DEVELOPMENT OF HARSH ENVIRONMENT NITROGEN OXIDES SOLID-STATE GAS SENSORS

DISSERTATION

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By

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ABSTRACT

The goal of this dissertation was to study and develop high temperature solid-state sensors for combustion based gases. Specific attention was focused on NO\textsubscript{x} gases (NO and NO\textsubscript{2}) as they are of significant importance with respect to the environment and the health of living beings.

This work is divided into four sections with the first chapter being an introduction into the effects of NO\textsubscript{x} gases and current regulations, followed by an introduction to the field of high temperature NO\textsubscript{x} sensors and finally where and why they will be needed in the future.

Chapter 2 focuses on the development of a gas sensor for NO\textsubscript{x} capable of operation in harsh environments. The basis of the sensor is a mixed potential response at 500/600°C generated by exposure of gases to a platinum-yttria stabilized zirconia (Pt-YSZ) interface. Asymmetry between the two Pt electrodes on YSZ is generated by covering one of the electrodes with a zeolite, which helps to bring NO/NO\textsubscript{2} towards equilibrium prior to the gases reaching the electrochemically active interface. Three sensor designs have been examined, including a planar design that is amenable to packaging for surviving automotive exhaust streams. Automotive tests indicated that the sensor is capable of detecting NO in engine exhausts.
Chapter 2 concluded that it is difficult to measure NO or NO₂ selectively especially when both gases are present at the same time thus we have developed a strategy in chapter 3 to measure the total NOₓ level (NO + NO₂) in a background of O₂ and N₂ at high temperatures with minimal CO interference by combining a catalytic filter bed with the existing YSZ sensor device. The filter bed was composed of a Pt catalyst dispersed onto a zeolite Y support placed before a YSZ sensor having an air reference with a Cr₂O₃ or Pt sensing electrode.

Chapter 4 explores the reasons for the difference in sensitivity of metal oxide electrodes, Cr₂O₃ and a mixed conducting perovskite La₀.₆Sr₀.₄Fe₀.₈Co₀.₂Oₓ, with the goal of ultimately developing a systematic method of electrode screening as compared to the random screening often found in the literature.
Dedicated to my parents

*Barbara* and *Frederick Szabo*

and grandparents

*Nida* and *Nicholas Coreno*
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1. Nicholas F. Szabo, Prabir K. Dutta, “Strategies for Total NOx Measurement with
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CHAPTER 1
INTRODUCTION

The development of miniaturized chemical sensors for a variety of species in the gas and liquid phases for different applications is an increasingly growing area of research [1]. The driving force towards chemical sensor development is the potential to be much cheaper, smaller and more “mobile” than traditional analytical instruments that are used today. A few examples of major areas where gas and liquid sensors have been used or will be needed are: emission and combustion processes monitoring in vehicles and for fire and smoke detection [2], emissions monitoring in industrial processes such as power plants [3], \textit{in vivo} measurements of biological systems (e.g. NO biosensors) [4, 5], explosive [6] and chemical warfare agent [7, 8] detection and engine oil degradation monitoring [9, 10].

This dissertation will concentrate on the development and study of high temperature solid-electrolyte NO$_x$ (NO and NO$_2$) gas sensors with an application towards combustion-based systems such as gasoline or diesel based vehicles and coal-fired boilers in power plants. The first part of Chapter 1 will discuss the general principles and issues of high temperature gas sensors, which will be followed by a more detailed account of the types of existing NO$_x$ sensors and the challenges for their development. In Chapter 2 attention will be focused on a "proof of concept" idea to create a simple laboratory based
NO or NO\textsubscript{2} potentiometric sensor utilizing a microporous zeolite and developing a prototype device to be tested in a real automotive engine. Chapter 3 will chronicle the development of a selective total NO\textsubscript{x} sensing system employing a zeolite catalytic filter bed. Finally Chapter 4 will detail fundamental studies to better understand the chemical processes of the NO\textsubscript{x} sensor mechanism using a metal oxide electrode system.

1.1 The need for harsh environment NO\textsubscript{x} sensors

1.1.1 The environmental, health effects and sources of NO\textsubscript{x}

NO\textsubscript{x} gases including both NO and NO\textsubscript{2} can have a negative impact on the environment as well as human and animal health [11]. The formation of smog commonly seen over large metropolitan areas arises from a combination of NO\textsubscript{x} species, hydrocarbons reacting with ultraviolet light. Photochemical smog can cause eye and lung irritation, reduced visibility, crop destruction and can lead to formation of corrosive compounds. The brown color in smog arises mostly from nitrogen dioxide (NO\textsubscript{2}) [11]. NO\textsubscript{x} gases and the sulfur oxides, SO\textsubscript{2} and SO\textsubscript{3} are precursors for acid rain, and can dissipate many miles from where they were initially produced. These gases react to form nitric (HNO\textsubscript{3}) and sulfuric (H\textsubscript{2}SO\textsubscript{4}) acids, respectively. Acid rain has impacted the environment and affected many natural biosystems. Some consequences of acid rain are forest destruction, respiratory problems in humans and animals, and corrosion of buildings and exposed equipment [11, 12].

There have been many studies on the health and physiological effects of NO and NO\textsubscript{2} in the biomedical field [13-17]. The recognized importance of nitric oxide is shown by the ever increasing number of academic publications devoted to this molecule, the
formation of an entire journal devoted to NO, *Nitric Oxide: Biology and Chemistry* [18], and a 1998 Nobel Prize in Physiology and Medicine for research on NO as a signaling molecule [19]. Medical studies have shown that NO can act as a vasodilator that relaxes smooth muscle, which is important for various cardiac conditions [15]. Inhalation of larger amounts of NO\textsubscript{x} can result in respiratory irritation, headache, nausea, vomiting, and may cause death due to pulmonary edema. Repeated exposure could result in a permanent decrease in pulmonary function [11, 20]. NO\textsubscript{2} is more toxic than NO in that inhalation of 50-100 ppm for several minutes to an hour can cause lung inflammation for 6-9 weeks. Direct exposure to 150-200 ppm can cause *brochiolitis fibrosa obliterans*, which is a fatal condition after 3-5 weeks and 500 ppm NO\textsubscript{2} can result in death within 2-10 days [11].

The main sources of anthropogenic NO and NO\textsubscript{2} are internal combustion engines such as the reciprocating types (gasoline and diesel) used in cars and trucks [21, 22], gas turbines in small power plants, and airplanes and tanks [23], as well as non-engine based uses such as coal-fired power plants [24], and process heaters [25, 26].

The NO\textsubscript{x} that is produced from these sources comes from three processes. When the air-fuel mixture is lean, N\textsubscript{2} in the ambient air can combine with molecular O\textsubscript{2} at high temperatures (thermal NO\textsubscript{x}), under air-fuel rich conditions N\textsubscript{2} can react with hydrocarbon radicals (prompt NO\textsubscript{x}), and finally N content in the fuel can react with O during combustion (fuel NO\textsubscript{x}) [27]. Ultimately the amount of NO\textsubscript{x} formation is dependent on fuel type, temperature, and air/fuel mixing. Figure 1.1 shows that the cycle of NO\textsubscript{x} formation in a combustion environment is a complex process with many intermediates. For a detailed description of pulverized coal combustion in boiler systems refer to the
book by Smoot et al [28] and for a discussion of internal combustion engine fundamentals and NOx formation refer to the book by Heywood [29].

NO and NO2 are the subject of this work, however it is important to mention another important NOx species called nitrous oxide (N2O) which has had many uses such as an anesthetic in the medical field (“laughing gas”) [30], a proposed rocket fuel component [31], and as an ingredient in whipped cream propellant cartridges [32]. The anthropogenic sources of N2O in the environment come from combustion emissions [33] as shown in Figure 1.1 [27] and from fertilizer sources [34]. Only two percent of the total NOx emission from automobiles is N2O and about 0.1% of the calculated temperature rise due to greenhouse gases is believed to be caused by N2O [35].

1.1.2 Legislation on NOx emissions

Due to the serious nature of environmental and health effects of NOx most governments around the world have imposed some type of regulations on the amount of emissions allowed [36]. Some of the main species that are regulated are: NOx (NO, NO2, N2O), SOx, CO, CO2, hydrocarbons (HC), and particulate matter and the specific rules and laws vary according to the country. The discussion in this section will focus on the U.S. but other large players such as the European Community [37] and Japan [36, 38] have parallel standards as well.

In 1970's the EPA was formed in the U.S. and set limitations on the amount of NOx that can be emitted from mobile and stationary sources by enabling the Clean Air Act [39]. The Clean Air Act is composed of various parts dedicated to different pollutants with Title IV addressing NOx emissions. Over the years there have been various changes
to the original Clean Air Act as in the Clean Air Act Amendments of 1990, with further modifications in 1997 regarding ozone destruction, and just recently in July of 2002 the Clear Skies Act was proposed by President Bush that modifies Title IV for better regulation of NO\textsubscript{x}, SO\textsubscript{x} and Hg emissions from coal-fired boilers in power plants. Although the Clean Air Act is a federal set of laws (encompassing over 400 pages), it allows individual states to impose even tighter emissions regulations if desired.

The two NO\textsubscript{x} sources that have received the most attention are vehicles (cars and trucks) and coal-fired boilers due to their leading role in global NO\textsubscript{x} emissions. The pie Chart in Figure 1.2 from a recent Clear Skies EPA report [40] shows a breakdown of where NO\textsubscript{x} emissions came from in the year 2000. It is clear that the largest NO\textsubscript{x} source was from vehicles and power plants and they deserve special attention.

In the US mobile source NO\textsubscript{x} emissions are determined by specific methods called the Federal Test Procedures (FTP) [41, 42] as outlined in Title 40 of the code of federal regulations (CFR) published in the federal register [43]. Table 1.1 shows the current EPA regulations for the total NO\textsubscript{x} emission (NO + NO\textsubscript{2}) over the duration of the FTP driving cycle from small passenger vehicles for the years 1975 to 2009. The table indicates that for newer model cars the regulations become increasingly stricter. The units for NO\textsubscript{x} emission from mobile sources are given as mass of total NO\textsubscript{x} emitted per distance traveled during the FTP cycle for example g NO\textsubscript{x}/mi or g NO\textsubscript{x}/km. Vehicle owners in major metropolitan areas are required to take their vehicles to an "E-check" station to see if the amount of emissions are in compliance with EPA regulations and they will receive a pass or fail grade [44]. The FTP involves putting the vehicle on a dynamometer and using a specified driving cycle depending on the vehicle make and
model defined in Title 40, part 86 of the CFR [43]. The total mass of NO\textsubscript{x} emitted over the distance of the drive cycle is typically acquired by a constant volume sampling (CVS) measurement. This involves filling a bag of known volume with an air diluted exhaust sample. Measuring equipment such as a chemiluminescence detector (CLD) or a Fourier Transform infrared analyzer (FTIR) [45] determine the NO\textsubscript{x} concentration inside the bag. By knowing the NO\textsubscript{x} concentration an equation can be used to calculate the total NO\textsubscript{x} level in g/mile. A paper by Adachi and references therein describes the method in further detail [45].

Interestingly today's vehicles emit 60-80% less pollution than in the 1960's but despite the implementation of the Clean Air Act, the overall pollution in the US has not decreased. This is due to a variety of reasons such as the number of total miles driven in a given year have quadrupled since the 1970's (1 trillion miles in 1970 verses 4 trillion in 2000), people live farther from work and there are relatively few commuter buses and subways, there is a lack of carpooling, bus and truck regulations have not been as strict as passenger car regulations and fuels have become more polluting since after phasing out lead new formulations emit more volatile organic compounds (VOCs) [39].

The Clean Air Act also established regulations for the various types of coal-fired boilers (a stationary source) shown in Table 1.2 [46] as defined in Title 40, part 76 of the CFR published in the federal register [47]. The recent Clear Skies Proposal [48] attempts to further tighten the allowed emissions from boilers by modifying Title IV of the Clean Air Act. It proposes to cut emissions of NO\textsubscript{x} from power plants by 67 percent more than the current Clean Air Act would in the next 10 years, from current emissions of 5 million tons/yr to a cap of 2.1 million tons/yr in 2008, and to 1.7 million tons/yr in 2018.
For stationary sources such as boilers the emission units are usually given as lb NO\textsubscript{x}/million Btu or lb NO\textsubscript{x}/MWh. Parts 75 and 76 of Title 40 in the CFR [47, 49] define the limits for total NO\textsubscript{x} emissions as shown in Table 1.2 and the rules for monitoring them. The owner or operator of a coal-fired boiler must follow various protocols and set up a continuous emissions monitoring system (CEMS) [50] that periodically measures the NO\textsubscript{x} concentration (NO + NO\textsubscript{2}) in ppm and also the emission rate in lb NO\textsubscript{x}/million Btu.

To meet the future emission requirements manufacturers have implemented a variety of solutions to control NO\textsubscript{x} as will be described in section 1.1.3.

1.1.3  Methods to control NO\textsubscript{x} emissions and where a NO\textsubscript{x} sensor is needed

1.1.3.1 Vehicles (mobile sources)

Exhaust gases in a typical spark ignition engine during high power use can reach temperatures as high as 900°C. During normal idle, the temperature range is around 300 to 400°C. On average, the engine exhaust temperature falls in the 400 to 600°C range [29]. Emissions including CO, HC, and NO\textsubscript{x} are formed in the engine cylinders and a typical exhaust gas composition contains ~12% CO\textsubscript{2} and H\textsubscript{2}O, 100 to 200 ppm NO, ~1 to 5% O\textsubscript{2}, 0.2 to 5% CO, 1000 to 6000 ppm HC, ~20 ppm SO\textsubscript{2} and low amounts of phosphorous and lead [29]. In gasoline automobiles 95% of the total emitted NO\textsubscript{x} is in the form of NO [51] due to its stability at high temperatures with the rest being in the form of NO\textsubscript{2} and N\textsubscript{2}O.

Traditional methods that have been utilized for treatment of the exhaust stream include oxidizing catalysts for HC and CO, and reduction catalysts for NO\textsubscript{x} species, or
three-way catalysts (TWC) composed of a mixture of Pt, Rh, Pd and metal oxides dispersed onto a monolith to treat all three types of pollutants. The TWC has its highest conversion efficiency at a certain O$_2$ level, near the stoichiometric air/fuel ratio (A/F) of 14.6, in the engine exhaust as shown in Figure 1.3. Modern fuels are made without lead because it can poison the TWC, which significantly reduces efficiency. An O$_2$ sensor is employed in a feedback loop with the engine computer to control the A/F in the combustion process in accordance with the TWC requirements. The O$_2$ sensor is also referred to as a lambda sensor because A/F is often shown as $\lambda$. Figure 1.4 shows a schematic of the O$_2$ sensor and the TWC placement in relation to the automobile engine adapted from the Bosch automotive handbook [52]. Figures 1.5 [53, 54] and 1.6 [55] show the oxygen sensor package and a schematic of it placed into the tailpipe of the engine. The actual physical design of the O$_2$ (A/F) sensor body is a small 1” length thimble shaped piece of yttria stabilized zirconia placed inside the package. Currently most commercial and research grade automotive chemical sensors are designed and built to fit into the type of standard packaging dimension of the O$_2$ sensor.

The O$_2$ sensor operates mainly in an on/off mode and not with a standard calibration curve (there are newer O$_2$ sensors that actually use a calibration curve). The lambda O$_2$ sensor gives an output voltage between 0-5V, which is dependent on the A/F of the combustion gas. The O$_2$ sensor tells the engine control unit (ECU) whether or not the gasoline mixture is rich or lean from stoichiometry i.e. high or low A/F. If there is a deviation from 14.6 the O$_2$ sensor signal quickly changes and this change will make the ECU tell the engine cycle to go back to the 14.6 ratio where there is optimal efficiency. Over time the precious metals and metal oxides in the converter can sinter and decrease
the conversion efficiency. In some newer cars a second O\textsubscript{2} sensor is placed after the TWC to monitor the catalyst efficiency to further improve combustion control. It would also be desirable to have direct NO\textsubscript{x} sensors before and after the catalyst for a more accurate measurement [22]. This TWC/O\textsubscript{2} sensor system is still widely used today in many cars but there are limitations in that the fuel efficiency of traditional gasoline engines needs to be improved. To increase efficiency there is a push for the development of alternative engine types such as lean-burn gasoline engines and diesel engines that consume less fuel for passenger vehicles. However, the TWC does not work as well in the lean regime and other leading methods for NO\textsubscript{x} control are being developed including direct decomposition catalysts, NH\textsubscript{3} or hydrocarbon selective catalytic reduction (SCR) and NO\textsubscript{x} storage devices [56].

With direct decomposition catalysts the idea is to develop a catalyst that can directly reduce NO\textsubscript{x} to the elements without the need for CO or hydrocarbons. This is the holy grail of NO\textsubscript{x} abatement research as it offers the simplest engineering approach. However there has been extensive research in this area and an ideal catalyst has not been found that performs well under real exhaust conditions. The materials that have been studied the most are zeolites, precious metals, and metal oxides [51]. A NO\textsubscript{x} sensor would monitor the performance of the DeNO\textsubscript{x} catalyst similar to monitoring the TWC.

SCR involves reducing the NO\textsubscript{x} compounds over a catalyst with NH\textsubscript{3} or hydrocarbons to form N\textsubscript{2} and water [57]. In the case of ammonia the overall reactions occur as:

\[ 4 \text{NO} + 4\text{NH}_3 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1.1) \]

\[ 6 \text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \quad (1.2) \]
In reality, storing NH$_3$ on a vehicle can be dangerous and urea, which is non-toxic and non-explosive, has been used as a starting material to generate NH$_3$ in-situ [58]. Similarly alkanes and alkenes have been used in HC-SCR using zeolites, oxides and noble metals [51]. In both these methods a NO$_x$ sensor is highly desirable to control the amount of NH$_3$, urea or HC that is injected so as not to have excess ammonia or hydrocarbons emitted from the tailpipe [21]. The NH$_3$/urea-SCR and HC-SCR methods have not been implemented on commercial vehicles yet.

