisms associated with electrical shorts and open circuits. Current and voltage contacts were fabricated using a Pt slurry deposited onto a alumina substrate with a subsequent heat treatment. The conductive thick-film Pt strips enabled good electrical contact from the sensor-RTD device through the combustion environment seal, provided by a rubber O-ring and compression fitting, and to the external electrical contacts. The sensor-RTD device was spot-

welded to wires attached to the conductive thick-film Pt strips via sinter bonding. Figure 4.2.39 shows the alumina substrate with thick-film Pt electrical contacts connected to the sensor-RTD device.

Fig. 4.2.39. The sensor-RTD device attached to the alumina substrate with thick-film Pt contacts. The compression seal and the electrical compression connector are also labeled.

An electrical connection to the conductive Pt contacts was made using a compression connector sandwiched over the end of the alumina substrate. Soldered wires from the compression connector then interfaced with the data acquisition unit using a female 9-pin circular electrical outlet. Current for the RTD was supplied via a power supply to the 9-pin circular outlet, and RTD voltages and sensor voltage response were measured from the same.

The maximum temperature of the package has not yet been established (the maximum temperature is currently limited by the existing rubber seal), but successful operation of the prototype has been shown in ambient temperatures below 100°C. As previously stated, the RTD-sensor device heats the sensor element to local temperatures as high as 900°C, allowing for sensitivity and response evaluation to NO and NO₂, including interference gases. The protective stainless steel sheath provides testing depths that can be modified. Currently, the sensor element can be inserted about 5 inches into the combustion gas zone.

4.3 Sensor Characterization in Laboratory and Combustion Testing

In Section 4.3.1, a combustion environment was simulated in the laboratory and sensors were tested for sensitivity and selectivity with laboratory introduced interference gases and water. Prototype repeatability is discussed, and sensitivity to changing gas conditions (e.g., gas flow rate).

Section 4.3.2 discusses the sensitivity and response time of hierarchical composite sensor architectures tested in a laboratory environment.

The hierarchical prototype sensors were selected for combustion testing and results reported in Section 4.3.3. GE sensor performance is compared to the gas analyzer data for the emissions gas testing.

4.3.1 Laboratory Testing of GE Sensors

To simulate combustion testing in the laboratory, gas was flowed at a rate of 500 sccm through a rig capable of holding three prototype sensors in series (Figure 4.3.1). The gas was composed of 3% O₂, 14% CO₂, 0-300 ppm of NO₂, 0-600 ppm NO, 0-10 vol% H₂O, 0-300 ppm CO, and balance N₂, which simulates combustion conditions. Heat was provided to the RTD in the prototypes by setting the voltage on a DC power supply. The rig holding the sensors was heated to 80°C with the heat tape under 10% H₂O conditions to prevent condensation. Gas composition was varied with mass flow controllers and the EMF was collected for each prototype with a data logger. For each gas composition, the sensor response was measured for 5 minutes, followed by a 5 minute “flush”, during which the prototype sensors were allowed to recover in 3% O₂ + 14% CO₂. The response to 300 ppm NO₂ was monitored at the beginning and end of the run to track sample drift over 4 hours, and the drift observed is minimal over the run time. Figure 4.3.2 shows the typical data collected for the GE NO₂ sensor under 3% O₂, 14% CO₂, 0% H₂O, 0-300 ppm of NO₂, 0-600 ppm NO, 0 ppm CO, and balance N₂. The markers signify where the sensitivity was recorded during each of the conditions.

**GE
Sensors**

Fig. 4.3.1. The laboratory testing rig for the prototype sensors developed at GE.

Fig. 4.3.2. EMF as function of time for GE prototype sensor under 3% O₂, 14% CO₂, 0% H₂O, 0-300 ppm of NO₂, 0-600 ppm NO, 0 ppm CO, and balance N₂ conditions. A 300 ppm NO₂ peak is shown at the beginning and end of the run to ensure steady baseline conditions.

The prototype repeatability is evaluated for the NO_x sensor prototype and the NO₂ sensor prototype through 2010 using the simulated combustion testing in the laboratory. For all tests, the gas flow rate through the prototype rig was maintained at 500 sccm. The gas was composed of 3% O₂, 14% CO₂, 0% H₂O, 0-300 ppm of NO₂, 0-600 ppm NO, and balance N₂, which simulates combustion conditions. Figure 4.3.3 shows the response of the NO₂ prototype sensors to NO and NO₂ (displaying NO₂ selective behavior). The NO₂ sensor prototypes displayed a sensitivity of 0.26 ± 0.01 mV/ppm NO₂.

Fig. 4.3.3. Response of the GE NO₂ sensor element prototypes to NO and NO₂. Baseline conditions are 3% O₂, 14% CO₂, 0% H₂O, and balance N₂. The sensors displayed the following sensitivity to NO₂: (a) 0.28 mV/ppm NO₂ @ 300 ppm NO₂; (b) 0.26 mV/ppm NO₂ @ 300 ppm NO₂; (c) 0.25 mV/ppm NO₂ @ 300 ppm NO₂; and (d) 0.25 mV/ppm NO₂ @ 300 ppm NO₂.

The prototypes were evaluated for their cross-sensitivity to CO. CO was put in as an interference gas using a similar protocol as shown in Figure 4.3.2, except that the baseline now contained 0,

20, or 100 ppm CO. Figure 4.3.4 shows the effects of the selectivity and sensitivity when CO is present. The selectivity for the GE sensor remained > 0.90 (for 300 ppm NO_2 relative to 300 ppm $\text{NO}_2 + 100$ ppm CO) for up to 100 ppm CO.

Fig. 4.3.4. Response of the GE NO_2 sensor element prototypes to NO and NO_2 with CO interference gas. Baseline conditions are 3% O_2 , 14% CO_2 , 0% H_2O , balance N_2 and (a) 0 ppm CO, (b) 20 ppm CO, and (c) 100 ppm CO.

10% H_2O was added to the simulated combustion gas. The NO_2 sensor shows a sensitivity of 0.16 mV/ppm NO_2 (Figure 4.3.5). There was negligible change from 0 ppm CO in sensor response for 20 and 100 ppm CO interference in 10% H_2O conditions. Despite heating the rig to prevent condensation, there was still some condensation present on the electrical contacts which caused noise in the NO_2 sensor response. Further development in the electronic packing should rectify this issue. The decrease in sensitivity with water in the combustion gas should improve with better packaging preventing condensation on contacts.

Fig. 4.3.5. Response of the GE NO₂ sensor element prototypes to NO and NO₂ with CO interference gas. Baseline conditions are 3% O₂, 14% CO₂, 10% H₂O, balance N₂ and (a) 0 ppm CO, (b) 20 ppm CO, and (c) 100 ppm CO.

At this point, only one oxygen level (3%) was studied for the sensor sensitivity and selectivity. To determine the GE NO₂ sensor sensitivity to O₂, a protocol similar to Figure 4.3.2 was run except that the baseline was changed to 6% O₂, 14% CO₂, and balance N₂. Figure 4.3.6 shows the difference in the response at 6% O₂ compared to the 3% O₂ GE NO₂ sensor. A few trends should be noted. First, the overall sensitivity is decreased with the higher (6%) O₂. Second, the sensitivity reduction depends on the NO and NO₂ content in the gas (it is not uniform through all levels of NO₂ or NO). The sensor becomes less selective to NO₂ at higher O₂ concentrations.

Fig. 4.3.6. Response of the GE NO₂ sensor element prototypes to O₂, NO, and NO₂. Baseline conditions are 3% or 6% O₂, 14% CO₂, 0% H₂O, and balance N₂.

Two conditions were studied across a wide range of O₂ conditions: 0 ppm NO_x and 600 ppm NO_x (300 ppm NO + 300 ppm NO₂). Figure 4.3.7 shows the effect of O₂ on the GE prototype NO₂ sensor. The baseline condition changed from 21 mV at 1% O₂ to 17 mV at 10% O₂. The 600 ppm NO_x condition changed from 100 mV at 1% O₂ to 40 mV at 21% O₂. Therefore, if there are changing O₂ conditions in the combustion environment, the O₂ must be measured to accurately predict sensor response. Furthermore, accurate models of NO and NO₂ response across multiple levels of NO, NO₂, and O₂ need to be collected to accurately predict the sensor response in changing O₂ conditions.

Fig. 4.3.7. Response of the GE NO₂ sensor element prototypes to O₂. Baseline conditions are 14% CO₂, 0% H₂O, and balance N₂.

The sensitivity of the prototypes to gas flow rate was evaluated to simulate the changing conditions in a combustion environment. The gas flow rate through the prototype rig was maintained at 250, 500, and 1000 sccm. The gas was composed of 3% O₂, 0% H₂O, 0 or 200 ppm of NO₂, 0 ppm NO, and balance N₂. For each flow rate condition, the sensor response at each flow rate under baseline conditions was measured for 15 minutes, followed by a 15 minutes of 200 ppm NO₂, and then repeated for the next flow rate condition. Figure 4.3.8 shows the response of the NO₂ sensor prototypes to 200 ppm NO₂ under three different flow rate conditions. Overall, the prototypes displayed a sensitivity of 0.33 ± 0.02 mV/ppm NO₂ for gas flow rates between 250 and 1000 sccm.

Fig. 4.3.8. Response of the GE NO₂ sensor element prototype to 200 ppm NO₂ under gas flow rate conditions of 250 sccm to 1000 sccm.