NO$_x$ storage devices are composed of precious metals (Pt,Rh), alkali, alkaline earth, and rare earth oxides on a support. The general idea is that the oxides can store the NO$_x$ at lean conditions [51, 56], and after a short burst of richer fuel composition, the metals will reduce the stored NO$_x$ to N$_2$ and regenerate the NO$_x$ trap. When the NO$_x$ storage device is saturated there will be a NO$_x$ "break through" and when this occurs the rich pulse can be initiated. A NO$_x$ sensor could be used to observe this breakthrough for precise timing of the trap regeneration [21].

The Clean Air Act requires all 1996 or later model year cars to have an on-board diagnostic (OBD) system for emissions monitoring and control [59]. For gasoline cars the dual oxygen sensors, and electronics that can store any fault information are key portions of the OBD system [60]. For example, the driver can be alerted if something is wrong with the converter performance or O$_2$ sensors and the check-engine light will come on. Any additional sensors for existing and new emissions control equipment would become part of the OBD system.

Diesel engines also operate in the lean region and the methods described above can also serve to minimize emissions from this type of engine. It has also been discovered
that by adding water to diesel fuel to form an emulsion the amount of NO production can be significantly reduced. The water lowers the combustion temperature, which reduces the NO formation although this can have an effect on the overall achievable power from the engine [61].

Research is also ongoing to model automobile emissions such as NO\textsubscript{x} for better vehicle exhaust control design [62].

1.1.3.2 Coal-fired boilers (stationary sources)

As shown in section 1.1.2 on NO\textsubscript{x} legislation there are various types of boilers for burning coal. In recent years low-NO\textsubscript{x} burner technology has been developed [46] that will reduce NO\textsubscript{x} formation at the source. Post formation NO\textsubscript{x} treatment in boilers is also accomplished by using NH\textsubscript{3}-SCR technology described earlier [51, 57, 58]. A NO\textsubscript{x} sensor is needed to monitor the NO\textsubscript{x} content to optimize the coal-burning process and control SCR.

1.2 Future NO\textsubscript{x} sensor requirements

There has been considerable research effort towards the development of an effective high-temperature NO\textsubscript{x} sensor due to the future needs described in section 1.1.3 earlier. A recent search in November 2002 of the Chemical Abstracts Database using SciFinder under keyword “NO\textsubscript{x} Sensor” gave 1324 total references with almost 60% as patents. The number of references has increased each year with 83 in 1996 to more than double that in 2001 with 180. Figure 1.7 shows number of publications for the top 17 years since 1980.
The general criteria for a NO\textsubscript{x} sensor is that it should selectively detect NO, NO\textsubscript{2}, at levels of 5-300 ppm NO and NO\textsubscript{2} [22, 63, 64] in a 3-8% O\textsubscript{2} environment with water vapor present. Since regulatory agencies have strict limits on emissions expressed as total NO\textsubscript{x}, sensors that provide a measure of the sum of NO and NO\textsubscript{2} as total NO\textsubscript{x} are also desirable. Physically the sensor should be stable at high gas flow rates, during large possible temperature swings (300-700°C depending on the engine type) and in a dirty soot (particulate) laden environment. The response time should be fast for combustion control (100 ms) while simple OBD diagnosis does not require as fast a response time. The sensor should be selective and not respond to fluctuating O\textsubscript{2} environments, CO, HC, SO\textsubscript{x}, H\textsubscript{2}O and NH\textsubscript{3}. A simple design is essential for low-cost manufacturing and commercialization. Of course each of the applications above will require specific criteria for sensor performance.

The difficulty in making a commercial, functioning sensor is the nature of the harsh environment. Only one company (NGK) has brought a total NO\textsubscript{x} sensor to market and its reliability is questionable. In addition the sensor must have similar properties to most analytical instrument detectors of quick response time, stability, recovery, and sensitivity. Ultimately, obtaining a stable sensor calibration curve is what has limited the development of these sensors.

There are three main research and development areas to make a final commercial sensor product, which includes first designing the sensor element with all the desirable properties such as selectivity and sensitivity. Next, an appropriate package must be designed. This includes a heating element for the sensor and a shield for the sensor element to protect against soot particles and water droplets in the exhaust as well as
minimizing the temperature fluctuations due to the high gas flow. The shield has a specially designed hole and slit architecture to allow gas to flow in a relatively controlled path to the sensor element. In addition the package must be properly designed to withstand high temperatures and maintain a proper heat distribution throughout the device as well as grounding when necessary [65, 66]. The third important area is the electronic control of the sensor which can include the heater feedback loops, signal processing, and other circuit control elements such as applied voltages and currents (i.e. in amperometric sensors or in biasing sensor electrodes to promote a particular chemical reaction). The sensor control circuit itself must have a fast rise time and often be able to do multiple tasks [67]. The design of the chemical sensor element is often the focus of academic journal papers due to the fundamental research nature and lower startup costs. While the latter two areas, which include the packaging and electronic circuit control design, are often the subject of patents by companies. Since the commercial sensor is a device, which includes all the above elements it must be ultimately cheap enough to sell in the marketplace and be durable enough to have a useful working life.

1.3 The existing types of high temperature NO\textsubscript{x} gas sensors

The majority of high temperature solid-state combustion gas sensors have been made from ceramic materials that have a high melting point to withstand the high temperatures of the application. Two main types of these sensors that have been studied are the solid electrolyte [68] and the semiconducting [69] designs. The solid electrolyte design will be the focus of this dissertation and is operated in potentiometric mode, which gives a voltage output signal depending on the NO\textsubscript{x} content like the original oxygen
sensor. The solid electrolyte type has also been used in amperometric mode in the literature. The semiconducting metal oxide sensors also known as resistance or conductance types give a change in resistance or conductance as their transduction signal. Their design is very simple generally consisting of an insulating substrate, typically alumina, with two Au electrodes, and a metal oxide layer on top of the electrodes. The metal oxide can be tailored to give the desired sensing properties by adding dopants, and controlling particle size and layer thickness. Although the semiconducting sensors have been successful for the detection of NO\(_x\) their advanced development has been limited due to material stability and lack of selectivity. Since they are an important NO\(_x\) sensor type, Table 1.3 lists various references about resistive type NO\(_x\) sensors along with the material used as the sensing layer. Refer to the references for a specific account of the sensor preparation and testing.

Examples of other types of chemical gas sensors which have also been used for NO\(_x\), such as the quartz crystal microbalance (QCM) [98], the capacitive type [99, 100], surface acoustic wave (SAW) devices [101], and gas sensors coupled with neural networks [102] or fuzzy logic [103] algorithms can be found in the corresponding references. The next sections will discuss in more detail the general principles of solid-electrolyte potentiometric gas sensors and their different designs as well as the existing challenges in the field.
1.4 Potentiometric sensors

1.4.1 Electrolyte types

The simplest form of a potentiometric solid-state gas sensor is a solid electrolyte on which is placed two electrodes as shown in Figure 1.8. The solid electrolyte is an ionic conductor and needs to be heated past a certain temperature for ionic conduction to occur and the temperature depends on the type of electrolyte. The literature has shown various electrolytes that conduct a variety of different ions used in gas sensor applications. A few of the many examples are: O\(^{2-}\) (Yttria stabilized zirconia (YSZ)) [68], Ce\(_{0.9}\)Gd\(_{0.2}\)O\(_{1.9}\) [104], Na\(^+\) (Na-\(\beta\)-alumina [105], NASICON [106]), Ag\(^+\) (Ag-\(\beta\)-alumina [107]), and even a nitrosonium ion conducting, NO\(^+\) (Ga\(_{11}\)O\(_{17}\) [108, 109]). In practice the solid electrolyte can be formed into any shape for the desired application within the limit of its machineability.

1.4.2 Sensor electrodes

The sensor electrodes can be placed anywhere on the surface of the electrolyte as long as they are on a heated portion. In addition often a third or even fourth electrode can be used to provide a reference or second sensing electrode can be used.

Various electrode materials have been utilized in the literature with some of the earliest being pure metals such as Au, Pt, and Ag. These metals have excellent mechanical stability and do not easily delaminate from the electrolyte. Pt has excellent high temperature stability and is still used in today’s O\(_2\) sensor. There has been a move to utilize metal-oxide electrodes (either electronic conducting or mixed conducting (ionic and electronic)) or even metal/ceramic composites (cermet electrodes) both of which
have seen applications in fuel cell research. These electrodes have the potential to offer better performance in sensing and can be cheaper than noble metal electrodes. Although one problem has been the mechanical stability of these electrodes in harsh environments as compared to metals.

1.4.3 Measurement principle

For a simple potentiometric gas sensor the potential difference between the two electrodes is measured versus time in a changing gaseous atmosphere. The potentiometric sensor signal is a voltage change, which represents a changing condition in the gas. The potential difference arises because there is an asymmetry in the chemical reactivity of the two electrodes towards the analyte gas. Electrochemical reactions that ultimately affect the electrochemical potential at each electrode are believed to take place at the triple point boundary (TPB) between the electrode, gaseous phase and the electrolyte. In the case of a mixed conducting electrode the triple point boundary phase can be extended into three dimensions above the surface of the electrolyte.

1.4.4 A real world example: the potentiometric O$_2$ sensor

As discussed earlier, one of the first commercial gas sensors was the O$_2$ sensor of which many ideas and sensor designs used today are based on. A brief discussion of the O$_2$ sensor principle will be useful as a foundation for the NO$_x$ sensor mechanism. The O$_2$ sensor is composed of the solid electrolyte YSZ ($O^{2-}$ anion conductor) and must be heated above 350-400°C to reach the activation energy of conduction. The sensor takes the form of an electrochemical cell with two porous electrodes, one being an air reference and the
other a sensing electrode exposed to the sensing gas. The sensing and reference electrodes are made of Pt and the electrochemical cell structure can be represented as:

\[ P_{O_2}(\text{air reference}), \text{Pt} | \text{YSZ} | \text{Pt}, P_{O_2}(\text{exhaust}) \]  

(1.3)

Two half-cell reactions occur at each electrode TPB, which involves an equilibrium between gaseous \( O_2 \) and \( O^{2-} \) ions from the YSZ lattice shown by equation 1.4:

\[ O_2 + 4e^-(\text{Pt}) \leftrightarrow 2O^{2-}(\text{YSZ}) \]  

(1.4)

This process on the YSZ electrolyte can be represented in Figure 1.9 [1].

Assuming complete ionic conduction in YSZ the resulting cell voltage between the two electrodes can be represented by the Nernst equation:

\[ \text{EMF} = \frac{RT}{4F} \ln \left( \frac{P_{O_2}^{\text{ref}}}{P_{O_2}^{\text{exhaust}}} \right) \]  

(1.5)

Thus by knowing the cell voltage, temperature, and the reference \( P_{O_2} \) (which is 21% from air) one can calculate the \( P_{O_2} \) of the sensing environment. Typical exhaust \( O_2 \) levels can be around 1-5%.

**1.5 Potentiometric NO\textsubscript{x} sensors in the literature**

Many of the early studies focused on NO\textsubscript{x} sensor designs that were primarily effective at lower temperatures below 400\degree C. The need for *in-situ* monitoring of combustion processes has pushed the temperature range higher. Leading the current trend is research involving high temperature sensing materials. In the following sections, examples of the main formats of potentiometric NO\textsubscript{x} sensors from the literature will be shown followed by an overview of the NO\textsubscript{x} sensor mechanism common to them.
A typical potentiometric NO\textsubscript{x} sensor from Lu et al is shown in Figure 1.10 [110]. It consists of a closed-end commercial YSZ tube with two electrodes in a stacking orientation (electrodes located on opposite sides of the electrolyte). The sensor is placed into a heated chamber with a controlled atmosphere at 550°C. The sensing electrode is a spinel metal oxide material, CdCr\textsubscript{2}O\textsubscript{4}, placed on top of a Pt conductor layer serving as an electrical contact and is exposed to the flowing sensing gas at 100 cm\textsuperscript{3}/min (NO or NO\textsubscript{2} + 21%O\textsubscript{2} + balance N\textsubscript{2}). The reference electrode is a Pt metal/Pt black combination exposed to static air. The sensor response of the device to 200ppm NO and NO\textsubscript{2} is shown in Figure 1.11. The response to NO and NO\textsubscript{2} are in opposite directions which is characteristic of these types of sensors. Also Figure 1.11 shows the response to NO\textsubscript{2} is higher than NO for the same concentration. An explanation given by Miura is that NO\textsubscript{2} is less thermodynamically stable than NO at higher temperatures and it will have a higher amount of conversion towards equilibrium resulting in a higher signal on the sensor [111]. As is typical of the literature usually many different metal oxides are screened for their response to NO\textsubscript{x} (Figure 1.12). In this particular paper 10 oxides were tested and CdCr\textsubscript{2}O\textsubscript{4} gave the largest signal to 200ppm NO\textsubscript{x} at 550°C [110] although no explanation for this was given in the paper.

A NO\textsubscript{x} sensor that uses a solid NaNO\textsubscript{2} reference instead of a fixed air reference was demonstrated by Imanaka et al [108]. This sensor was interesting in that a new nitrosonium ion (NO\textsuperscript{+}) conducting Ga\textsubscript{11}O\textsubscript{17} electrolyte was utilized. The two electrodes were made of Pt as exhibited in Figure 1.13. The reference electrode was sealed by a small Pyrex glass chamber holding solid NaNO\textsubscript{2} which provided a fixed NO\textsubscript{x} concentration determined by the temperature. An earlier study was done by the
Schoonman group [107] using a Ag\textsuperscript{+}-β\textsuperscript{"} alumina electrolyte with a AgNO\textsubscript{3}/Pt sensing electrode and a sealed solid reference electrode composed of Ag metal.

A planar design using a MgO stabilized zirconia and Pt paste and Ba(NO\textsubscript{3})\textsubscript{2}-CaCO\textsubscript{3} electrodes was used by Kurosawa et al [112]. A Pt mesh and Au mesh served to transport electrons from the electrodes. In this design both electrodes were exposed to the sensing gas without a fixed reference (either air or a packed solid) as shown in Figure 1.14. The advantage of this design is that the sensor is simpler to fabricate and can be made much smaller with a larger number of placement possibilities.

Potentiometric sensors have also been used in a three-electrode arrangement. The general idea is to apply a voltage or current to a set of electrodes to suppress or enhance a particular reaction to create selectivity. Miura used a YSZ pellet having three Pt electrodes consisting of a reference electrode (RE), a counter electrode (CE), and a sensing electrode (SE), which was covered by a CdCr\textsubscript{2}O\textsubscript{4} spinel layer shown in Figure 1.15 [111]. In this design a polarizing voltage $V_{s-c}$ was applied between SE and CE and the sensor signal $E_s$ was measured between SE and RE. It was observed that for 200ppm NO or NO\textsubscript{2} in air at 500°C when $V_{s-c}$ was +100mV the sensor responded primarily to NO and when $V_{s-c}$ was -60 mV the sensor responded mainly to NO\textsubscript{2}. In this case the Pt reference electrode (RE) was not a true reference because it was also exposed to the sensing gas and Pt has been shown to respond to NO\textsubscript{x} gases before [113].

Amperometric type NO\textsubscript{x} sensors using solid electrolytes have been a subject of various journal articles and patents. In the academic literature, Yamazoe [114] and Göpel [115] have developed designs where a current or voltage is applied to a set of sensor electrodes. The sensor signal is then measured as a voltage or current, respectively. For
example, Yamazoe developed a device to detect ppb levels of NO\textsubscript{2} at 150\degree C in air shown in Figure 1.16 [116]. This device has some similar elements to the one in Figure 1.15. It consisted of a NASICON pellet with three Au electrodes consisting of a reference electrode (RE), a counter electrode (CE), and a working/sensing electrode (WE). The counter electrode was covered by a NaNO\textsubscript{2} layer and the reference electrode was covered by an inorganic adhesive. The reference electrode was created by using a sealant so NO\textsubscript{x} (or any test gas presumably) could not reach it, although in the paper the group did not specifically mention what the sealant was made of or its source and the mechanism of how the potential remains fixed at RE. When a voltage of -150mV was applied between WE and RE a current of 30nA developed between WE and CE for 80ppb NO\textsubscript{2}. The sensor was also tested for 0.1ppm NO and showed about 4nA interference. Reinhardt has developed a YSZ based device that can measure O\textsubscript{2} and NO\textsubscript{x} simultaneously [117]. The device was a hollow single closed-end YSZ tube with two Pt electrodes painted on the inside circumference and two Pt electrodes painted on the outside (Figure 1.17). At the open end of the YSZ tube a diffusion channel was created. Electrode 1 (E1) biased at voltage \(U_1\) detected the O\textsubscript{2} reduction current \(I_1\) and electrode 2 (E\textsubscript{2}) biased at \(U_2\) detected the NO reduction current \(I_2\). The approach was to let the gas mixture diffuse in and reduce all the O\textsubscript{2} at the first electrode by choosing a potential where NO would not be reduced. The remaining NO was then reduced at the corresponding potential (\(U_2\)) at E\textsubscript{2} without interference from O\textsubscript{2}. Table 1.4 lists the major potentiometric and amperometric NO\textsubscript{x} sensor references from the literature and the materials that they were made from. It is observed that earlier sensors generally operated at lower temperatures and there is a push to develop NO\textsubscript{x} sensors that can withstand higher temperatures.
The patent literature has many references for NO\(_x\) sensors that differ significantly from that seen in the academic literature [54, 67, 142-155]. The main design that has been pushed for development has been the multilayer amperometric type because they can be made reasonably selective to NO\(_x\) over O\(_2\). In addition all the incoming NO\(_x\) is converted to NO or NO\(_2\) and detected as such or by reduction for a "total NO\(_x\)" signal. A couple of the major designs will be shown next to demonstrate the state of the art.

Figure 1.18 shows a schematic of a sensor adopted from a patent by Riken [149]. The sensor was fabricated by using multiple layers of YSZ bonded to each other. The device contains three chambers where gas can pass through. The first chamber is exposed to the exhaust test gas through a small diffusion hole so the gas consisting of NO\(_x\) and O\(_2\) can enter. In chamber 1 the O\(_2\) level is reduced to a low level (~1ppm) by an applied current, I\(_1\), between electrodes E\(_1\) and E\(_2\) (E\(_1\) composed of Pt, E\(_2\) composed of a metal oxide). In chamber two, Pt electrode 3 (E\(_3\)) is an oxygen sensing electrode in conjunction with the air reference Pt electrode 4 (E\(_4\)) located in chamber 3. When the signal for the E\(_3\)/E\(_4\) couple, V\(_2\) indicates there is less than 1ppm O\(_2\) in chamber two then the pumping current between E\(_1\)/E\(_2\) will stop. Thus throughout the measurement the current application at E\(_1\)/E\(_2\) is in a constant feedback loop with the O\(_2\) sensing couple E\(_3\)/E\(_4\). At the same time while reducing the O\(_2\) levels the NO\(_2\) in the NO\(_x\) gas is reduced to NO at E\(_2\). The patent mentioned that care must be taken so that NO is not also reduced. Finally the NO gas flows into chamber two and is electrochemically reduced to the elements at the Pt electrode 5 (E\(_5\)) polarized by V\(_1\). The current, I\(_2\), given by the E\(_5\)/E\(_6\) couple is due to the O\(^{2-}\) formed and discharged and is proportional to the NO reduced. Since all the incoming NO\(_x\) was converted to NO the final signal gives the “total NO\(_x\)” of the original.
gas content. The original O$_2$ level is reduced to 1ppm to facilitate NO$_2$ reduction and to minimize the background current contribution in chamber 2.

A second sensor design in the same Riken patent [149] is a modified version of the first using a similar principle but with improved parameters. Figure 1.19 shows the design, which also has three chambers and six electrodes (E$_1$-E$_6$). The difference is that E$_6$ is brought inside the second chamber. This serves to eliminate the air reference of this couple, which will significantly reduce any signal fluctuations due to O$_2$ if there is any still present since any O$_2$ changes at E$_5$ and E$_6$ should cancel each other out. After the NO gas enters into chamber 2 it contacts the E$_5$/E$_6$ couple. In this design now the voltage at E$_5$/E$_6$ is measured (there is no applied current or voltage here). E$_5$ is composed of a CuMnO$_4$ compound that is more sensitive to NO than the Pt electrode E$_6$. In this design NO is oxidized to NO$_2$ by O$^{2-}$ from the YSZ lattice at each electrode via the reaction NO + O$^{2-}$ $\rightarrow$ NO$_2$. Due to the asymmetry between E$_5$/E$_6$ a net signal for NO is measurable that corresponds to the original total NO$_x$ content. Figure 1.20 shows a commercial ad from NGK [53] for a packaged NO$_x$ sensor still under development based on its various patents with a design similar to the RIKEN group. NGK has teamed up with Horiba to market a non-sampling type NO$_x$ analyzer for exhaust gas called the MEXA-120 consisting of its YSZ based sensor design [156, 157]. Generally these multi-layered YSZ devices are more complicated and expensive than what the academic literature has demonstrated and other issues such as clogging of the diffusion hole in the first chamber [148], electrode signal drift, and O$_2$ control have been challenges to their mass commercialization.
There have also been many NO\textsubscript{x} gas sensor SAE Technical Paper Series presentations [64, 113, 127, 130, 157-159] at the Society for Automotive Engineers conference each year [160]. Generally these papers deal with the applied aspect of the sensors in field tests and are funded by companies with the subject matter often based on their patent contents.

1.6 Mechanism of potentiometric NO\textsubscript{x} sensor response

Potentiometric solid electrolyte (SE) gas sensors operate by two main sensing principles: equilibrium potential or mixed potential [68]. Weppner classified these gas sensors into three types depending on the nature of electrochemical interactions between the SE and the sensing gas [161] [68]. Type I utilizes a SE that has a mobile ion in common with the target gas. Type II employs a SE with immobile ions related to the sensing gas. Type III sensors have no direct relation between the SE and target gas. This type uses an attached auxiliary phase (AP) to provide sensing properties. Table 1.5 gives various examples of the sensor types along with the chemical reactions that enable gas sensing [68, 161]. The Type III sensor can be further divided into three subtypes based on the nature of the SE and AP depending on whether the mobile ion of the SE and AP are the same (Type IIIa), the mobile ions are different but the same sign (Type IIIb), or if the ions have different signs (Type IIIc).
1.6.1 Operating principles of potentiometric designs

1.6.1.1 Equilibrium potential type sensors

The most widely used design based on the equilibrium-potential sensing mechanism is the commercial oxygen sensor (see section 1.4.4). This sensor is composed of YSZ with Pt electrodes. One side of the sensor has an air reference and the other is exposed to the sensing gas [68]. The arrangement for the oxygen sensor results in a concentration cell that can be represented by:

\[
P_{O_2}(\text{reference}), \text{Pt} \mid \text{YSZ}(O^{2-}\text{ conductor}) \mid \text{Pt}, P_{O_2}(\text{sensing})
\]  \hspace{1cm} (1.6)

At the three-phase contact of the porous Pt electrode, YSZ, and gas phase, oxygen undergoes the following equilibrium:

\[
\frac{1}{2}O_2 + 2e^{-}(\text{Pt}) \leftrightarrow O^{2-}(\text{YSZ}) \hspace{1cm} (1.7)
\]

The EMF value of the sensor can be measured by the Nernst equation as shown earlier [68]:

\[
\text{EMF} = \frac{RT}{4F}\ln\left(\frac{P_{O_2}^{\text{sensing}}}{P_{O_2}^{\text{reference}}}\right) \hspace{1cm} (1.8)
\]

Table 1.5 lists examples of various types of equilibrium potential type sensors.
1.6.1.2 Mixed potential type potentiometric sensors

The sensor mechanism in this dissertation involves a mixed potential as will be shown in Chapters 2-4 thus it will be instructive to lay a foundation for this type of sensor.

To understand mixed potential sensors it is instructive to look at the equilibrium potential design first. When another gas such as NO is present in the case of the oxygen sensor, two situations must be considered. If the Pt electrodes completely oxidize NO towards equilibrium (and NO\(_2\) does not further react), then the local O\(_2\) concentration simply decreases due to reaction with NO [68]. Since the original amount of NO is very small (ppm level) compared to the O\(_2\) (% level), the change in observed sensor signal should be minuscule. This is in effect the equilibrium potential case giving the same result as the O\(_2\) sensor. An interesting case occurs if the NO is not completely oxidized towards equilibrium, which may be due to the bulk electrode having a low catalytic activity or if the temperature is not ideal for the conversion. When NO is left to react (i.e. not fully equilibrated) at the triple point boundary it also takes part in the overall cell reactions which can significantly affect the sensor voltage. The simultaneous occurrence of multiple electrochemical reactions for O\(_2\) and NO on the electrode creates a mixed potential. The mixed potential results in an "anomalous EMF" which generally does not follow the Nernst equation. The final steady state mixed potential is observed when all of the anodic and cathodic electrochemical reactions proceed at an equal rate [68]. In the case of multiple gases present the reaction scheme can become very complex.

The anomalous EMF was first reported in the late 1970’s [162] and since then various researchers have discussed and tested mixed potential type sensors [68, 110, 126, 25]...
The majority of studies have been done on YSZ type devices with a fixed air reference on one side and the other side exposed to air mixed with NO₅, CO, or HC.

An illustrative example of a mixed potential sensor for NO₅ was studied by Lu et al. [110]. The sensor was constructed as shown in Figure 1.10 and had the following cell structure:

\[
\text{air, Pt | YSZ | CdCr}_2\text{O}_4 \text{, Pt, NO or NO}_2 \text{ in air} \quad (1.9)
\]

The following reaction schemes were assumed to occur at the TPB:

\[
\begin{align*}
\text{O}_2 + 4e^- & \rightarrow 2\text{O}^{2-} \quad (1.10) \\
\text{NO} + \text{O}^{2-} & \rightarrow \text{NO}_2 + 2e^- \quad (1.11) \\
\text{NO}_2 + 2e^- & \rightarrow \text{NO} + \text{O}^{2-} \quad (1.12) \\
2\text{O}^{2-} & \rightarrow \text{O}_2 + 4e^- \quad (1.13)
\end{align*}
\]

The observed EMF values for transients of 200ppm NO or NO₂ at 550°C are shown in Figure 1.11. The potential difference that is measured is composed of an equilibrium potential electrode (the Pt air reference) and a mixed potential electrode (the CdCr₂O₄). It was found that for linearly increasing concentrations of NO or NO₂ up to 800ppm the sensor gave a logarithmic voltage response, in that at lower NO₅ levels the signal change was larger than at higher NO₅ levels.
The mixed potential arises when the gases are not thermodynamically equilibrated and is ultimately determined by the electrode kinetics. Jones stated that on an electrically conducting electrode "isolated potentials" cannot exist and the final potential is determined when the rates of all reactions are equal [171]. Figure 1.21 shows a representation of the mixed potential on an electrode by Göpel [115]. He uses a case for a CO sensor where O₂ and CO are present but this can be adapted for the NO sensor shown in Figure 1.10. The diagram in Figure 1.21 is for the simplest case of only two gases present (O₂, NO) on the sensor electrode. It shows the equilibrium potential (E_{O₂}, E_{NO}) for the two electrode reactions, 1.10 and 1.11. The equilibrium potentials can been calculated from thermodynamic data [115, 117]. At the mixed potential, E_{mix}, the anodic and cathodic reactions have the same rate which occurs when the anodic (iₐ) and cathodic (iₖ) currents of the two reactions are equal, e.g. |i_{NO}| = |i_{O₂}| making the overall net current zero, iₐ + iₖ = 0. It is impossible to calculate an exact solution for the mixed potential even for the simplest case of two gases because the heterogeneous catalytic activity of the bulk electrode, all kinetic parameters, and the current voltage properties of the reactions must be known [115]. Therefore, there has been very little quantitative work done in the literature regarding the mixed potentials with only approximate models being developed [110, 172].

Lu et al. [110] employed quantitative expressions for the anodic (i_{NO}) and cathodic (i_{O₂}) current densities to explain why E_{mix} changes linearly with the logarithm for changing concentrations of NO and NO₂ for the sensor in Figures 1.10 and Figures 1.11. Considering the case for NO based on reactions 1.10 and 1.11 expressions for i_{NO} and i_{O₂} were determined:
\[ i_{\text{NO}} = i_{\text{NO}}^\circ \exp\{2\alpha_1 F(E-E_{\text{NO}}^\circ)/RT\} \quad (1.14) \]
\[ i_{\text{O}_2} = -i_{\text{O}_2}^\circ \exp\{-4\alpha_1 F(E-E_{\text{O}_2}^\circ)/RT\} \quad (1.15) \]

where \( E \) is the electrode potential, \( E^\circ \) is the electrode potential at equilibrium, \( i^\circ \) corresponds to the exchange current density, \( \alpha \) is the transfer coefficient and \( F, R, \) and \( T \) have the same meanings as defined earlier. Lu employed further kinetic expressions for \( i^\circ \) assuming that it can be represented by:

\[ i_{\text{NO}}^\circ = B_1 C_{\text{NO}}^m \quad (1.16) \]
\[ i_{\text{O}_2}^\circ = B_2 C_{\text{O}_2}^n \quad (1.17) \]

where \( C \) is the \( \text{NO} \) or \( \text{O}_2 \) concentration, and \( B_1, B_2, m \) and \( n \) are constants. By equating \( |i_{\text{O}_2}| = |i_{\text{NO}}| \) and combining equations (1.14-1.17) the mixed potential \( E_{\text{mix}} \) can be expressed as:

\[ E_{\text{mix}} = E^\circ - mA \ln C_{\text{NO}} + nA \ln C_{\text{O}_2} \quad (1.18) \]

where \( E^\circ \) and \( A \) are defined as:

\[ E^\circ = \frac{RT}{(2\alpha_1+4\alpha_2)F}(\ln(B_1/B_2)+\alpha_1 E_{\text{NO}}^\circ+2\alpha_2 E_{\text{O}_2}^\circ)/(\alpha_1+2\alpha_2) \quad (1.19) \]
\[ A = \frac{RT}{(2\alpha_1+4\alpha_2)F} \quad (1.20) \]
Equation 1.18 shows that when either the NO\textsubscript{2} or O\textsubscript{2} concentration is fixed then E\textsubscript{mix} should change linearly with the change in the logarithm of concentration of the other gas. Lu et al. found the experimental result to be in agreement with what was expected from equation 1.18. All of the sensors in Figures 1.10-1.17 and 1.19 have a mixed potential electrode.

1.7 Issues of selectivity between NO an NO\textsubscript{2} in existing NO\textsubscript{x} sensors

One of the drawbacks of most existing NO\textsubscript{x} sensors is the lack of selectivity between the two main NO\textsubscript{x} components, NO and NO\textsubscript{2}. Even though there is generally more NO present it has been observed that only a small amount of NO\textsubscript{2} can give a large signal [113]. This can be a problem since electrochemical sensors usually give a signal response to both NO and NO\textsubscript{2} typically in opposite directions because NO gets oxidized and NO\textsubscript{2} reduced on the sensor [110]. A few examples are known where the sensor response to NO and NO\textsubscript{2} are in the same direction. An electrochemical sensor using the reaction of Ba\textsuperscript{2+} with NO or NO\textsubscript{2} to form Ba(NO\textsubscript{3})\textsubscript{2} provided EMF signals that were in the same direction for NO and NO\textsubscript{2} [112]. A resistance-based sensor using Si\textsubscript{3}N\textsubscript{4} also gave sensor output responses to NO and NO\textsubscript{2} in the same direction, though the mechanism of sensing action was not explained [88] and mixtures of the gases were not tested. Nevertheless, since these sensors respond to both gases, it would be difficult to determine the level of NO and NO\textsubscript{2} in a mixture.

Some solutions to the selectivity problem are to develop a sensor that only responds to one of the species, convert one of the NO\textsubscript{x} species to the other so that the total NO\textsubscript{x} can be measured, or utilize a sensor that gives a signal response in the same direction for both
species that is additive so as to also get the total NO\textsubscript{x} concentration. For the former two solutions this sensor can then be coupled with another sensor that is selective for one of the species making it possible to determine both NO and NO\textsubscript{2} concentrations.

Several strategies have been reported for improving selectivity. By polarizing the sensing metal oxide electrode relative to a Pt reference electrode for a YSZ based sensor at different voltages, the currents produced by the device upon exposure to NO or NO\textsubscript{2} could be modulated to produce a selective NO\textsubscript{x} sensor [111]. Besides selectivity to specific NO\textsubscript{x} components, gases such as CO, which are present in a combustion environment interfere with the signal for NO\textsubscript{x} [113]. Thus to measure an accurate level of NO\textsubscript{x}, the CO cross-sensitivity must be minimized.

Some groups have focused on developing a total NO\textsubscript{x} sensor as discussed earlier and this method and its variations have been extensively reported in the patent literature [67, 115]. Finally, filters have been placed before the sensor to convert NO to NO\textsubscript{2} or vice versa [106, 173] to improve selectivity. Chapter 3 will discuss the use of filters in more detail to create a total NO\textsubscript{x} sensing system.
FORMATION AND REDUCTION OF NITROGEN OXIDES IN COMBUSTION; MECHANISTIC PATHWAYS

Figure 1.1. Diagram of NO$_x$ formation during combustion process [27].
Source of Nitrogen Oxides in Year 2000

* Other stationary combustion includes residential and commercial sources.

Figure 1.2. Year 2000 source breakdown of NOx emissions [40].
### Coal-Fired Boiler NOx Emission Limits lb/million Btu (Title IV)

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<th>Implementation Period</th>
<th>Phase I</th>
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<td>Enacted</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group 1 Boilers</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Bottom Wall-Fired</td>
<td>0.50</td>
<td>0.46</td>
</tr>
<tr>
<td>Tangentially Fired</td>
<td>0.45</td>
<td>0.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group 2 Boilers</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Bottom Wall-Fired</td>
<td>NA</td>
<td>0.84</td>
</tr>
<tr>
<td>Cyclone Fired</td>
<td>NA</td>
<td>0.86</td>
</tr>
<tr>
<td>Vertically Fired</td>
<td>NA</td>
<td>0.80</td>
</tr>
<tr>
<td>Cell Burner</td>
<td>NA</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 1.2. Federal emissions standards of total NOx from coal-fired boilers [46].
Figure 1.3: Catalytic converter efficiency versus air/fuel ratio [29].

Figure 1.4: Layout of components in an engine system, 1: Air-flow sensor, 2: Engine, 3: Lambda sensor, 4: Catalytic converter, 5: Injection valves, 6: Lambda closed-loop sensor, $U_s$: sensor voltage $U_v$: Valve actuation voltage, $V_c$: Injection quantity [52].
Figure 1.5. Packaged O₂ sensor (NTK) [53][54].