Four GE sensor elements were connected in series in an effort to measure the sensor sensitivity. For comparison, a single sensor element was also measured during the same test. For this test, the gas flow rate through a furnace rig was maintained at 500 sccm. The gas was composed of 3% O₂, 14% CO₂, 0% H₂O, 0-300 ppm of NO₂, 0-600 ppm NO, and balance N₂, which simulates combustion conditions. Heat was provided to the sensors by heating in a tube furnace. Gas composition was varied with mass flow controllers and the EMF was collected for each sensor with a data logger. For each gas composition, the sensor response was measured for 5 minutes, followed by a 5 minute “flush”, during which the prototype sensors were allowed to recover in 3% O₂ + 14% CO₂. The response to 300 ppm NO₂ was monitored at the beginning and end of the run to track sample drift over 4 hours, and the drift observed is minimal over the run time. Figure 4.3.9 shows the response of the sensor elements connected in series (Figure 4.3.9 (a)) compared to one single sensor element (Figure 4.3.9 (b)) in the furnace rig test. The results show that the sensitivity to NO₂ was enhanced by 3x by connecting the sensor elements in series.

Fig. 4.3.9. Response of the GE NO₂ sensor elements to 0-300 ppm NO₂ and 0-600 ppm NO in the furnace rig (a) 4 GE elements connected in series (b) one GE element. Baseline conditions are 3% O₂, 14% CO₂, 0 % H₂O, % CO, and balance N₂.

4.3.2 Laboratory Testing of Hierarchy Sensors

Hierarchical sensing electrode structures have at least two phases, where at least one phase is an ionic conductor such as YSZ, and multiple size scales. Hierarchical sensor architectures were created to decrease the recovery time of the sensor after exposure to NO₂. When compared to a single phase sensing electrode under the same experimental conditions, a hierarchical electrode showed significantly faster response times.

The hierarchical sensors were evaluated in laboratory simulated combustion conditions. The gas flow rate through the laboratory prototype rig was maintained at 500 sccm. The gas was composed of 3% O₂, 14% CO₂, 0% H₂O, 0-300 ppm of NO₂, 0-600 ppm NO, 0 and 100 ppm CO, and balance N₂. Heat was provided to the RTD in the prototypes by setting the voltage on a DC power supply. Gas composition was varied with mass flow controllers and the EMF was collected for each prototype with a data logger. For each gas composition, the sensor response was measured for 5 minutes, followed by a 5 minute “flush”, during which the prototype sensors were allowed to recover in 8.5% O₂ + 14% CO₂. The response to 300 ppm NO₂ was monitored at the beginning and end of the run to track sample drift over 4 hours, and the drift observed was minimal over the run time.

The benefits of the hierarchical structure can be observed in the recovery time. Table 4.3.1 summarizes the performance of the various sensing hierarchy electrode structures using a Pt reference electrode in a single atmosphere configuration and compared to single phase GE electrodes. Response and recovery times are calculated by taking the time to reach 90% of full signal or baseline, respectively. Only the GE Hierarchy-1 sensor incorporates both faster response and recovery times with high (>50 mV) sensitivity at 300 ppm NO₂.

Figures 4.3.10 and 4.3.11 show the 300 ppm NO₂, 0 ppm NO peak at 800°C for all sensors. Figure 4.3.11 is plotted with the sensitivity scaled to 1.0 for a 300 ppm NO₂, 0 ppm NO peak for all sensors. Figure 4.3.10 shows the difference in sensitivity for all electrode structures.

Table 4.3.1. The performance of various electrode structures.

Electrode	Processing Temperature	Operating Temperature	NO _x Gas Concentration	90 % Response (seconds)	90% Recovery (seconds)	Sensitivity (mV)
GE	1400°C	800°C	300 ppm NO ₂	63	300	82
GE Hierarchy-1	1400°C	800°C	300 ppm NO ₂	56	180	65
GE Hierarchy-2	1400°C, 900°C	800°C	300 ppm NO ₂	23	81	35
GE Hierarchy-3	1400°C, 900°C	800°C	300 ppm NO ₂	43	484	86
GE Hierarchy-4	1400°C	800°C	300 ppm NO ₂	67	106	48

Fig. 4.3.10. Response of sensors at 800°C for a 5 minute 300 ppm NO₂, 0 ppm NO, 3% O₂, 14% CO₂, balance N₂ peak. (scaled sensitivity to 1.0)

Fig. 4.3.11. Response of sensor EMF (in V) at 800°C for a 5 minute 300 ppm NO₂, 0 ppm NO, 3% O₂, 14% CO₂, balance N₂ peak.

At 800°C, the time to which the sensor reaches 90% of the voltage after NO₂ exposure is about 300 seconds when using a single phase GE sensing electrode. When hierarchy is added to the electrode structure, the time for 90% recovery is decreased to 180 seconds. With additional modifications to the hierarchy in GE Hierarchy-2, the 90% recovery time decreases to 81 seconds. However, the GE Hierarchy-3 electrode displays <50% of the sensitivity as the GE electrode structure. The GE Hierarchy-2 sensor showed good selectivity for NO₂ (Figure 4.3.12) however subsequent runs with this sensor showed increasing sensitivity and unstable performance, most likely due to coarsening of the structure. Overall, the GE Hierarchy-1 sensors performed the best with high sensitivity of 65 mV @ 300 ppm NO₂ and were the chosen electrode structure for combustion testing of GE prototype sensors.

Fig. 4.3.12. Response of GE Hierarchy-2 sensor with varying NO₂, NO concentration at 800°C (sensor is selective to NO₂)

4.3.3 Combustion Testing of Hierarchy Sensors

The hierarchical prototype sensors were selected for combustion testing due to the high sensitivity (near GE sensors) and reduced recovery time (~50% improvement over GE prototype sensors). Prior to combustion testing, the hierarchical sensors were evaluated in laboratory simulated combustion conditions. The gas flow rate through the laboratory prototype rig was maintained at 500 sccm. The gas was composed of 8.5% O₂, 14% CO₂, 0% H₂O, 0-300 ppm of NO₂, 0-600 ppm NO, 0 and 100 ppm CO, and balance N₂, which best simulates the diesel locomotive combustion conditions. Heat was provided to the RTD in the prototypes by setting the voltage on a DC power supply. Gas composition was varied with mass flow controllers and the EMF was collected for each prototype with a data logger. For each gas composition, the sensor response was measured for 5 minutes, followed by a 5 minute “flush”, during which the prototype sensors were allowed to recover in 8.5% O₂ + 14% CO₂. The response to 300 ppm NO₂ was monitored at the beginning and end of the run to track sample drift over 4 hours, and the drift observed was minimal over the run time.

The response of the hierarchical prototype NO₂ sensor in the laboratory environment is shown in Figure 4.3.13. Figure 4.3.13 (a) shows the response at 0 ppm CO and Figure 4.3.13 (b) shows the response at 100 ppm CO. The hierarchical prototype NO₂ sensor is displaying high sensitivity and is selective to NO₂. Previously it was shown that the GE sensor element displayed decreased selectivity above 3% O₂, however the RTD of the sensor was adjusted so that selectivity could be obtained in an 8.5% O₂ gas environment.

Fig. 4.3.13. Response of GE hierarchical NO₂ prototype sensor under simulated combustion conditions with (a) 0 ppm CO and (b) 100 ppm CO. Baseline conditions are 8.5% O₂, 14% CO₂, 0% H₂O, and balance N₂.

The response was modeled by a second-order polynomial equation using a regression analysis where the response (in EMF) was dependent on the [NO₂]. The R-squared value of the fit was 98.5%. Figure 4.3.14 shows the EMF response of the GE hierarchical NO₂ sensor as a function of [NO₂] for the polynomial fit and the collected data.

Fig. 4.3.14. Δ EMF as function of NO_2 for the GE hierarchical NO_2 sensor for 0 and 100 ppm CO conditions in the laboratory rig. Also shown is the polynomial fit of the NO_2 response.

The Δ EMF (in V) from Figure 4.3.14 was fit to a polynomial equation as a function of $[\text{NO}_2]$ in ppm:

$$\Delta\text{EMF} = 1.17 \times 10^{-3} + 6.00 \times 10^{-4} [\text{NO}_2] - 1.15 \times 10^{-6} [\text{NO}_2]^2 \quad (\text{Eq. 25})$$

The measured EMF response of the GE NO_2 sensor includes both the background level of 26 mV (from laboratory test data under 0 ppm NO_x) and the Δ EMF from the response of the sensor to NO_x :

$$\text{EMF}_{\text{measured}} = \Delta\text{EMF}_{\text{NO}_2 \text{ Sensor}} + \text{Baseline}_{\text{NO}_2 \text{ Sensor}} \quad (\text{Eq. 26})$$

Although the fit to the laboratory simulated combustion gas stream is quite good, a few things should be noted. First, the fit is to data collected at 8.5% O_2 and 14% CO_2 . Previous studies on these sensors have shown that there is a measurable O_2 dependency and negligible CO_2 and CO on the EMF response. Second, there is no laboratory data on this sensor exceeding 100 ppm CO. Further work would include expanding the CO range and including the O_2 dependency over various CO and NO_x conditions in the regression analysis.

After laboratory qualification, the GE hierarchical NO_2 sensor was tested during emissions gas sampling of combustion emissions at GEGR (Figure 4.3.15). The combustion emissions gas composition (NO_x , CO, CO_2 , O_2 , unburned hydrocarbons) were tracked by an analyzers during the lifetime of the test. In addition, the EMFs of the GE sensors and the ambient temperature in the test rig were also tracked during the test. The sensor prototype was put in-line with the gas analyzers and emissions gas flow to the prototype was maintained at 500 sccm. Heat was provided to the RTD by setting the voltage on a DC power supply. Gas composition data was

collected at 30 sec intervals and the EMF was collected at 1.0 sec intervals. The testing spanned over 4 hours.