Figure 1.6. Cross section of exhaust gas O₂ sensor placement [55].
Figure 1.7. NO$_x$ sensor publications per year using the keyword "NO$_x$ sensor" in the SciFinder Chemical Abstracts database.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensor Material</th>
<th>Temp (°C)</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO/NO₂</td>
<td>SnO₂</td>
<td>200</td>
<td>1979</td>
<td>[70]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>LaNiO₃</td>
<td>350</td>
<td>1987</td>
<td>[71]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Al₂O₃·V₂O₅</td>
<td>400</td>
<td>1989</td>
<td>[72]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>SnO₂·Al₂O₃</td>
<td>100</td>
<td>1990</td>
<td>[73]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Pb-phthalocyanine</td>
<td>330</td>
<td>1990</td>
<td>[74]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>In-SnO₂</td>
<td>325</td>
<td>1990</td>
<td>[75]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>WO₃</td>
<td>300</td>
<td>1991</td>
<td>[76]</td>
</tr>
<tr>
<td>NO₂</td>
<td>2at.%Cd·SnO₂</td>
<td>250</td>
<td>1991</td>
<td>[77]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Ga·ZnO</td>
<td>400</td>
<td>1992</td>
<td>[78]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>In₂O₃·SnO₂(9:1)</td>
<td>300</td>
<td>1992</td>
<td>[79]</td>
</tr>
<tr>
<td>NO₂</td>
<td>SnO₂</td>
<td>280</td>
<td>1993</td>
<td>[80]</td>
</tr>
<tr>
<td>NO₂</td>
<td>5at.%Al·SnO₂</td>
<td>300</td>
<td>1994</td>
<td>[81]</td>
</tr>
<tr>
<td>NO₂</td>
<td>5mol%(Sc₂O₃)·Ni·Cu·O</td>
<td>600</td>
<td>1994</td>
<td>[82]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Bi₂Sr₂CaCu₂O₈+x</td>
<td>350</td>
<td>1994</td>
<td>[83]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>In·TiO₂</td>
<td>450</td>
<td>1994</td>
<td>[84]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Yb₂Cu₂O₅·Tm·Cu₂O₅</td>
<td>550</td>
<td>1994</td>
<td>[85]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>BaWO₃·BaCO₃(Ba/W=1.5)</td>
<td>600</td>
<td>1995</td>
<td>[86]</td>
</tr>
<tr>
<td>NO</td>
<td>5wt%(K₂O)·SnO₂</td>
<td>400</td>
<td>1996</td>
<td>[87]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>8mol%Y₂O₃·Si₃N₄</td>
<td>750</td>
<td>1999</td>
<td>[88]</td>
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<tr>
<td>NO</td>
<td>WO₃+B₂O₃</td>
<td>325</td>
<td>1999</td>
<td>[3]</td>
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<tr>
<td>NO/NO₂</td>
<td>ZnO+Er₂O₃·Pd/V</td>
<td>400</td>
<td>2000</td>
<td>[89]</td>
</tr>
<tr>
<td>NO</td>
<td>WO₃+oxide dopants</td>
<td>350</td>
<td>2000</td>
<td>[90]</td>
</tr>
<tr>
<td>NO</td>
<td>WO₃+MoO₃</td>
<td>450</td>
<td>2000</td>
<td>[91]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>WO₃</td>
<td>300</td>
<td>2000</td>
<td>[92]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Zn·Sn·Sb·O</td>
<td>600</td>
<td>2001</td>
<td>[93]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Te</td>
<td>25</td>
<td>2001</td>
<td>[94]</td>
</tr>
<tr>
<td>NO₂</td>
<td>In₂O₃ + TiO₂</td>
<td>400</td>
<td>2001</td>
<td>[95]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>WO₃, In₂O₃, SnO₂</td>
<td>226</td>
<td>2002</td>
<td>[96]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>WO₃</td>
<td>400</td>
<td>2002</td>
<td>[97]</td>
</tr>
</tbody>
</table>

Table 1.3. Examples of resistive type/semiconducting sensors in the literature. The sensor materials are listed in the form of the most sensitive material tested in the paper. All sensor designs consisted of putting a sensing layer on top of an insulating layer (i.e. Al₂O₃) with two electrodes. Temp: the maximum temperature the sensor was tested at.
Figure 1.8. Simple planar form of potentiometric gas sensor.

Figure 1.9: Triple point boundary concept on a solid electrolyte sensor. Adapted from Madou [1].
Figure 1.10. Example of a closed-end tube potentiometric sensor for NO\textsubscript{x} with electrodes in stacking configuration [110].

Figure 1.11. Typical sensor response to 200 ppm NO\textsubscript{2} or NO at 550°C [110].
Figure 1.12. Screening various metal oxides for NO\textsubscript{x} response [110].

Figure 1.13. Sealed reference type potentiometric sensor for NO\textsubscript{x} [108].
Figure 1.14: Planar type potentiometric sensor [112].

Figure 1.15. Planar NOx sensing device with three electrodes [111].
Figure 1.16. Configuration of a NASICON-based device using a NaNO₂ layer for amperometric sensing [116].

Figure 1.17. Schematic view of a tubular type amperometric cell with two working electrodes [117].
<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensor Material</th>
<th>Mode</th>
<th>Temp (°C)</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>Ba(NO₃)₂+1%AgCl</td>
<td>P</td>
<td>481</td>
<td>1977</td>
<td>[118]</td>
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<tr>
<td>NO₂</td>
<td>Ag-β'-alumina/NaNO₃</td>
<td>P</td>
<td>150</td>
<td>1986</td>
<td>[119]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Na-β/β&quot;-alumina/NaNO₃</td>
<td>P</td>
<td>150</td>
<td>1987</td>
<td>[105]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Ag/Ag⁺-β&quot;'-alumina/AgNO₃</td>
<td>P</td>
<td>200</td>
<td>1992</td>
<td>[107]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/Nasicon/Au+NaNO₃-Ba(NO₃)₂</td>
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<td>450</td>
<td>1993</td>
<td>[120]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Pt/Nasicon/Au+NaNO₂-M₂CO₃ (M=Na, Li)</td>
<td>P</td>
<td>150</td>
<td>1994</td>
<td>[121]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/MSZ/Au+Ba(NO₃)₂-CaCO₃</td>
<td>P</td>
<td>450</td>
<td>1994/5</td>
<td>[112, 122]</td>
</tr>
<tr>
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<td>P</td>
<td>463</td>
<td>1994</td>
<td>[123]</td>
</tr>
<tr>
<td>NO/NO₂</td>
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<td>700</td>
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<td>[124]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/CdMn₂O₄</td>
<td>P</td>
<td>500</td>
<td>1996</td>
<td>[125, 126]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt</td>
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<td>650</td>
<td>1996</td>
<td>[127]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Au/Nasicon/Au+NaNO₂-NaNO₃</td>
<td>A</td>
<td>200</td>
<td>1996</td>
<td>[128]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt+CdCr₂O₄</td>
<td>P</td>
<td>600</td>
<td>1997</td>
<td>[110]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Au/CeO₀.₈Sm₀.₂O₁.₉/Au+NaNO₂</td>
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<td>900</td>
<td>1998</td>
<td>[129]</td>
</tr>
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<td>150</td>
<td>1998</td>
<td>[116]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/CdCr₂O₄</td>
<td>P</td>
<td>600</td>
<td>1998</td>
<td>[111]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt+CdCr₂O₄/Pt+WO₃</td>
<td>P</td>
<td>550</td>
<td>1998</td>
<td>[132]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt</td>
<td>A</td>
<td>550</td>
<td>1999</td>
<td>[111, 114]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt</td>
<td>P</td>
<td>550</td>
<td>1999</td>
<td>[130]</td>
</tr>
<tr>
<td>NO</td>
<td>NaNO₃/NO⁺-Ga₁₁O₁₇/Pt</td>
<td>P</td>
<td>190</td>
<td>1999</td>
<td>[88]</td>
</tr>
<tr>
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<td>Pt/β'-alumina/Au</td>
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<td>700</td>
<td>1999</td>
<td>[21]</td>
</tr>
<tr>
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<td>Pt/YSZ/Pt</td>
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<td>596</td>
<td>2000</td>
<td>[131]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt+WO₃</td>
<td>P</td>
<td>700</td>
<td>2000</td>
<td>[132]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Au/Nasicon/Au+WO₃+Pt-SiO₂/Au+NaNO₂</td>
<td>A</td>
<td>150</td>
<td>2000</td>
<td>[106]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/Nasicon/Pb₂Ru₁.₉V₀.₁O₇₋ₓ</td>
<td>P</td>
<td>400</td>
<td>2000</td>
<td>[133]</td>
</tr>
</tbody>
</table>

Table 1.4. Examples of solid electrolyte NOₓ sensors in the literature. The sensor materials are listed in the form of reference electrode/electrolyte/sensing electrode/counter electrode (if applicable). P: Operated in potentiometric mode, A: Operated in amperometric mode. Temp: the maximum temperature the sensor was tested at.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensor Material</th>
<th>Mode</th>
<th>Temp (°C)</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Pt/YSZ/Pt/Pt + diffusion layer</td>
<td>A</td>
<td>650</td>
<td>2000</td>
<td>[134]</td>
</tr>
<tr>
<td>NO₂</td>
<td>SmFeO₃+Au-Pd/Nasicon/Pt</td>
<td>P</td>
<td>400</td>
<td>2000</td>
<td>[135]</td>
</tr>
<tr>
<td>NO</td>
<td>Pt/YSZ/Pt+MgAl₂O₄</td>
<td>A</td>
<td>700</td>
<td>2001</td>
<td>[136]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Pt+LaFeO₃/YSZ/Pt</td>
<td>A/P</td>
<td>450</td>
<td>2001</td>
<td>[137]</td>
</tr>
<tr>
<td>NO</td>
<td>Au/(Na⁺,NO⁻⁺)-B''-alumina/Au</td>
<td>P</td>
<td>250</td>
<td>2001</td>
<td>[109]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/NiCr₂O₄/Pt</td>
<td>P</td>
<td>650</td>
<td>2001</td>
<td>[138]</td>
</tr>
<tr>
<td>NO₂</td>
<td>Au+sealant/Nasicon/Au/Au+NaNO₂</td>
<td>A</td>
<td>150</td>
<td>2001</td>
<td>[139]</td>
</tr>
<tr>
<td>NO</td>
<td>Pt/(Al₀.₂Zr₀.₈)₂₀/₁₉Nb(PO₄)₃⁺YSZ/Eu₂O₃+KNO₂</td>
<td>P</td>
<td>450</td>
<td>2002</td>
<td>[140]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/ZnFe₂O₄</td>
<td>P</td>
<td>700</td>
<td>2002</td>
<td>[141]</td>
</tr>
<tr>
<td>NO</td>
<td>Pt/YSZ/La₁₋ₓSrₓMnO₃</td>
<td>A</td>
<td>700</td>
<td>2002</td>
<td>[117]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt/YSZ/Pt+zeolite NaY</td>
<td>P</td>
<td>500</td>
<td>2002</td>
<td>[113]</td>
</tr>
</tbody>
</table>

Table 1.4 continued. Examples of solid electrolyte NOₓ sensors in the literature. The sensor materials are listed in the form of reference electrode/electrolyte/sensing electrode/counter electrode (if applicable). P: Operated in potentiometric mode, A: Operated in amperometric mode, Temp: the maximum temperature the sensor was tested at.
Figure 1.18. Schematic diagram of a multi-layer YSZ based amperometric total NOx sensor from Kunimoto et al. in the patent literature [149].
Figure 1.19. Schematic diagram of a multi-layer YSZ based amperometric total NOx sensor from Kunimoto et al. in the patent literature [149].
Figure 1.20. NTK 2001 brochure ad for NOx sensor [53].

<table>
<thead>
<tr>
<th>Sensing Principle</th>
<th>Typical Cell Structure</th>
<th>Gas-Sensing Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Equilibrium Potential</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>(RE) O₂, Pt/YSZ/Pt, O₂</td>
<td>1/2O₂ + 2e⁻ \leftrightarrow O²⁻</td>
</tr>
<tr>
<td>Type II</td>
<td>(SE) CO₂+O₂, Au/K₂CO₃/Au, CO₂+O₂</td>
<td>2K⁺ + CO₂ + 1/2O₂ + 2e⁻ \leftrightarrow K₂CO₃</td>
</tr>
<tr>
<td>Type III</td>
<td>O₂, Au/Nasicon/NaNO₂-Au, NO₂+O₂</td>
<td>Na⁺ + NO₂ + e⁻ \leftrightarrow NaNO₂</td>
</tr>
<tr>
<td><strong>Mixed Potential</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>O₂, Pt/YSZ/ZnO(Pt), H₂+O₂</td>
<td>2H₂+O₂⁻ \rightarrow H₂O + 2e⁻</td>
</tr>
<tr>
<td>Type II</td>
<td>O₂, Pt/YSZ/WO₃(Pt), NO₂+O₂</td>
<td>1/2O₂ + 2e⁻ \rightarrow O²⁻</td>
</tr>
</tbody>
</table>

Table 1.5. Examples of the two main types of potentiometric based sensors [68], [161].
Figure 1.21. Theoretical schematic adapted from Göpel [115] showing the mixed potential in the case of only two gases (O₂, NO). The mixed electrode potential (E_{mix}) occurs at the point of net zero current of the two reactions that have different equilibrium potentials (E_{NO} and E_{O₂}).
Chapter 2 focuses on the development of a non-selective gas sensor for NO$_x$ detection that is capable of operation in harsh environments, as exemplified by automotive exhaust streams. The basis of the sensor is generation of a mixed potential response by exposure of gases to a platinum-yttria stabilized zirconia (Pt-YSZ) interface. The asymmetry between the two Pt electrodes on YSZ is generated by covering one of the electrodes with a zeolite, which helps to bring NO/NO$_2$ towards equilibrium prior to the gases reaching the electrochemically active interface. The mixed potential generated is logarithmically related to NO concentration (0-1000 ppm) at sensor temperatures between 500-600°C, the optimum temperature being 500°C. The microporosity of the zeolite makes it permeable to oxygen, thus minimizing the interference to O$_2$. The sensor shows interference from CO and NO$_2$. Three sensor designs have been examined, including a planar design that is amenable to packaging for surviving automotive exhaust streams. Automotive tests indicate that the sensor is capable of detecting NO in engine exhausts.

A class of compounds called zeolites show promise for use in harsh environment gas sensors. Zeolites are crystalline, microporous, hydrated aluminosilicates of interlinked SiO$_4$ and AlO$_4$ tetrahedra, in an infinitely extended three-dimensional network.
Zeolites have high internal surface area and porosity and have been used as catalysts for many reactions, and in particular for the removal of noxious constituents present in automobile exhaust [2]. There have also been several accounts of utilizing zeolite materials for gas sensing at high temperatures. For example, CO detection at 300°C was accomplished using Au-La$_2$O$_3$/SnO$_2$ covered with a layer of the zeolite, ferrierite [3]. The addition of the zeolite served as a catalyst filter to allow selectivity for CO in the presence of H$_2$, CH$_4$, C$_2$H$_4$, i-C$_4$H$_{10}$ and C$_2$H$_5$OH. Zeolites deposited on a quartz crystal microbalance (QCM) have been utilized as sensors for gaseous molecules e.g. Cu-ZSM-5 was used to detect NO in He at 348K [4]. A similar study done at 423K involving a thin layer of the zeolite faujasite on a QCM detected SO$_2$ in the presence of O$_2$ [5].

The purpose of this study was to develop a high-temperature NO sensor, without the need for an air reference, with minimal interference from changing O$_2$ concentrations and a simple design. We accomplished this objective by using YSZ packed or coated with a layer of microporous zeolite Y. We have examined zeolite Y, which is made of interconnected supercages of 13Å sharing 7Å windows (Figure 2.1). For this study, the Na$^+$ exchanged form of the zeolite was used and is labeled henceforth as NaY.

2.1 Experimental

2.1.1 Sensor designs

We first made and tested a sensor design without a zeolite that was similar to the commercial O$_2$ sensor (see Chapter 1). This was to demonstrate the limitations of a sensor with an air reference and to investigate the Pt electrode response to NO and NO$_2$. To verify if the sensing system would give a Nernstian response for a sensor with a fixed air
reference, an oxygen sensor was constructed using a hollow commercial YSZ tube (10.5 mol% Vesuvius McDanel) with one end closed. The design and preparation was similar to that used by other researchers [6, 7]. The tube was approximately 18 inches in length, 6 mm O.D. and 4.5 mm I.D. Pt ink (Englehard corporation, lot# A4731) was hand painted on the inside and outside of the tube (Figure 2.2a). On the outside of the tube a Pt wire (Englehard corporation, 31 AWG) was attached to the wet ink by forming a Pt mesh and wrapping around the end (Figure 2.2b). The ink was then cured in a Lindberg Blue box furnace at 1250°C for 2hrs with a heating and cooling rate of 6°C/min and the resulting electrodes had a metallic grey color. The inside electrode was connected via mechanical contact by a Pt wire inside a small bore alumina tube.

Three sensor designs without an air reference based on the same sensing principle using zeolite NaY were tested. The first (type I), displayed in Figure 2.3, consisted of a YSZ pressed pellet with Pt electrodes mounted onto an alumina tube packed with zeolite NaY (LZY-52 from Union Carbide). The YSZ pellet was made from commercial YSZ powder (HSY-8, Zirconia Sales Inc., 8 mol% YSZ). The pellet was formed in a stainless steel die (Carver inc.) under 10,000 psi on a Carver pellet press. The green pellet was put onto an alumina plate and sintered in a Lindberg Blue high temperature box furnace at 1450°C for 6 hrs with 6°C/min heating and cooling rates. The final pellet dimensions were approximately 9 mm diameter and 2 mm thickness and had a white color. Pt ink was painted on both sides of the pellet and Pt lead wires were set into the wet Pt ink and heat treated as described above. The pellet was then mounted onto an alumina tube (Coors Ceramics), approximately 1 inch in length, with a high temperature inorganic adhesive, Ceramabond 569 (Aremco). Thus one lead wire was on the outside of the tube.
and the other wire on the inside. The Ceramabond was then left to dry for 1-2 hrs at room temperature. The purpose of the tube is to hold zeolite powder, which was then packed on the inside as to cover the Pt electrode. After final assembly the sensor was put into a tube furnace at 500°C for a few hours to thermally stabilize before testing.