Fig. 4.3.15. GE sensor in the combustion test rig for sampling combustion emissions gas. Emissions gas was kept at a flowrate of 500 sccm using a mass flow controller (not shown). A thermocouple located inside the test rig monitored the test rig ambient temperature during the lifetime of the test.

Figure 4.3.16 shows the gas analyzer data (in ppm and %) during the 4 hour segment of the emissions testing. Total NO_x (in blue) was measured by the gas analyzers, and at some points during the test, the gas analyzer was switched to measure the NO gas composition (red), for a total of 11 NO_x/NO switches.

Fig. 4.3.16. Gas composition during emissions testing measured by gas analyzers.

The unburned hydrocarbons (UHC) were low (<75 ppm UHC) throughout the lifetime of the test. The CO₂ varied from 4.75 – 10%. The CO was higher than expected, with a range of 70 ppm to 530 ppm. NO_x varied from 40 ppm to 1100 ppm, with most of the test around 200 ppm NO_x. The O₂ varied from 6% to 12%, with most of the test around 9% O₂.

Table 4.3.2 Combustion emissions data collected from gas analyzers and GE sensor. Also shown are the % error for the three sensors tested.

Point	GAS ANALYZER									GE NO ₂ SENSOR			
	Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)	O ₂ (%)	CO (ppm)	CO ₂ (%)	HC (ppm)	Ratio (NO ₂ /NO _x)	NO ₂ Sensor (V)	Temp (°C)	NO ₂ calc (ppm)	Accuracy - GE NO ₂ % error
1	51	130	112	242	8.48	519	8.95	38	0.463	0.0426	76.1	82	26.9
2	61	138	119	257	8.53	446	8.88	37	0.463	0.0466	76.5	92	22.6
3	90	70	107	177	7.99	354	9.25	10	0.606	0.0500	77.2	98	9.2
4	108	97	95	192	8.79	273	8.62	13	0.495	0.0527	77.3	110	16.1
5	135.5	178	79	257	9.37	260	8.35	18	0.306	0.0523	77.5	113	43.8
6	177	101	97	198	8.87	198	8.7	16	0.489	0.0515	77.8	107	11.4
7	209.5	84	131	215	7.91	188	9.4	8	0.609	0.0535	77.7	107	18.6
8	228	151	113	264	8.46	332	8.97	30	0.428	0.0495	77.6	99	12.1
9	236.5	340	118	458	9.96	195	7.84	30	0.258	0.0578	77.5	134	13.7
10	239.5	423	140	563	10.58	178	7.4	31	0.249	0.0612	77.6	151	7.9
11	242.5	570	206	776	11.78	138	6.55	67	0.265	0.0623	77.5	165	20.0
												Average	18.4

The gas stream in the laboratory rig was fixed at 500 sccm and was held at a constant temperature (65.1°C), which contributes to a constant temperature in the rig and a fixed background EMF level. Equation 26 adjusts for the background level in the regression analysis of the laboratory data. In the combustion rig, the temperature of the gas stream was changing, and the background level thus changed over the lifetime of the test. Thus, the background adjustment is more complicated in the combustion rig than in the laboratory rig. The temperature in the combustion rig location where the sensors were located was recorded during the life of the test from a K-type thermocouple. The background was collected prior to combustion emissions testing in the combustion emission rig as the sensors were exposed to air. Figure 4.3.17 (a) shows the response of the GE sensor in air as a function of the combustion rig temperature. Figure 4.3.17 (b) shows the actual variation in temperature during the emissions testing where NO_x data was collected.

(a)

(b)

Fig. 4.3.17. (a) Response of GE NO₂ sensor in air with temperature (measured in the combustion rig) and (b) variation in temperature in the combustion rig over the lifetime of the emissions test.

For each of the 11 NO/NO_x switch data points, a background level was calculated using the equations generated from a fit to the collected data in Figure 4.3.18. This estimates the background level for each of the 11 switch conditions, since the rig conditions were changing (unlike the laboratory testing, where the background level was stable and fixed). Additionally, the background level was corrected for oxygen dependency.

The EMF of the background level as a function of oxygen concentration was measured using the laboratory rig. At conditions of 0 ppm NO_x and 1-10% oxygen, the EMF of the GE NO₂ sensor was measured. For the GE NO₂ sensor, the background level measured in the laboratory rig changed by < 0.5 mV for 0 ppm NO_x, and O₂ ranging from 6-10% O₂.

Fig. 4.3.18. EMF of the background level (0 ppm NO_x) as a function of oxygen concentration (measured in the laboratory rig).

The transfer function to convert the EMF from the combustion rig to NO₂ levels are based on data collected at 8.5% O₂. Therefore, the signals from the sensors during combustion emissions testing also need to be adjusted for oxygen dependency. The background level (0 ppm NO_x) and signals with NO_x do not respond in the same way to oxygen so these calculations were done separately. To estimate the oxygen dependency on the GE NO₂ sensor in the presence of NO_x as a function of oxygen, the dependency in Figure 4.3.19 was used. This dependency was collected on similar sensors in the laboratory rig under 600 ppm NO_x with a 0.50 NO₂/NO_x ratio.