The second sensor design (type II) (Figure 2.4), consisted of a cylindrical piece of 8 mol% YSZ (Vesuvius McDanel), approximately 20 mm length, 6 mm O.D., 4.5 mm I.D., cut with a diamond saw (Leco). Pt electrodes were prepared in a similar manner as the type I design. After the sensor body was prepared, zeolite NaY powder was packed into the inside as to cover the inside electrode. The final sensor was then heated at 500°C in a tube furnace to achieve thermal equilibrium before testing.

The third design (type III) (Figure 2.5) consisted of a YSZ pellet with two Pt electrodes on the same side (planar structure) with one of the Pt electrodes coated by a layer of zeolite. The YSZ pellet and electrodes were prepared using the same materials and method as the type I and type II designs. A viscous zeolite paste was prepared by mixing zeolite NaY powder with terpineol solvent. The paste was applied with a paint brush over one of the Pt electrodes. After the paste application, the sensor was heated in a tube furnace at 500°C for 2 hrs to evaporate the terpineol solvent and stabilize the coating.

2.1.2 Sensing apparatus and testing

The gas sensing experiments were performed within a quartz tube located inside a high temperature tube furnace (Lindberg Blue model, Figure 2.6). The sensor rested on a quartz base shown in Figure 2.7 while the two sensor wires were connected to two Pt
wires threaded through the quartz tube, which led outside the furnace. Figure 2.8a shows a closer view of the tube furnace and the quartz sensor holder. The tube furnace was used to heat and cool the sensor at a programmed rate as well as maintaining at a temperature between 500-700°C depending on the experiment. Air, N\textsubscript{2} and combustion gases such as NO (2000 ppm source tank), NO\textsubscript{2} (1000 ppm source tank), and CO (2000 ppm source tank), were metered through Sierra brand mass flowmeters (Figures 2.6 and 2.8b) to form gas mixtures of various compositions, with a volumetric flow rate of 100cc/min. The voltage output of the sensor response to changes in the gas concentrations was monitored by a Hewlett Packard multimeter (34401A) and recorded by Hewlett Packard Benchlink software on a Windows based PC.

2.1.3 Prototype design for automotive exhaust gas sensing

An experimental test probe was designed for field testing in an actual automobile engine. The commercial oxygen sensor packaging was used as a model for the test probe design. The sensor element was composed of a modified version of the type III planar design.

A smaller version of the planar type III sensor was constructed in a similar manner as described in section 2.1.1. Since the zeolite material does not adhere to the Pt electrode surface very readily, especially in the high flow environment of an automobile engine a zeolite pellet was put on top of the zeolite powder. The zeolite pellet was made in a Carver die on a Carver die press machine in a similar manner as the YSZ pellet. The zeolite pellet was pressed under 0.5 ton psi resulting in a pellet approximately 0.05 mm thick and 7.5 mm in diameter. The final zeolite pellet was cut with an x-acto knife to a
size that would cover the Pt electrode and zeolite powder. The zeolite pellet was then glued around the edges to the YSZ pellet with Ceramabond 569. Care was taken as to not get Ceramabond onto either of the electrodes (Figure 2.9a). Thus, the final sensor consisted of a mechanically stable zeolite layer able to withstand higher gas flow rates. This sensor was then mounted onto a four-bore mullite tube using Ceramabond 569. The sensor wires were brought through two of the two bores and came out of the other end of the mullite tube. In addition several prototype designs were made using a resistive heater on the backside of the sensor. The heater was linked in a feedback loop with a type K thermocouple that was mounted on the surface of the sensor near the electrodes (shown in Figure 2.9a). The thermocouple wires were placed in two extra grooves etched onto the outside of the mullite tube and bonded down with Ceramabond 569. This unit was then also mounted in a stainless steel holder for testing in an engine shown in Figure 2.10a. The metallic holder had a standard thread to screw into the exhaust pipe and served to protect the sensor from high gas flow rates, soot, and water droplets. Figure 2.10b shows a diagram of how the sensor temperature was maintained using an omega temperature controller with the signal measured by HP Benchlink software of Labview.

The automotive sensor testing was done at the Center for Automotive Research (CAR). The sensor device was put into the exhaust pipe of a V-8 engine upstream of the three-way catalyst (Figure 2.11). The engine parameters such as throttle and air to fuel ratio were controlled by a dynamometer. Exhaust gases were also monitored with an in-situ IR gas analyzer in conjunction with the sensor testing.
2.2 Results

The sensor designs developed in this study are based on the well-known principles of mixed potential generation upon exposure of a Pt-YSZ interface to NO [8, 9]. The two redox reactions at the Pt-YSZ surface upon exposure to NO/O\textsubscript{2} are:

\[
\begin{align*}
\text{NO} + \text{O}^{2-} &\rightarrow \text{NO}_2 + 2\text{e}^- \quad (2.1) \\
\text{O}_2 + 4\text{e}^- &\rightarrow 2\text{O}^{2-} \quad (2.2)
\end{align*}
\]

Using these reactions as the basis, we have focused on a sensing strategy outlined below, along with sensor results, interference effects, novel sensor designs and testing of sensors in engine exhausts.

2.2.1 Testing with a YSZ air reference based sensor

The standard air reference based sensor with two Pt electrodes (Figure 2.2) was first tested for its response towards varying O\textsubscript{2} levels at 500°C with a gaseous flow rate of 100cc/min. The results are shown in Figure 2.12a starting with a baseline of 1%O\textsubscript{2}/N\textsubscript{2} (in this dissertation the term "baseline" is the point where the gas mixture consists of only O\textsubscript{2} in a balance of N\textsubscript{2}). It is seen that the sensor signal changes upon changing the O\textsubscript{2} level to 3%, 5% and 10%. In addition, the response compares well with that expected from the Nernst equation (see Table 2.1) as can be seen in the calibration curve in Figure 2.12b. The individual points were fit with a logarithmic trendline and the fitting equation is displayed. The t\textsubscript{90} response time was 13.25 minutes from 1 to 3% O\textsubscript{2}. The slow response time is probably due to the low gas flow rates that we employ for our tests and is expected to be faster in an environment with high gas flow rates. Also, it is noted that the closer the test gas is to 21%O\textsubscript{2} the closer the signal is to zero since the ∆p\textsubscript{O\textsubscript{2}} between
the two electrodes becomes less. We further tested the O₂ sensor at 650°C and the calibration curve slope increased (Figure 2.13) and the response time was faster with a t₉₀ for 1% to 3%O₂ of 4.98 minutes most likely due to the increased ionic conduction and electrode kinetics. The experimental values matched well with the theoretical values as shown in the calibration curve in Figure 2.13. Since the experimental calibration curves match closely with the Nernst equation, the Pt sensing electrode is behaving as an equilibrium electrode and fully equilibrates the O₂ reaction (see Chapter section 1.6.1.1).

After confirming that the sensor gave a Nernstian response, we tested for NO sensitivity. Figure 2.14a shows the result of the NO sensing test at 500°C for 200, 400, 600, and 800ppm NO in 10%O₂-N₂. The sensor responded to NO and the signal increased (more positive voltages) with increasing NO content. The signal also had a logarithmic response, in that sequentially higher concentrations of NO gave lower signal changes and is consistent with that observed in the literature [6]. In real situations, such as an automotive tailpipe or a smokestack, the O₂ content fluctuates depending on the combustion parameters. This makes it important to test the NO sensor response in different background oxygen levels. Figure 2.14b shows the sensor data plotted as calibration curves for three O₂ background levels of 3%, 5%, and 10%O₂-N₂. The 10%O₂ data is taken from Figure 2.14a. As expected from the earlier O₂ sensing test (Figure 2.12) the background signal level shifts with different O₂ content. The result is that the whole NO calibration curve moves on top of the background shift. In a real application, this is something to consider as significant error could be introduced in the NO measurement.
In addition to the shift in background, the change in the response to NO is also important, as this can be measured by the slope of the calibration curve. Figure 2.14b shows that the slopes are relatively similar with slight decrease at 10%O2.

Other gases that are important to consider as interferences are NO2, CO and various hydrocarbons. There is also some interest in NH3 interference because of its use in SCR technology to reduce NOx to the elements. In this dissertation we focused primarily on NO2 and CO as interfering gases.

The YSZ air reference sensor with Pt electrodes was tested again for NO and for NO2 in 3%O2-N2 at 500°C. Figure 2.15 shows that the response to NO and NO2 was in opposite directions with NO2 giving a larger response at an equal concentration. This is because in addition to reactions (2.1) and (2.2), the reverse electrochemical reaction of 2.2 can also occur,

\[ \text{NO}_2 + 2e^- \rightarrow \text{NO} + \text{O}^{2-} \]  \hspace{1cm} (2.3)

altering the mixed potential due to the oxidizing nature of NO2. This large NO2 interference also can cause a serious error in NO measurement. In a real combustion system, NOx is composed of both NO and NO2 with NO typically making up 90% of the total NOx. For a total NOx of 1000 ppm around 100ppm NO2 would be present. However, even 100ppm NO2 causes a significant change of 40mV from the 3%O2 baseline so it cannot be neglected. We further tested mixtures of NO and NO2, which closely resembles a realistic situation. Figure 2.16a shows the result of testing mixtures of NO and NO2 at a total NOx of 600 ppm in 3%O2. Finally we tested the sensor for response to CO gas in 3%O2 as shown in Figure 2.16b and observed that the response was quite significant due to the electrochemical reaction:
The CO response was in the same direction as NO due to its reducing nature and the response was larger than NO for the same concentration.

These results show that Pt as an electrode material can detect NO, NO\(_2\), CO as well as changing O\(_2\) concentrations on a YSZ electrolyte at 500°C. The large size and nature of the YSZ air reference based sensor is not attractive to miniaturization so we decided to develop new designs without an air reference having both electrodes exposed to the sensing gas (Figures 2.3-2.5). Without an air reference, if both electrodes are identical, then there should be no signal generated because the extent of the electrochemical reactions would be the same on each electrode. The identical reactions would change the electrochemical potential equally at each triple phase boundary and no potential difference would arise. Thus, it is necessary to create asymmetry between the two electrodes to get a signal for NO\(_x\). One approach to do this in the literature is to use two different electrode materials that promote the reaction of NO or NO\(_2\) at different rates. The method that we have chosen is to place a catalytic filter on one of the electrodes and leave the other uncovered. The uncovered electrode would see the native NO\(_x\) sensing gas while the covered electrode would see an altered NO\(_x\) concentration because the filter equilibrates the NO or NO\(_2\). The net result is a different NO\(_x\) level at each electrode and a measurable potential difference.

Before we used the filter, we fabricated a device where we could simulate a sensor without an air reference to prove our concept would work and is shown in Figure 2.17a. With this device we can control the gaseous atmosphere contacting both electrodes. In the first test, we exposed both electrodes to a 3%O\(_2\)-N\(_2\) background, which
gave a signal close to zero millivolts in the early part of Figure 2.17b since both see the same gas (i.e. without an air reference). Next 800ppm NO was added to the gas mixture on the outside and the signal shifted by -21mV from the baseline. This result models what the uncovered Pt electrode response would be (i.e. in the absence of the filter) and compares with the air reference based sensor earlier shown in Figure 2.14a (Note that the signal has changed direction for NO, i.e. going in a negative direction, and this is due to switching of the polarity on the multimeter connections for this experiment). Next we introduced a mixture of 800ppm NO and 100ppm NO\(_2\) that would simulate a filter covered electrode. For example if 900ppm NO passed through the filter a portion would be converted to NO\(_2\) and a mixture of the two gases would result. The mixture test result can be seen in Figure 2.17c and results in a shift of -10mV from the baseline and is less than the -21mV shift from 800ppm NO alone. If we treat these results as two separate electrode responses with one seeing 800ppm NO and the other seeing 800ppm NO + 100ppm NO\(_2\) then there would be a measurable potential difference between the two of -11mV (i.e. [-21]-[-11]) implying that the use of a filter to create asymmetry will work.

2.2.2 Testing of a planar sensor blank (Type III)

We first tested the planar design shown in Figure 2.5b with two blank Pt electrodes for response to NO at 500°C in 3%O\(_2\). As expected, there is very little change in signal (less than 1mV) as shown in Figure 2.18 from 3%O\(_2\) to 3%O\(_2\) + 800ppm NO because both electrodes see the same gases.

The utility of a filter covering one of the Pt electrodes and how it would create asymmetry is shown in Figure 2.19. Using chemiluminescence, 100 mg of zeolite NaY
powder was found to have a 10% conversion of 800ppm NO to NO\textsubscript{2} in 3%O\textsubscript{2} making it a good starting material as a filter to create asymmetry.

2.2.3 Type I, II, III testing results

2.2.3.1 NO sensing

Figure 2.20a clearly shows that when the NaY is placed onto one of the Pt electrodes there is a larger sensor signal for NO as compared to the blank. The sensitivity data in Figure 2.18 came from the blank response in Figure 2.20a. All three of the sensor designs exhibited similar behavior towards NO, as demonstrated in Figure 2.20b for a tubular (type I) design. Due to the asymmetry provided by the zeolite layer, it becomes possible to expose the complete sensor to the sensing gases without the need for a reference. Figure 2.20c compares the sensitivity plots for the three designs showing that the voltage follows a linear dependence with the logarithm of the NO concentration. The reproducibility of sensor performance is typified by the insert in Figure 2.20C for data obtained from three planar sensors where the signal variation for one standard deviation is shown. The variations are likely due to factors in the fabrication process, including the size and thickness of the Pt electrodes, and the zeolite film thickness and packing.

2.2.3.2 Interference effects

2.2.3.2.1 Oxygen

Since YSZ is an oxygen ion conductor, any imbalance of O\textsubscript{2} on the two Pt electrodes will alter the baseline. This was demonstrated by using a YSZ closed-end tube type sensor with an air reference where the oxygen inside the tube is at 21%, and the
outside of the sensor was exposed to NO (200-1000 ppm) at varying oxygen levels similar to a combustion environment. Figure 2.21B again shows the NO calibration curves for the air reference sensor (the same data from Figure 2.14B). If a similar experiment is done with a zeolite-based sensor (e.g. type II in Figure 2.4), the calibration curves collapse to approximately the same line (Figure 2.21C), demonstrating that the level of O$_2$ at both Pt electrodes is similar, primarily because the microporosity of zeolite allows for O$_2$ transport to the underlying Pt electrode. Another manifestation of the same effect can be seen in Figure 2.20A for the planar sensor (type III), where a changing O$_2$ level from 3% to 10% does not alter the background signal.

### 2.2.3.2.2 Carbon monoxide

Figure 2.22A shows the calibration curves obtained with CO using sensor type II and its dependence on the O$_2$ concentration of the background gas. There is a strong signal from CO due to the electrochemical reaction $\text{CO} + \text{O}^2- \rightarrow \text{CO}_2 + 2\text{e}^-$. However, the slope of the calibration curve, which is a measure of sensitivity, decreases with increasing O$_2$ concentration. Figure 2.22B shows the sensor trace to both CO and NO in 21% O$_2$, where the sensor appears to be almost insensitive to CO. Our explanation for the gradual decrease in CO signal with O$_2$ is that the CO gets oxidized on the Pt surface at higher background O$_2$ levels, before it can reach the Pt-YSZ triple point boundary interface for the electrochemical reaction and the oxidation product CO$_2$ is electrochemically inactive.
2.2.3.4 Nitrogen dioxide

Figure 2.23 compares the potentiometric response of a planar sensor (Type III) to 400 ppm NO and 400 ppm NO + 100 ppm NO\textsubscript{2} in 3\% O\textsubscript{2} at 500°C. It is clear that in the presence of NO\textsubscript{2}, the signal for NO is considerably diminished, indicating significant interference.

2.2.3.3 Temperature effects

Using the sensor type I in Figure 2.3, we measured the NO response in a fixed O\textsubscript{2} concentration (3\%) at temperatures varying from 500-700°C. This temperature range throughout this chapter was chosen because YSZ begins to show significant ionic conduction only above 450°C and zeolite Y retains its crystalline structure up to 750°C. It was observed that the sensitivity of the sensor to 200-1000ppm NO decreased with increasing temperature with virtually no sensor response at 700°C. We propose two possible reasons, preferential oxidation of NO at the Pt surface rather than the Pt-YSZ boundary at the higher temperatures, and also diminished adsorption of NO at the triple points on the Pt-YSZ at higher temperatures. This temperature dependence is consistent with previous measurements, e.g. on CdCr\textsubscript{2}O\textsubscript{4} electrodes on YSZ, a significant loss of sensitivity at 600°C was reported [10].

2.2.4 Sensor characterization

The zeolite NaY filter material was investigated after being used in a type II sensor for 2 days. Figure 2.24 shows the results of the powder x-ray diffraction pattern for fresh commercial NaY powder out of the bottle and the used powder taken from the
sensor. The diffraction patterns are similar suggesting that no amorphous phase was formed at 500°C as expected since zeolite NaY maintains its crystal structure up to 700°C.

Electron microscope images were taken of the sensors and electrodes to give an idea of the microstructure. The images are all of typical polycrystalline sensors prepared in the manner described earlier and those used from the data that was shown above. Figure 2.25 is a secondary electron microscope (SEM) image of a typical sensor surface at the edge of the Pt electrode on the YSZ. It can be seen from this image that the Pt electrode is not completely continuous and shows some porosity. The Pt ink upon drying and sintering appears to crack. Figures 2.26-2.28 show back scattered electron (BSE) images of the electrode surface of a second sensor at various magnifications. It can also be seen from these images that the electrode is cracked and porous. Figures 2.29 and 2.30 show BSE images of the lead wire connection to the electrode surface. The images show that close to the wire the Pt from the electrode tends to separate and crack away from the wire. The wires used in these images were all 31 AWG (approximately 230 µm). The larger the wire the more stress is created at the interface of the connect as well as causing stress on the zeolite film that covers the wire. If the zeolite thick film is to completely cover the electrode then it must also cover the wire, thus the film must be thicker than the wire and in this case that would mean greater than 230 µm. In an attempt to minimize the thickness of the wire on type III sensors, the end was flattened before connecting as can be seen from the two images (Figures 2.29-2.30). It was found that even with a flatter wire the zeolite film would still crack. Figure 2.31 shows an SEM image of the zeolite thick film surface at 5000X which shows that the zeolite particles are
less than 1 µm in size. The zeolite layer thickness could not be readily determined as the film was very delicate. Any attempt to cut a cross section would destroy the film.

The thickness of a typical Pt electrode was determined by optical microscopy. The sensor was cut through the Pt electrode with a diamond coated circular saw-blade (Leco). To obtain an ideal cross section, the sample should be mounted in bakelite or lucite to minimize stress on the electrode by the saw. The method used here without the mount gives a general idea of the electrode thickness. Figure 2.32 shows a cross section of a Pt electrode towards the center. The brighter portion of the image is the Pt electrode on which the thickness is labeled at various points and at the top of the image is the Pt/YSZ interface. From Figure 2.32 it can be seen that the thickness of the electrode is about 200 µm at the center. Figure 2.33 shows that away from the center of the electrode the thickness can decrease to 21 µm and that the electrode is not uniform due to the hand painting method.

2.2.5 Engine exhaust testing

The interest in NO sensors arises because of their possible utility in sensing gases in high temperature combustion processes. Of particular interest to the community is sensing NO emissions from automotive engines. Because of the high temperatures and the presence of high flow rates and particulates in the exhaust, the sensor needs appropriate packaging. The planar sensor (type III) lends itself to a possible packaging design that can survive the harsh environment. Figure 2.11-2.13 showed how the planar sensor has been incorporated into a package for engine exhaust sensing.
This sensor was tested in the automotive engine set-up shown in Figure 2.13. An on-line IR analyzer was used to verify the sensor response. In the first test, the engine rpm was changed from 2000 to 3000 (Figure 2.34a) and at the same time, the IR signal for NO (Figure 2.34b) was compared to the sensor signal (Figure 2.34c). It is clear as the rpm is increased the amount of NO increases as measured by the IR. The sensor signal also follows the NO trace from the IR reasonably well, although it is very noisy, possibly due to the vibrations from the engine.

In the second test, the level of NO in the exhaust was altered by adjusting the engine rpm speed by quick throttles (2 = 1000rpm, 1,5 = 2000rpm, 3,4 = 4000rpm) and the NO emission profile as measured by the IR is shown in Figure 2.35a. The output of the NO sensor during the throttling is plotted in Figure 2.35b and the sensor peaks follow a similar time profile as the IR output (except for event 2, where no response of the NO sensor is observed). These preliminary data are encouraging, in that the sensor packaging survived repeated tests. The response time of the sensor is comparable to that of the IR detector. There is a delay in the response of the IR due to the length of the gas transfer line, which accounts for the small absolute time difference in the sensor and IR signals. The temperature of the exhaust stream fluctuated as the engine speed was altered and could be responsible for the changing backgrounds. Better heating control of the YSZ sensor element to minimize the effect of the temperature fluctuations is currently being investigated.
2.3 Discussion

Potentiometric sensors that exploit the differences in mixed potential between two electrodes for gas sensing have been extensively studied. Usually, the strategy is to use two different electrodes for providing asymmetry and hence a measurable emf response upon NO introduction [9, 11]. The strategy that we have proposed here is to use two similar Pt electrodes, but provide asymmetry via a chemical reaction that alters the species interacting with the two electrodes. Our choice of zeolite to alter the NO/NO\textsubscript{2} balance was based on several studies that show zeolites as excellent catalysts for NO oxidation. The role of zeolites as catalysts for selective catalytic reduction of NO\textsubscript{x} has been extensively studied [12] and it has been observed that the reduction is enhanced in the presence of O\textsubscript{2}. Mechanistic studies have shown that zeolites promote the oxidation of NO to NO\textsubscript{2}, the latter being involved in subsequent decomposition reactions to N\textsubscript{2} and O\textsubscript{2}. Amongst the zeolites that have been examined for NO to NO\textsubscript{2} oxidation are NaY, NaZSM-5, H-ZSM-5, H-mordenite and CuZSM-5 [12-15].

For all of the sensor types tested it is assumed that the relevant reaction at the zeolite/gas interface for NO\textsubscript{x} is:

\[ 2\text{NO} + \text{O}_2 \leftrightarrow 2\text{NO}_2 \]  

(2.5)

Chemiluminescence studies indicated that about 10% of the NO is converted to NO\textsubscript{2}. Equilibrium calculations [10, 16] predict that at 500°C, the ratio of NO/NO\textsubscript{2} in 5% and 0.5% O\textsubscript{2} are 4.9 and 32, respectively, whereas at 3% O\textsubscript{2}, we observe the ratio to be close to 8 indicating that the zeolite is helping establish the NO/NO\textsubscript{2} equilibrium. Thus, with the zeolite coating, there is an asymmetry of NO/NO\textsubscript{2} profiles at the two Pt electrodes. This asymmetry leads to sensing of NO. However, this also leads to the
observation that if NO\textsubscript{2} is present in the sensing stream and its concentration changes, then the NO signal is altered. Thus, the present sensor system cannot be used for sensing NO in gas streams where NO\textsubscript{2} concentration is also changing. Yamazoe and coworkers have shown that by using a three-electrode system with chromates as the sensing electrode, selectivity towards NO or NO\textsubscript{2} could be accomplished by applying a bias voltage to the sensing electrode relative to a Pt counter electrode, while measuring the voltage relative to a Pt-reference electrode [10, 17].

A major advantage of the zeolite-based design is the fact that NO response is insensitive to changing O\textsubscript{2} profiles in the gas stream. This arises from the porous nature of the zeolite, which allows for the penetration of O\textsubscript{2} to the Pt-YSZ interface. A part of the oxygen reacts with NO to form NO\textsubscript{2}, but considering the significant excess of O\textsubscript{2} over NO, the O\textsubscript{2} concentration change is very small. Another strategy for detecting NO in changing O\textsubscript{2} levels is based on multielectrode amperometric sensors, in which diffusion-limited passage of gases to multiple electrodes held at different potentials ensures that oxygen gets completely reduced at the first electrode, followed by NO reduction at the second electrode [18].

Interference from CO can be significant, but under the lean conditions that result in NO formation, the levels of CO should be small. Also, the fact that at high O\textsubscript{2} backgrounds, the effect of CO is minimized due to oxidation to CO\textsubscript{2} provides possible pathways for minimizing the CO interference. This may be especially useful for future lean-burn engine applications where there is more O\textsubscript{2} present.

The strategy of using a catalyst to suppress interference is well recognized in the sensor literature. Ono et al. used a Na\textsuperscript{+} conductor (NASICON) as the electrolyte and a
WO₃ and Pt/SiO₂ catalyst layer to detect NO and NO₂ at 150°C [19]. Zeolite filters have been used to minimize cross species interferences by chemically reacting the gas to undetectable species [3]. Our strategy is somewhat different, since we are using the zeolite to promote the sensing characteristics.

The zeolite-based sensor can also be fabricated with several designs, including a convenient planar design that was incorporated into a breadboard assembly for measuring NO in automotive exhausts.

All the sensor designs tested showed the ability to detect NO in the concentration range of 0-1000 ppm in 1-10% O₂ at 500°C. On average, the sensor response for 1000ppm NO was between 10-15mV from the baseline of O₂/N₂. The response to NOₓ from sensors in the literature varies widely depending on the materials used and testing conditions. For comparison only the sensors that could withstand high temperatures above 500°C will be considered. From a sensitivity standpoint, the zeolite-based sensor is not as good as the best mixed potential sensors made by using two different electrode materials. Yamazoe found that for a three electrode YSZ plate sensor, where a CdCr₂O₄ sensing electrode was polarized at 100mV with respect to a Pt counter electrode, the sensing electrode signal verses a Pt reference electrode gave a voltage change of around 30mV for 200ppm NO in air [10]. Whereas for a similar planar design (but without the applied voltage), the zeolite sensor produces a response of approximately 7mV. The response/recovery times of the zeolite-based sensor for laboratory tests is of the order of minutes, while it appears faster in the automotive exhaust tests, presumably because of much higher gas flows.
2.4 Conclusions

By using a microporous aluminosilicate zeolite that establishes the NO/NO₂ equilibrium at temperatures of 500°C and higher, an asymmetry was generated between two Pt electrodes on YSZ. This asymmetry led to a mixed potential signal, which was proportional to NO concentration (0-1000ppm) with a logarithmic dependence. The sensor response was stable in varying O₂ concentrations, but showed interference from CO and NO₂. The range of temperatures over which signals could be measured was 500-600°C with better sensitivity at the lower temperatures. Several sensor designs were tested, including a planar sensor that was packaged into a spark-plug type assembly and tested in an automotive exhaust train. The sensor response followed the NO concentration, with comparable response times as the infrared detector.
Figure 2.1. Schematic representation of a supercage of zeolite Y.
Figure 2.2. A. Closed-end O$_2$ sensor with an air reference. B. Optical microscope image of a Pt electrode on the outside tip of closed-end sensor.
Figure 2.3. A. Type I sensor. YSZ pellet and pellet mounted on an alumina tube. B. Side view of cross section of closed-end pellet design.
Figure 2.4. A. Type II sensor side view of a cross section of open-end tube type sensor. B. Optical microscope image of an open-end tube sensor.
Figure 2.5. A. Side and top view of the Type III planar sensor design. B. Optical microscope image of the top of a typical planar sensor without zeolite. C. Optical image of a planar sensor with zeolite NaY coating over one Pt electrode.
Figure 2.6. Diagram of the experimental set-up.

Figure 2.7. Side view of quartz sensor testing platform.
Figure 2.8. A. Picture of a Lindberg tube furnace used to heat the sensors in the lab. An inner quartz tube holder for the sensor is placed on top of the furnace. In the furnace is an outer quartz tube jacket where the sensor holder is placed to form a closed atmosphere. B. Picture of Sierra mass flowmeters mounted onto plexiglass and connected to Swagelok fittings and valves.
Figure 2.9. A. Optical picture of sensor element showing version with thermocouple and zeolite NaY pellet. B. Experimental sensor design for auto exhaust testing based on sensor type III.

Figure 2.10. A. Picture of final sensor assembly with protective chamber. B. Schematic of sensor temperature control and measurement scheme.
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Table 2.1. Theoretical slopes and voltages of O₂ sensor for (1-10% O₂) at 500 and 650°C.

<table>
<thead>
<tr>
<th>O₂%</th>
<th>mV(500°C)</th>
<th>mV(650°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope</td>
<td>-16.65mv/decade</td>
<td>-19.88mv/decade</td>
</tr>
<tr>
<td>1</td>
<td>50.69</td>
<td>60.53</td>
</tr>
<tr>
<td>3</td>
<td>32.40</td>
<td>38.69</td>
</tr>
<tr>
<td>5</td>
<td>23.89</td>
<td>28.53</td>
</tr>
<tr>
<td>10</td>
<td>12.35</td>
<td>14.75</td>
</tr>
</tbody>
</table>

Figure 2.13. Comparison of experimental and calculated calibration curves for O₂ sensor at 650°C.

$y = -19.149\ln(x) + 57.462$: experimental

$y = -19.882\ln(x) + 60.531$: theoretical
Figure 2.14. A. Sensor transient response at 500°C to varying NO concentration in a 10%O₂-N₂ background at 100cc/min flow rate. B. Calibration curves for NO response (200,400,600,800,1000ppm) at 500°C in a 3%, 5% and 10%O₂-N₂ background.
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**Figure 2.18.** Response of the blank sensor without a covering on the Pt electrode.

**1.** Heterogeneous gas-phase reaction over zeolite towards equilibrium.

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

**2.** TPB electrochemical reactions

\[ \text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-} \]

\[ 2\text{NO} + 2\text{O}^{2-} \rightarrow 2\text{NO}_2 + 4\text{e}^- \]

**Figure 2.19.** Mechanism schematic of non-air reference based planar sensor with a zeolite filter on one electrode and the other uncovered.
Figure 2.20. A. Sensor response for Type III sensor with and without zeolite and exposed to NO between 0-800 ppm. B. Sensor response for type II sensor. C. Comparison of Type I-III sensor responses to NO. (Insert shows the standard deviation of the data obtained from three different Type III sensors). All data at 500°C.
Figure 2.21. A. Air reference sensor diagram. B. NO calibration curves for varying O₂ concentrations on the outside. C. NO calibration curves for a Type II sensor with varying O₂ concentrations. All data at 500°C.
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Figure 2.23. Demonstration of interference from NO$_2$ for NO sensing on a planar type III design at 500°C.
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Figure 2.25 SEM image of a typical planar sensor surface at the Pt electrode edge on the YSZ.

Figure 2.26 BSE image of Pt electrode surface and lead wire edge at 100X.
Figure 2.27 BSE image of Pt electrode surface at 1250X.

Figure 2.28 BSE image of Pt electrode surface at 5000X.
Figure 2.29 BSE image of Pt lead wire and electrode interface at 25X.

Figure 2.30 BSE image of Pt lead wire and electrode interface at 100X for another sensor.
Figure 2.31 SEM image of zeolite NaY film on top of Pt electrode at 5000X.
Figure 2.32 Optical microscope image of cross section of center of Pt electrode.

Figure 2.33 Optical microscope image of cross section of center of Pt electrode away from the center.
Figure 2.34. Top. Rpm perturbation verses time via the dynamometer. Middle. IR analyzer response to NO during the rpm change. Bottom Sensor response during the rpm change.
Figure 2.35. A. IR gas analyzer response for NO to five engine throttles. B. Sensor response for the same five engine throttles.
CHAPTER 3

Development of a Selective Total NO\textsubscript{x} Sensing System Using a Pt Loaded Zeolite Y Catalytic Filter Bed

Chapter 2 concluded that it is difficult to measure NO or NO\textsubscript{2} selectively especially when both gases are present at the same time. Thus, we have developed a strategy in chapter 3 to measure the total NO\textsubscript{x} level (NO + NO\textsubscript{2}) in a background of O\textsubscript{2} and N\textsubscript{2} at high temperatures with minimal CO interference by combining a catalytic filter bed with the existing YSZ sensor device. The filter bed was composed of a Pt catalyst dispersed onto a zeolite Y support and placed before a YSZ with Cr\textsubscript{2}O\textsubscript{3} or Pt sensing electrodes. The zeolite filter acts as both a NO\textsubscript{x} equilibration and CO oxidation catalyst, oxidizing the incoming CO before it reaches the sensor. We found that the sensor signal could be magnified by keeping the filter bed and sensor at different temperatures.

3.1 Introduction: Filters Used in Conjunction with Sensors

There are several reports in the literature of using filters prior to the sensor for improving selectivity. These filters can be generally classified into two groups: adsorption or chemical filters. The adsorption filters remove interferents by adsorption, as in the use of a zeolite filter for removing isoprene from breath for breath analyzers [1]. Chemical filters can be further classified into two categories: reactant filters or catalytic filters. Reactant filters react with the gas in a stoichiometric fashion, e.g. Mo filters for
converting NO\textsubscript{2} to NO [2] or KMnO\textsubscript{4} for converting NO to NO\textsubscript{2} [1], and are consumed over time. Catalytic filters have been used to oxidize or equilibrate gases. The advantage of the catalytic filter is that it is not consumed in the reaction. A Pt-SiO\textsubscript{2}/WO\textsubscript{3} catalyst layer was used in an amperometric design to equilibrate NO\textsubscript{x} to NO\textsubscript{2} at 150\(^\circ\)C but the effect of higher temperatures was not investigated [3]. Pt on cordierite, Mn\textsubscript{3}O\textsubscript{4}, and Co\textsubscript{3}O\textsubscript{4} have been used as catalytic filter ahead of a resistive SnO\textsubscript{2} sensor for total NO\textsubscript{x} sensing in the patent literature [4].

In addition to the zeolite filter for isoprene there are other examples of use of zeolites as filters. For a NASICON-based CO\textsubscript{2} sensor, the zeolite acted as a filter to remove CO and ethanol, presumably by physical adsorption, though this was unclear from the paper [5]. Another study reported the use of a zeolite filter ahead of a resistive SnO\textsubscript{2} sensor for removing interference from ethanol by physical adsorption, and therefore needed regeneration to remove the adsorbed ethanol [6]. A chemically active zeolite filter that converted ethanol to C\textsubscript{2}H\textsubscript{4} decreased the interference from ethanol in CO detection by a resistive SnO\textsubscript{2} sensor [7]. Another example of a chemical filter is Nafion, which has also been found to discriminate against ethanol for CO detection by acid-catalyzed decomposition of ethanol [8].

We report in this chapter a system that can measure total NO\textsubscript{x} in a background of O\textsubscript{2} and N\textsubscript{2} at high temperatures with minimal CO interference. We have used a filter composed of a Pt catalyst dispersed onto a zeolite Y support placed before a YSZ air reference sensor with a Cr\textsubscript{2}O\textsubscript{3} sensing electrode. The zeolite acted as both a NO\textsubscript{x} equilibration and CO oxidation catalyst, oxidizing the incoming CO before it reached the
sensor. The sensor signal could be magnified by keeping the filter and sensor at different temperatures.