Fig. 4.3.19. EMF of the GE NO₂ sensor at 600 ppm NO_x as a function of oxygen concentration. EMF shown is adjusted so that the difference in EMF due to change in O₂ from 8.5% O₂ condition can be easily visualized.

Figure 4.3.20 shows the performance of the GE NO₂ sensor compared to the gas analyzer NO₂ data during the combustion emissions test. The average error of all 11 test points is 18%. The predicted response is in the same ballpark as the actual response, however there are still some differences that need to be resolved.

As mentioned previously, the predicted response was not fit to CO concentrations greater than 100 ppm, and all test points during the emissions testing were at CO concentrations of 138 ppm to 519 ppm CO (i.e., > 100 ppm CO). Second, there are other constituents in the emissions gas that are not tested in the laboratory simulation (such as SO_x species and unburned hydrocarbons). The GE NO₂ sensor response is dependent on O₂ present, so the NO₂ calculation is dependent on an accurate O₂ data. It is also not known the response of the sensors under changing O₂ and NO₂/NO_x conditions – only one condition ([NO₂/NO_x] = 0.50) was used to adjust the data set for oxygen dependence. The error analysis also assumes that the gas analyzer data is accurate, and previous analysis showed that the GE sensors respond faster than chemiluminescence gas analyzers in changing NO_x conditions.

Fig. 4.3.20. Performance of GE NO₂ sensor compared to gas analyzer NO₂ sensor during combustion emissions testing. The dashed lines show the $\pm 10\%$ accuracy window. The GE NO₂ sensor had an average error of 18% compared to the gas analyzers.

The key elements to a more accurate NO₂ sensor are an accurate background signal measurement and robust transfer functions that relate EMF to NO₂ at the ranges of CO, NO₂/NO_x and O₂ in the test. All testing was done on cooled (<100°C emissions gas) due to the limitations of the chemiluminescence NO_x sensor, which was used to quantify the GE sensors response. A large thermal gradient exists at the GE sensor electrode/emissions gas interface at these low emissions

gas temperatures. Operation of GE sensors in a real combustion environment would thus reduce the thermal gradients because the gas would naturally be at higher temperature, and the background and noise level would be significantly reduced. The noise could be further reduced with a more robust ceramic-package design with heaters designed to keep the sensor at constant temperature instead of constant voltage.

Figure 4.3.21 shows the response time for GE sensor element prototype compared to the response time of the stationary gas analyzer, which is based upon chemiluminescence (Signal USA, Model 4000VM). The manufacturer specification for response time of the gas analyzer is 1.5 sec. To measure response time, the probe inside the combustion environment was moved from one physical location containing 1400 ppm NO_x to another location containing 2200 ppm NO_x. The timestamp of the probe movement was compared to the EMF response of the GE sensor and the gas analyzer NO_x reading.

The GE sensor prototype responded to the change in the gas concentration (inferred from change in probe position) faster and with less lag time than the NO_x gas analyzer. These results suggest that the sensor response is faster than measured in lab testing conditions, which are limited in flow rates and by the rate of change in the gas mixes by the mass flow controllers. Because the response is faster and without the lag time of the gas analyzer, the GE NO₂ sensors may have less error than calculated previously because the error in these sensors was based on the assumption that the NO_x reading from the gas analyzer was the correct NO_x value. If conditions were changing rapidly, the NO_x analyzer data could be inaccurate. Future testing would include testing with the gas analyzer and GE NO₂ sensors for a fixed period of time (~1 minute) to let the NO_x signal stabilize and reduce error in the gas analyzer.

Fig. 4.3.21. Response of one GE sensor element prototype (pink) and gas analyzer (blue) in real time. The probe position was moved from 1400 ppm NO_x concentration to a 2200 ppm NO_x concentration over a period of 6 seconds. The gas analyzer took ~2x as long as the GE sensor element prototype to change concentration (or EMF in case of the GE sensor prototype).

5. BENEFITS ASSESSMENT

The successful development of nanoengineered harsh-environment sensors would enable a new generation of combustion-process heating systems with increased efficiency, expanded fuel flexibility, more reliability, and reduced cost. With very conservative assumptions on the potential for energy savings, this technology is expected to result in annual energy savings of about 24 trillion Btu.

Combustion processes accounted for more than 70% of the total energy used in six U.S. industry sectors —petroleum, chemicals, steel, aluminum, glass, and metal casting [Energetics, Inc, 1998, 1999, 2000a, 2000b, 2002]. In aggregate, these industries consumed 5.8 quads of energy, 92% in the form of fossil fuels and 8% in electricity, for process heating.

With its wide and varied industrial use, process heating directly and indirectly affects the employment of an estimated 16 million people in the United States at more than 300,000 establishments, with total annual sales and shipments worth \$3.8 trillion [Capital Surini Group, 2001]. The ubiquity of process heating operations throughout industry means that even relatively small improvements in the efficiency of combustion-based process heating systems can lead to significant energy savings and emissions reductions.

The estimates provided in this analysis are based on conservative assumptions. Only a 0.5% efficiency gain is assumed, rather than the 5 to 30% estimate used in the Roadmap for Process Heating technologies. This is based on GE's experience with commercial balancing systems for coal boiler power plants which has shown that automation can produce a sustainable increase in combustion efficiency of at least 0.5% and as much as 2%, while also increasing availability.

At market saturation (80%), nanoengineered harsh-environment sensor systems could result in annual energy savings of at least 24 trillion Btu, assuming a conservative 0.5% improvement in efficiency. In addition, one million metric tons total carbon equivalent (TCE) of CO₂; 5,500 metric tons of SO₂; 3,000 metric tons of NO_x; 2,000 metric tons of particulates; 1,600 metric tons of CO; and 430 metric tons of volatile organic compounds (VOCs) would be avoided annually due to reduced fuel use.

6. COMMERCIALIZATION

The path for commercialization for the GE NO₂ sensor is to follow the established technology development process. The technology will be evaluated in the New Technology Introduction process against the technology development milestones according to a Technology Readiness Level (TRL) assessment. The technology is currently assessed to be at a TRL5. Additional testing of the sensor technology in a variety of services conditions will be required. For example, the sensor should be tested in a wider range of NO_x combustion environment with the prototype at the temperature of the service environment. Further assessment is needed that includes operating temperature range, and the performance of the sensor in a variety of combustion gas environment ranges. The performance will be assessed against product requirements and optimal markets identified.

7. ACCOMPLISHMENTS

During the project the following milestones were achieved:

- 1) Hierarchical, porous electrode structures were synthesized.
 - Eight structures were produced with surface area $> 1 \times 10^8 \text{ m}^2/\text{m}^3$ ($> 10\times$ over the baseline)
- 2) Processes were developed for synthesizing sensing nanomaterials:
 - Eight oxide materials were synthesized with $< 100 \text{ nm}$ crystallite sizes using combustion synthesis, wet chemical methods and post-processing techniques
- 3) Catalytic nanomaterials capable of operating in harsh environments were identified and synthesized
 - Three nanomaterials were produced that showed catalytic activity for NO_x using temperature-programmed-reaction and temperature-programmed-desorption at temperatures above 400°C .
 - 15 oxide sensing materials were screened for high temperature sensing activity for NO_2 with 5 materials identified with greater than $10 \text{ mV} / 100 \text{ ppm}$ sensitivity at temperatures greater than 600°C .
- 4) A process for functionalizing hierarchical structures was developed
 - Co-synthesized $\text{LaFeO}_3/\text{YSZ}$ structures were produced with 50% volume fraction of LaFeO_3 phase with both phases containing $< 100 \text{ nm}$ crystallite sizes
- 5) The materials performance was demonstrated in a sensing element
 - Sensitivity and selectivity was demonstrated for NO_x in the temperature range $400\text{-}800^\circ\text{C}$ of $\pm 10 \text{ ppm}$ ($0\text{-}100 \text{ ppm}$) in a gas blending rig
 - Sensitivity and selectivity for NO_2 for the prototype sensors were determined in a lab rig for $0\text{-}10\% \text{ H}_2\text{O}$, $0\text{-}300 \text{ ppm NO}_2$, $0\text{-}600 \text{ ppm NO}$, $3, 6$ and $8.5\% \text{ O}_2$, and $0, 20$ and 100 ppm CO
- 6) The materials performance was validated in a simulated service environment
 - Sensitivity and selectivity was demonstrated for NO_x in a combustion gas rig
 - Sensor prototypes were produced that displayed 18% accuracy in predicting NO_2 in actual combustion environment with $79\text{-}206 \text{ ppm NO}_2$ and $70\text{-}570 \text{ ppm NO}$ conditions using simple models based on laboratory testing.

Presentations, Publications, and Patents

- "Combustion Synthesis of LaFeO_3 and LaMnO_3 Perovskite Nanopowders for Functionalized Nanostructures" was presented at the 33rd International Conference & Exposition on Advanced Ceramics and Composites on January 23, 2009 by Todd Striker of GE Global Research.
- "TPD/TPR Evaluation of Oxide Nano-Materials for Sensor Applications," was presented at the 33rd International Conference & Exposition on Advanced Ceramics and Composites on January 23, 2009 by Eric Armstrong of University of Florida.