3.2 Experimental Description

3.2.1 Sensor designs and preparation

Two different sensor electrode arrangements (sensor#1 and sensor#2) for detecting total NO\textsubscript{x} were tested. Sensor#1 consisted of a single closed-end YSZ tube (Vesuvius McDanel, 8mol\% YSZ) that was 30cm long and had an i.d. of 8mm and a wall thickness of 2mm (Figure 3.1a). Two different materials were used for the sensing and reference electrodes. Pt served as an air reference electrode (R) made from Pt ink (Englehard corporation, lot# A4731) and was painted onto the inside of the YSZ tube. The Pt ink was then cured at 1250°C for 2 hours with a 6°C/min heating and cooling rate. Electrical contact with the Pt reference electrode was made by inserting a small alumina tube containing a Pt wire to make contact mechanically. The Pt sensing electrode (S) was prepared in the same manner as the reference electrode. S\textsubscript{2} was made from Cr\textsubscript{2}O\textsubscript{3} powder (Alfa Aesar) consisting of a 50 wt/wt\% mixture of the oxide and terpineol organic solvent. A Pt wire was wrapped around the outside of the YSZ tube and the Cr\textsubscript{2}O\textsubscript{3} paste was painted on top of the wire in a band around the tube circumference. The Cr\textsubscript{2}O\textsubscript{3} paste was then cured in air at 750°C for 2 hours with a 6°C/min heating and cooling rate.

Figure 3.1b shows sensor#2, which is also a closed end YSZ tube utilizing an internal Pt air reference electrode (R). On the outside of the tube, two Pt wires were wrapped around the circumference and Pt paste was painted on top of a portion of each of the wires in a square shape. The Pt paste was cured at 1250°C for 2hrs to form two Pt
electrodes in the planar configuration ($S_1$, $S_2$). A Pt loaded zeolite Y (PtY) powder was mixed with terpineol solvent in a 50 w/w% mixture to form a paste and painted directly onto $S_2$. The sensor was then heated to 500°C for 1hr to evaporate the solvent. The potential difference of the three possible electrode combinations ($S_1$,R), ($S_2$,R), ($S_1$, $S_2$) was measured.

### 3.2.2 Sensor Testing Set-up

The sensor testing set-up consisted of the sensor being placed into a controlled atmosphere quartz tube located inside a tube furnace and was the same as that described in chapter#2. The sensor furnace was connected to an external catalytic filter bed and a chemiluminescence analyzer as detailed in the next section and in Figure 3.2.

#### 3.2.2.1 Catalytic filter bed chamber

In the tests using the catalytic filter, a second quartz tube separately heated was connected to the tube with the sensor by metal to glass fittings. The second quartz tube had dimensions of 4.8 mm i.d. and 23 cm length and was set in a vertical position. Inside the center of the quartz tube was a porous quartz frit where 70 mg of zeolite powder (either PtY or NaY) was placed. The quartz chamber was maintained between 25-700°C by wrapping with a heater tape and a type K thermocouple that were connected to an Omega controller in a feedback loop. Figure 3.2 shows a schematic of the complete sensor testing system including the quartz tube holding the catalyst filter bed. The gas flow system was designed so that the test gas from the mass flow controllers could either flow directly onto the sensor or through the catalyst bed to the sensor.
3.2.2.2 Catalytic activity measurements of the filter bed via chemiluminescence and gas chromatography

The activity of the filter materials towards NO\textsubscript{x} equilibration ability was investigated by chemiluminescence and CO oxidation was determined by gas chromatography.

NO\textsubscript{x} measurements were done on an ECO Physics CLD 70S NO/NO\textsubscript{x} analyzer system with the ability to measure in either NO or total NO\textsubscript{x} mode outlined in Figure 3.2. 80mg of PtY or NaY catalyst was tested under a flow rate of 200 cm\textsuperscript{3}/min, as per the instrument requirement, while the catalyst was heated to 500-700\degree C. The analyzer was calibrated with gas standard of 600 ppm NO/balance N\textsubscript{2} (Praxair). EcoPhysics NO\textsubscript{x}View software provided the output of the NO or NO\textsubscript{x} levels in ppm values.

CO oxidation measurements were done on a Shimadzu GC-17A gas chromatograph (GC) with a Supelco Carboxen 1006 0.32 mm i.d. capillary column 30 m in length, a He carrier gas and a TCD detector. The detector was calibrated with a series of CO\textsubscript{2} concentrations in the range of 0-7000 ppm. 80 mg of PtY or NaY was placed into the quartz tube heated to 500\degree C. A typical experiment involved flowing 0-1000 ppm CO in a background of 3\% O\textsubscript{2}/He at 100 cc/min over the catalyst bed and CO\textsubscript{2} production was monitored by injecting a portion of the outgoing gas onto the GC column as shown in Figure 3.3a.
3.2.2.3 Catalytic microporous filter preparation

Two different forms of zeolite Y were tested as filter material. The first was composed of a powder (LZY-52 from Union Carbide) of commercial Na\(^+\)-exchanged zeolite Y (NaY). The second material used was a Pt loaded zeolite Y and was prepared as follows [9]. First, 1.0 g of commercial NaY powder was dried at 100\(^\circ\)C for 4 hours. A 5 mM solution of \([\text{Pt(NH}_3\text{)}_4]\text{Cl}_2\) was prepared and the 1.0 g of NaY was added to 100 ml of the solution for ion-exchange. This mixture was stirred at room temperature for 24 hours and then centrifuged and washed with distilled water. The resulting powder was dried at 70\(^\circ\)C overnight and then calcined at 300\(^\circ\)C for 2 hours. Finally the zeolite powder was exposed to a flowing gas mixture of 5% H\(_2\) (balance N\(_2\)) to reduce the Pt compound to Pt metal. The resulting zeolite PtY powder had a dark brown appearance. Elemental analysis using ICP optical emission spectroscopy determined the Pt content to be 10.9 wt%. Figure 3.3b shows SEM images of the PtY particles. Pt metal particles of sizes from 20-80 nm diameter were observed on the surface of the zeolite crystals. TEM analysis of similar PtY samples by other researchers in the group observed additional Pt particles smaller than 20 nm in diameter.

3.3 Results

3.3.1 Sensor\#1 response to NO\(_x\) mixtures without filter

In chapter 2, our primary sensing electrode was made from Pt. In this chapter, we also continued to use Pt metal as well as a Cr\(_2\)O\(_3\) metal oxide electrode. We chose to use a metal oxide electrode because the material will be easier to work with when doing electrode studies and it is ultimately cheaper than Pt. We specifically chose Cr\(_2\)O\(_3\) based
on literature studies that demonstrated compounds of Cr₂O₃ had a good response towards NOₓ [10]. We found in chapter 2 that the presence of both NO and NO₂ can cause a decrease in the sensor signal on Pt making it difficult to get a reliable calibration curve. Here, we wanted to further investigate the electrode response in NOₓ mixtures. We used several of sensor type#1 in our study.

Sensor#1a was tested using a Cr₂O₃ and Pt sensing electrode simultaneously (from Figure 1a). The sensor was tested for 0-1000 ppm NO and NO₂ at 500°C in 3%O₂/N₂. The transient plots for the Cr₂O₃ response are shown in Figure 3.4. It is obvious that the response to NO and NO₂ are in opposite directions. Figure 3.5 shows the transient plot for the Cr₂O₃ response to a series of mixtures of NO and NO₂ that were tested at a total NOₓ of 1000 ppm. In the NOₓ mixtures, the signal decreased from that compared to just NO or NO₂ alone. At a mixture ratio of 700/300 the signal crosses the baseline. Figure 3.6a shows the sensitivity plot of the results from Figures 3.4 and 3.5 for the Cr₂O₃ and the response of the Pt electrode. It is interesting to note that the Cr₂O₃ electrode signal is higher than the Pt signal on this sensor. Figure 3.6b compares the response of the Cr₂O₃ and Pt electrode. At higher NO concentrations both electrodes became “saturated” in that the sensitivity remained unchanged or actually decreased. The Pt electrode in sensor#1a also gave a diminished signal when exposed to mixtures of NO and NO₂ at 1000 ppm total NOₓ (not shown). The mixture ratio that gave a signal closest to the baseline for Pt was for 600 ppm NO/400 ppm NO₂ giving a voltage of 25 mV, which was close to the 25 mV baseline of just 3% O₂.

The sensitivity trend for Cr₂O₃ and Pt in not always the same as can be seen from the plots for sensor#1b in Figures 3.7 and 3.8a. This is the same design as sensor#1a but
now gives a Pt signal higher than the Cr$_2$O$_3$ for 100-1000 ppm NO or NO$_2$ in 3% O$_2$ at 500°C. This could be due to the way the electrodes are prepared each time as they are made by hand. Mixtures of NO and NO$_2$ were again tested again at a total NO$_x$ of 600 ppm and the same general trend was observed (similar to Figure 3.6a) with the point closest to the baseline at a 500 ppm NO to 100 ppm NO$_2$ ratio for both Cr$_2$O$_3$ and Pt.

Figure 3.8b shows that for the Cr$_2$O$_3$ electrode, the response of sensor#1b is linear versus the logarithm of the NO or NO$_2$ concentration.

### 3.3.2 Evaluation of NO conversion over zeolite catalytic filter beds by chemiluminescence

As discussed in the introduction, we decided to employ a catalytic filter to overcome the problem of the opposite response of NO and NO$_2$.

The conversion of NO to NO$_2$ was examined after passage through the filter bed at temperatures of 500, 600, and 700°C. Two zeolite filter materials, NaY and PtY, were tested. Zeolite Y was chosen because of its high internal microporosity ensuring interaction of the gas with the catalyst in the pores. Data for the conversion of 600 ppm NO/3% O$_2$/N$_2$ flowing over the PtY filter bed are shown in Table 1 and compared with the calculated values using thermodynamic parameters [11]. The average conversions (with the variation for one standard deviation) of 600 ppm NO/3%O$_2$/N$_2$ flowing over the PtY filter bed at 500, 600, and 700°C are listed. At 500°C for five trials the observed conversion was 13.61 ± 0.80% and comparable with the calculated value of 13.66% using thermodynamic parameters [11]. Therefore with PtY as the filter material, the oxidation of NO reached close to its calculated equilibrium value. Using NaY as the filter material
at 500°C, full equilibration of 600 ppm NO was not achieved (3.80% conversion to NO2). Thus, we focused primarily on PtY for the rest of the experiments with the filter.

3.3.3 Total NO\textsubscript{x} sensing utilizing zeolite catalytic filter with sensor

3.3.3.1 Sensor and filter bed at same temperature of 500°C

The simplest combination of using a filter and sensor together is to test them at the same temperature. We continued to use the second sensor with a Cr\textsubscript{2}O\textsubscript{3} and Pt electrode, sensor#1b, and tested it at 500°C with the catalyst filter bed also at 500°C. First we wanted to make sure the empty quartz catalyst reactor (“blank”) that holds the filter bed had minimal activity on NO\textsubscript{x} conversion and it was tested using the set-up in Figure 3.2. 600ppm NO or NO\textsubscript{2} in 3% O\textsubscript{2} flowed directly onto the sensor to give an absolute signal of -55 mV for NO and +35 mV for NO\textsubscript{2} with the baseline at -34 mV (3% O\textsubscript{2}/N\textsubscript{2}) for the Cr\textsubscript{2}O\textsubscript{3} electrode as shown in Figure 3.9a. The Pt electrode gave a larger signal as observed earlier. When the gas was directed through the empty heated reactor, there was less than a 1% decrease in the Cr\textsubscript{2}O\textsubscript{3} response to NO, whereas NO\textsubscript{2} exhibited a diminished signal of 13%. The conversion for NO\textsubscript{2} may be expected since it is less stable thermodynamically at higher temperatures and is possibly reacting on the walls of the empty quartz reactor.

The quartz reactor was then filled with NaY and heated to 500°C and tested with the sensor. There was a decrease in the sensor signal for both 600 ppm NO in Figure 3.9b (about 1.5% for the Cr\textsubscript{2}O\textsubscript{3} electrode) and NO\textsubscript{2} in Figure 3.9c (about 18% for the Cr\textsubscript{2}O\textsubscript{3} electrode), and the NO and NO\textsubscript{2} responses remained in opposite directions.
Next, the quartz reactor was filled with PtY and tested for response to 400, 600, and 1000 ppm NO and NO\textsubscript{2} through the PtY bed or the bypass. The sensor transient plot is shown in Figure 3.10.

Figure 3.11a compares the sensor\#1a response as change in emf from the baseline (3\%O\textsubscript{2}/N\textsubscript{2}) for 1000 ppm NO and 1000 ppm NO\textsubscript{2} (data from Figure 3.7) and the same gases passed through the PtY catalytic filter (data from Figure 3.10). It is clear that without the filter NO and NO\textsubscript{2} signals are in the opposite direction, but with the PtY filter the signals for NO and NO\textsubscript{2} are almost similar in magnitude and direction with a shift from the baseline (-34 mV) of about -5 mV.

The PtY was also tested with total NO\textsubscript{x}, but different ratios of NO and NO\textsubscript{2}. Data for four different ratios at a total NO\textsubscript{x} of 1000 ppm are shown in the inset of Figure 3.11a. The signals are of comparable magnitude, despite different starting ratios of NO and NO\textsubscript{2}. Figure 3.11b shows the calibration curve for the Pt and Cr\textsubscript{2}O\textsubscript{3} electrodes at 500\textdegree C to NO\textsubscript{x} and the filter at 500\textdegree C based on the data in Figure 3.10.

3.3.3.2 Investigation of the nature of the response with filter and sensor at same temperature

It was interesting to note that when the sensor and the filter were at the same temperature there was still a small residual signal to changing NO\textsubscript{x} levels (Figure 3.11B). This change could be due to small changes in the O\textsubscript{2} concentration when mixing the sensing gases, a small difference in temperature between the filter and sensor or a chemical effect. We decided to investigate the possibility of changing O\textsubscript{2} levels.

One method to monitor changing O\textsubscript{2} levels is to use a commercial O\textsubscript{2} analyzer to measure the O\textsubscript{2} concentration when the NO or NO\textsubscript{2} gases are introduced at different
levels. We connected a commercial Amptech O$_2$ analyzer in series with the gas stream from the flowmeters and observed a maximum change of 3.0% O$_2$ to 3.11% O$_2$ when changing the NO$_x$ from 100 to 1000 ppm. In addition, no interference from NO or NO$_2$ was observed on the analyzer. Thus it appears that the O$_2$ level in the gas stream does not vary considerably. Looking at Figure 3.11b for sensor#1b it is seen that for Pt the EMF change from the baseline (3%O$_2$/N$_2$) to 1000 ppm NO or NO$_2$ + 3%O$_2$/N$_2$ gave a change of -10 mV and for the Cr$_2$O$_3$ electrode the change was -2.5 mV. We also did an additional experiment using a Co$_3$O$_4$ electrode on YSZ coupled with the PtY filter bed in the same experiment as with the Pt and Cr$_2$O$_3$ electrodes. We observed and EMF change from the baseline of -5.5 mV for both 1000 ppm NO and NO$_2$. Considering the Nernst equation expression in Chapter 2 we can calculate the O$_2$ concentration change that would be required to induce a change of 10 mV, 2.5 mV and 5.5 mV respectively. Any O$_2$ change that occurs in the sensing gas should affect each electrode equally assuming they have a Nernstian response towards O$_2$. But it is observed that each electrode has a different response suggesting a possible temperature or chemical effect.

Using the Nernst equation:

$$\text{EMF} = \frac{RT}{4F}\ln\left(\frac{P_{O_2}^{\text{sensing}}}{P_{O_2}^{\text{reference}}}\right)$$  \hspace{1cm} (3.1)$$

with T = 500°C (773K), P$_{O_2}^{\text{reference}}$ = 21% O$_2$ and P$_{O_2}^{\text{sensing}}$ = 3% O$_2$ the EMF observed should be -32.4 mV. For a ΔEMF of 10 mV to -42.4 mV it would give a P$_{O_2}^{\text{sensing}}$ = 1.6% O$_2$ for a change of 1.4% O$_2$. Similarly a ΔEMF of 2.5 mV corresponds to a 0.35% O$_2$ change. Whereas the maximum change indicated by the O$_2$ analyzer was 0.11% O$_2$.  

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To further verify that $O_2$ changes are not the cause of the small response to $NO_x$, we fabricated a third sensor, sensor#1c, using only a $Cr_2O_3$ electrode and heating it to higher temperatures to observe the response to $NO_x$ and $O_2$ up to 750°C. The advantage of testing at higher temperatures is that the response to $NO_x$ diminishes significantly as observed in chapter 2 and the response to $O_2$ should increase based on the Nernst equation 3.1. At a temperature where there is no response to $NO_x$, only the effect of $O_2$ would be observed.

The sensor was tested at 500, 600, 700, and 750°C for varying $O_2$ levels of 1, 3, 5, and 10%$O_2$ and for levels of NO and NO$_2$ in 3% $O_2/N_2$. Figure 3.12 shows the experimental calibration curves of sensor#1c obtained for $O_2$, NO and NO$_2$. For $O_2$ the curves are close to the theoretical values and it is evident that as the temperature increases the slope of the calibration curve increases. For NO and NO$_2$ it is seen that the responses decrease with an increase in temperature and are close to zero above 700°C.