- “NO_x Adsorption Behavior of LaFeO₃ and LaMnO_{3+δ} and Its Influence on Potentiometric Sensor Response,” E.N. Armstrong, T. Striker, V. Ramaswamy, J.A. Ruud, and E.D. Wachsman, manuscript submitted to Sensors and Actuators B.
- “Effect of fuel choice on the aqueous combustion synthesis of lanthanum ferrite and lanthanum manganite,” T. Striker and J.A. Ruud, J. Am. Ceram. Soc. v93 (9), 2622-2629 (2010).
- “Kinetic and catalytic characterization of lanthanum ferrites and manganites for gas sensor and fuel cell applications,” Eric. N. Armstrong, University of Florida, Ph.D. Thesis, 2010.
- Patent application: Selective gas sensor device and associated method, Docket 235379-1

8. CONCLUSIONS

Conclusions are presented below for hierarchical sensor electrodes, sensing material synthesis and mechanisms, and sensor testing.

Hierarchical Nanoceramic Sensor Electrodes

- Eight structures were produced with surface area $> 1 \times 10^8 \text{ m}^2/\text{m}^3$.
- A new high speed linear array x-ray detector for time-resolved x-ray powder diffraction and a high temperature furnace allowed higher temperature for accelerated aging tests of hierarchical nanostructures and faster measurement capabilities for measuring the products from the synthesis of the catalytic nanomaterials.

Sensing Material Synthesis and Mechanisms

- Processes were developed for synthesizing sensing nanomaterials and eight oxide materials were synthesized with $< 100 \text{ nm}$ crystallite sizes using combustion synthesis, wet chemical methods and post-processing techniques.
- Aqueous combustion synthesis produced lanthanum manganite and lanthanum ferrite nanopowders with a high degree of crystallinity and chemical homogeneity after calcination. For stoichiometric amounts of fuel and oxidizers, where the volume combustion synthesis mode is typical, using glycine resulted in higher surface areas and lower crystallite sizes for lanthanum manganite powders compared with using ethylene glycol as the fuel.
- From TPD, TPR, and DRIFT results, LaFeO_3 and LaMnO_3 were shown to have complex nitrite and nitrate surface formation when NO or NO_2 are adsorbed. NO_x sensor mechanisms on LFO and LMO are proposed to have semiconducting mechanism contributions related to the formation of surface species and Differential Electrode Equilibria is proposed to explain the sensor performance of semiconducting oxides.
- LaFeO_3 based sensors had a higher EMF than those using LaMnO_3 sensing electrodes at temperatures known to have significant NO_2 generated surface adsorbents consistent with the Differential Electrode Equilibria theory.
- Two design considerations were determined to be critical for sensing of NO_x gas at high temperatures: 1) materials with semiconducting behavior caused by gas adsorption at low temperatures ($< 400^\circ\text{C}$) do not contribute to sensor response in the temperature ranges of interest, and therefore should not be considered as potential electrodes; and 2) materials with high gas-phase catalytic activity reduce the mixed-potential response and are also not in consideration for sensing electrode.
- Using the design considerations, metal oxide samples were screened for use in high temperature NO_2 , NO and CO gas sensors. Of the samples screened, five metal oxide materials were found to have sensitivity and selectivity for sensing NO_2 at temperatures of 600°C and 700°C .

Laboratory and Combustion Testing of Sensors

- Sensitivity and selectivity for NO_2 for the prototype sensors were determined in a lab rig for 0-10% H_2O , 0-300 ppm NO_2 , 0-600 ppm NO , 3, 6 and 8.5% O_2 , and 0, 20 and 100 ppm CO
- Sensor to sensor repeatability was displayed for NO_2 sensor prototypes
- A method of enhancing GE sensor sensitivity by 3x was demonstrated in laboratory rig

- Sensor prototypes were displayed 18% accuracy in predicting NO₂ in real combustion environment with 79-206 ppm NO₂ and 70 -570 ppm NO conditions using simple models based on laboratory testing.
- Sensor prototypes displayed similar or better response time as a commercial chemiluminescence gas analyzer.

9. RECOMMENDATIONS

This project demonstrated feasibility of a solid state NO₂ sensor starting from applied research (TRL 2) through technology development in the laboratory environment and laboratory testing of a semi-integrated system (TRL 5) with prototype sensors. Further testing and modifications are recommended to move the GE hierarchical sensor to TRL 6 (technology demonstration) and beyond.

In this project, the feasibility of the sensor was demonstrated in the laboratory environment and validated in a dried and cooled real combustion gas. Further testing on this sensor should include testing in the combustion chamber where moisture is present ($T > 400^{\circ}\text{C}$). Testing in this way reduces thermal gradients on the sensors and evaluates the sensor in a real combustion environment where humidity is present. Qualification of a sensor across a wider range of O₂, NO, NO₂, CO should be completed to develop a more comprehensive transfer function of the response of the sensor that encompasses the entire range of constituents present in the combustion gas. Specific market applications can be targeted based on the specific operating profile of the sensor.

In addition, in order to move to TRL 6 and beyond, an integrated ceramic package design would be required that optimizes the functionality of the sensor and provides durability and insensitivity to transient operating conditions.

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