Sensor#1c was cooled to 500°C and then tested for its response to $NO_x$ with the PtY filter bed also at 500°C. Figure 3.13 shows the calibration curve obtained for 0-1000 ppm NO and NO$_2$ in 3% $O_2/N_2$. With this particular sensor, the change from 0-1000 ppm NO or NO$_2$ is only about 1.5 mV in magnitude compared with a 2.5 mV change for the $Cr_2O_3$ electrode on sensor#1b in Figure 3.11. However the lower signal of sensor#1c may be expected since at 500°C sensor#1b give a higher signal to NO and NO$_2$ (shown in Figure 3.7) than did sensor#1b (shown in Figure 3.12). This could be due to a slight difference in the electrode properties during preparation. In any case, the 1.5 mV change for 1000ppm NO and NO$_2$ at 500°C in Figure 3.13b is larger than what was observed for a change due
to O$_2$ at 750°C of 0.5 mV shown in Figure 3.13a. We can conclude that this residual signal could be due to a small temperature difference between the filter and the sensor.

### 3.3.3.3 Sensor and filter bed at different temperatures

The small signal that was obtained when the sensor and the filter were at the same temperature is not very practical for real applications. Thus, we considered the idea that if the filter and sensor were maintained at different temperatures, the NO$_x$ gas could equilibrate first on the filter at a temperature $T_1$ and then re-equilibrate on the sensor electrode at temperature $T_2$.

NO and NO$_2$ at concentrations between 0-1000 ppm in 3%O$_2$ were passed over the PtY filter bed at temperatures ranging from 400-700°C, with sensor#1b at 500°C. These data are shown for the Cr$_2$O$_3$ electrode in Figure 3.14. A set of measurements were also made with sensor#1c at 400°C, while the PtY filter bed was varied from 400-600°C, and the data is shown for the Cr$_2$O$_3$ electrode in Figure 3.15. Several conclusions can be reached from these data. First, the smallest sensor signals are observed when the filter and sensor are at the same temperature, as observed earlier. Second, the signals due to NO and NO$_2$ overlap well under all concentration ranges. Third, the direction of the signal is dependent on the temperature of the filter relative to that of the sensor. For filter temperatures lower than the sensor, the signal is more positive compared to the baseline with just 3%O$_2$, whereas the reverse is true if the temperature of the filter is higher than that of the sensor. Fourth, the magnitude of the sensor signal is directly proportional to the temperature difference between the filter and the sensor.
3.3.3.4 Total NO\textsubscript{x} sensor design using a pseudo reference electrode

To get the largest sensor signal in a system with two electrodes, the ideal case would be where electrode 1 gives no signal for the gas of interest and electrode 2 gives the largest possible signal. A true reference electrode would not change potential due to any species present. In reality for metal oxide based sensors, it has been difficult to find a material that is insensitive to every gas. As discussed earlier, one method to make a fixed potential electrode in potentiometric YSZ based sensors has been to use a fixed air reference [10] or a sealed reference [12] (see Chapter 1 Figures 1.10 and 1.13). The problem with the air reference is that it can dramatically increase the size of the sensor and limit the placement possibilities. The fixed reference allows for reduced size and increased placement options but the high temperature stability of the seals is questionable. Some groups have simply covered the sensing electrode with an inorganic adhesive so that no gas can get through to the electrode [13]. Other research has involved using materials that inherently do not give a response to the gas of interest. The Yamazoe group has found various oxides that give a low response to NO\textsubscript{x} including MgFe\textsubscript{2}O\textsubscript{4} [14], numerous perovskites such as DyCrO\textsubscript{3}, NdCrO\textsubscript{3}, SmMnO\textsubscript{3}, LaFeO\textsubscript{3}, LaCoO\textsubscript{3}, LaNiO\textsubscript{3}, YbMnO\textsubscript{3}, [15] and single metal oxides including MoO\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, Nd\textsubscript{2}O\textsubscript{3} [16]. No investigation as to why these oxides gave a low signal was undertaken. In this section we have proposed the idea of using the PtY to create a pseudo-reference electrode on our sensor.

The idea was first tested by using a bare Cr\textsubscript{2}O\textsubscript{3} and Pt electrode (on sensor#1a) and observing their response to NO\textsubscript{x} as shown in Figure 3.4 and Figure 3.6 and

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subsequently coated them with a layer of the PtY. We observed that the signal for NO$_x$ drastically decreased in both cases. For the uncovered Cr$_2$O$_3$ electrode it gave a mixed potential signal from the baseline of -15 mV for 1000 ppm of NO and 90 mV for NO$_2$ and when covered the signal decreased to -1.2 mV and -1.2 mV for NO and NO$_2$ respectively. A similar result was observed for the Pt electrode which gave a mixed potential signal from the baseline when uncovered of -15 mV for 1000 ppm of NO and 70 mV for NO$_2$ and when covered the signal decreased to -10 mV and -5 mV for NO and NO$_2$ respectively. There was a slow recovery time for the PtY covered electrodes upon turning off the NO or NO$_2$ gas. We decided that further test this idea by making a new sensor and leaving one electrode uncovered and one covered simulating a planar device on an air reference based sensor.

Sensor design#2 which is represented in Figure 3.1b was examined. It had two Pt electrodes, one was bare Pt (called S$_1$), the other covered with a layer of PtY paste (called S$_2$). The sensor side (S$_1$ and S$_2$) was exposed to 560 ppm NO$_x$ at 100 cm$^3$/min, with a static air reference at the internal Pt electrode (R). Three simultaneous emf values were recorded upon exposure to NO$_x$, (S$_1$,R), (S$_2$,R) and (S$_1$,S$_2$) and shown in Figure 3.16a with the sensor at 500°C and the PtY filter at 600°C. It is seen that for (S$_2$,R) no response was observed when exposed to NO or NO$_2$ in 3% O$_2$. For, (S$_1$,R) with the bare Pt sensing electrode, the response to NO or NO$_2$ was similar in magnitude and direction. When the signal between the two electrodes (S$_1$,S$_2$) is considered, it also shows the same signal for the two NO$_x$ species.

We also measured the NO and NO$_x$ (NO + NO$_2$) levels with the chemiluminescence NO$_x$ analyzer in parallel with the sensor measurement at the time.
The result is shown in Figure 3.16b and follows the same pattern that of the sensor. A few interesting things can be obtained from this graph. For the 560 ppm NO response between 4 and 11 min we can see that the total NO\textsubscript{x} reads 560 ppm on the analyzer. Since this gas has passed through the PtY filter the total NO\textsubscript{x} is not only in the form of NO it also has a portion of NO\textsubscript{2}, as observed when measuring in the NO mode which reads 500 ppm. The remaining NO\textsubscript{x} is 60 ppm NO\textsubscript{2} and the final signal from the sensor is due to the mixture of these two gases. The spike that occurs near reading#500 in Figure 16b is due to switching between the NO\textsubscript{x} and NO mode since the analyzer only has one channel and during the switch, the counting stops temporarily. Similarly the sensor trace for 560 ppm NO\textsubscript{2} sent through the filter follows the NO\textsubscript{x} analyzer well, indicating 560 ppm total NO\textsubscript{x} as well as 500 ppm NO. The other “spikes” in the analyzer signal appear to be due to mixing of the gas in the stainless steel tubes. When the NO\textsubscript{2} is first introduced a sudden pressure pulse occurs resulting in a temporary higher concentration. Also it takes time for the gases to mix in the lines and stabilize to a constant concentration. This may explain the same spikes observed on the sensor around 20 min and the spikes observed on many of our sensor tests (see Chapters 2-4).

In addition to the PtY covered Pt we tried to create a pseudo reference in another manner by coating Ceramabond 569 and 617 on top of a Pt electrode to make a gas tight seal. Both of these did not work and still gave a signal for NO. The material is known to be porous and can leak although it was used successfully in the study of mixed potential CO sensors [17]. Miura et al. used an inorganic adhesive covering an electrode to create a fixed reference for NO\textsubscript{2} although the concentration was on the order of ppb thus if any leak occurred it should cause little interference [13].
In Chapter 4 we will test an electrode material that inherently has a low sensitivity for NO\textsubscript{x} without the use of filters or coatings. This is an advantage as it makes for a simpler electrode system and may also serve as a possible pseudoreference electrode.

### 3.3.4 CO Interference Studies

Sensor #1a with the Cr\textsubscript{2}O\textsubscript{3} sensing electrode was tested at 500°C, and the data is shown in Figure 3.17 for 0-1000 ppm CO. The direction of the sensor response to CO is in the same direction as that of NO. However, unlike the dependence of the signal on the logarithmic value of the concentration of NO or NO\textsubscript{2} shown in Figure 3.6, the response had a linear relationship with CO concentration, and is consistent with previous studies [18, 19].

#### 3.3.4.1 Evaluation of CO conversion over filters by gas chromatography

The influence of the external zeolite filters on CO oxidation chemistry was examined using the system in Figure 3.3a. The filter was heated to 500°C and the CO\textsubscript{2} formation was monitored by GC. Initially the blank heated quartz reactor at 500°C was tested with 7000 ppm CO/3%O\textsubscript{2} and its conversion to CO\textsubscript{2} was minimal (4%). PtY had a high conversion for 7000 ppm of CO and a complete conversion for 1000 ppm CO to CO\textsubscript{2} whereas NaY did not. Table 3.2 shows the percent conversion for the two zeolites for the two concentrations of CO tested.
3.3.4.2 Utilization of the filter to oxidize CO before the sensor

Flowing the gas through the empty heated reactor showed no signal for 600 ppm CO/3% O₂. The sensing tests were then repeated with CO passing first through the filter bed. With 80 mg of NaY zeolite, the signal decreased to -39 mV from -35 mV. For 80 mg of PtY zeolite however, there was no net signal for CO, as shown in Figure 3.18. The sensor was exposed to 600 and 1000 ppm of CO directly and then the CO was diverted through the PtY catalytic filter bed prior to the sensor.

Tests with mixtures of CO and NO together were done. Figure 10 shows the change in response from the baseline when sensor#1a and the PtY filter are at 500°C for 400 ppm CO, 600 ppm NO and 400 ppmCO + 600 ppm NO with and without the PtY filter. In the presence of CO and NO, the emf signal is greater than the sum of the two individual gases. When passing over the PtY, however, it is seen that the interference of CO on NO is virtually eliminated.

3.4 Discussion

The discussion is divided into various sections: N₂, O₂, and NOₓ thermodynamics and kinetic properties, mixed potential nature of the signal, role of the zeolite filter and enhancement of signal by differential temperature measurement.
3.4.1 NO\textsubscript{x} chemistry

3.4.1.1 NO properties

3.4.1.1.1 Physical characteristics of NO

NO is blue in color in its liquid and solid forms and colorless in the gaseous state. NO is usually encountered in the gaseous form due to its boiling point of -151.77\degree C (melting point at -163.65\degree C). Molecular orbital theory assigns NO an electron configuration with an unpaired electron in an antibonding orbital (2\pi\textsuperscript{*}) making it a free radical. The result of this odd electron gives NO paramagnetic characteristics [20]. NO has a bond length of 1.14 Å which is in between a typical carbon double bond (1.18 Å) and carbon triple bond (1.06 Å) [21]. NO in the gas phase does not form a polymer like structure like many other free radical complexes, but exhibits this behavior to an extent in the liquid and solid forms [20]. The low ionization potential [21] of NO (9.25 eV) compared to other similar gases CO (14.0 eV), O\textsubscript{2} (12.1 eV), and N\textsubscript{2} (15.6 eV) can result in ionization to the nitrosonium cation NO\textsuperscript{+}. The NO\textsuperscript{+} ion has a shorter and stronger bond than NO, which suggests the antibonding nature of the lone electron in the NO molecule [22].

3.4.1.1.2 Homogeneous formation and decomposition of NO

The direct formation of NO from the elements N\textsubscript{2} and O\textsubscript{2} at room temperature is difficult due to the large positive Gibbs free energy of formation required (+20 kcal/mol) [21]. This reaction:

\[
N_2 + O_2 \rightarrow 2\text{NO}
\] (3.2)
has a very small equilibrium constant at 25°C ($K_f = 4.6 \times 10^{-31}$) thus it produces a very small concentration of NO at equilibrium. A catalyst is of little help because it will only enable equilibrium to be reached more quickly [23]. At 2000°C, the equilibrium constant becomes larger so that about 0.4% NO is formed at equilibrium. To obtain NO in this case, the reaction mixture must be quickly cooled otherwise decomposition can take place via:

$$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2 \quad (3.3)$$

Reaction 3.3 has a very large equilibrium constant at 25°C ($K_b = 2.2 \times 10^{30}$) but at moderate temperatures, the rate of dissociation is too slow to be of much significance [23] due to a high activation energy of 364 kJ/mol[24].

### 3.4.1.1.3 Reactions involving NO with O₂

At moderate temperatures (i.e. < 700°C) NO can react with oxygen to form NO₂:

$$2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \quad (3.4)$$

This reaction has been well characterized as a third order reaction following a simple third order rate law [25]:
\[-\frac{d[NO]}{dt} = k[NO]^2[O_2]\] (3.5)

A specific characteristic of this reaction is that the rate constant has a negative temperature coefficient in the range of 413-923°C [25]. In fact in the presence of O₂, NO and NO₂ are in equilibrium with each other and the NO/NO₂ ratio is defined by the temperature and pO₂. Figure 3.20 shows a graph from the literature of the calculated thermodynamic percent conversion in 20%O₂ of NO to NO₂ or NO₂ to NO in reaction 3.4 over a range of temperatures. It is observed that NO is more stable at high temperatures (this is the reason why more NO forms in the cylinder of an engine) and NO₂ is more stable at low temperatures.

### 3.4.1.2 NO₂ properties

**3.4.1.2.1 Physical characteristics of NO₂**

NO₂ is a reddish brown gas with a boiling point of 21.2°C and a melting point of -11.2°C [20, 23]. The molecule has a bent V-shaped structure similar to ozone (O₃) and has a free electron on nitrogen resulting in a paramagnetic species. NO₂ has an N-O bond distance of 1.19Å and a bond angle of 134° [20].

**3.4.1.2.2 Decomposition of NO₂ to form NO and O₂**

At lower temperatures NO₂ is in equilibrium with N₂O₄ but above 150°C NO₂ begins to decompose leading to complete decomposition around 600°C via the following reaction scheme [23, 26]:

\[2NO₂ \rightarrow 2NO + O₂\]
The theoretical conversion of NO₂ to NO is shown in Figure 3.20. This figure does not account for the formation of the dimer, N₂O₄.

### 3.4.1.2.3 Equilibrium of NO and N₂O₄

NO₂ is produced on an industrial scale in the second step of the Ostwald process reaction scheme [23]. The NO₂ that is formed is then dissolved in water to form nitric acid and nitric oxide. NO₂ exists in equilibrium with dinitrogen tetroxide:

\[
\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2 \quad (3.6)
\]

which is a colorless compound. This reaction is exothermic, thus at low temperatures N₂O₄ is predominant but at temperatures above 140°C, equilibrium lies favorably toward NO₂ [23].

### 3.4.2 The nature of the mixed potential sensor response to NOₓ

A major advancement in improving the sensitivity of YSZ solid electrolyte sensors has been the use of metal oxide sensing electrodes [3, 10, 15, 19, 27]. Many metal oxide sensing electrodes have been investigated for NO/NO₂ detection with a large variation in sensitivity [14, 28].
In this study, we used Cr$_2$O$_3$ as the sensing electrode system, primarily because previous studies have shown that several compounds of chromium demonstrate high sensitivity [10, 28]. For metal oxide electrodes, it is well recognized that the response for NO and NO$_2$ are usually in opposite directions with the NO$_2$ response being larger [15] as observed in Figure 3.4. The electrochemical reactions at the TPB are shown below:

\[
\begin{align*}
2\text{NO} + 2\text{O}^{2-} &\rightarrow 2\text{NO}_2 + 4\text{e}^- \quad (3.8) \\
2\text{NO}_2 + 4\text{e}^- &\rightarrow 2\text{NO} + 2\text{O}^{2-} \quad (3.9) \\
\text{O}_2 + 4\text{e}^- &\rightarrow 2\text{O}^{2-} \quad (3.10)
\end{align*}
\]

For these gases, the mixed potential ($E_m$) at a fixed O$_2$ concentration takes the form shown in equations (3.11) and (3.12) for NO and NO$_2$, respectively [10]:

\[
\begin{align*}
\text{NO: } E_m &= \text{constant} - k_{\text{NO}}\ln[\text{NO}] \quad (3.11) \\
\text{NO}_2: E_m &= \text{constant} + k_{\text{NO}_2}\ln[\text{NO}_2] \quad (3.12)
\end{align*}
\]

where the constants $k_{\text{NO}}$ and $k_{\text{NO}_2}$ are determined by adsorption properties of the gases, as well as electrochemical parameters.

Figure 3.8b shows that the Cr$_2$O$_3$ indeed had a linear response versus $\ln[\text{NO}_X]$, with the slopes of NO and NO$_2$ having opposite sign, suggesting a mixed potential behavior.

Figure 3.6a also shows that for mixtures of NO and NO$_2$, signals intermediate between that of NO or NO$_2$ alone are observed. Chapter 1 showed that the mixed potential has been approximated by using Butler-Volmer expressions [10]. For a mixture of gases, both NO and NO$_2$ need to be simultaneously considered in the Butler-Volmer equation. The treatment we develop here is similar to what has been done in the
corrosion/dissolution literature [29, 30]. For a gas mixture with NO\textsubscript{2} in excess of the equilibrium concentration (NO, NO\textsubscript{2}, O\textsubscript{2}) at a fixed temperature T and potential E, the anodic (\(i_a\)) and cathodic (\(i_c\)) currents are:

\[
i_a = k_o [O_2] \exp\left[\frac{\alpha_o FE}{RT}\right] \tag{3.13}
\]

\[
i_c = k_{NO} [NO] \exp\left[\frac{\alpha_{NO} FE}{RT}\right] - k_{NO_2} [NO_2] \exp\left[\frac{-(1-\alpha_{NO}) FE}{RT}\right] \tag{3.14}
\]

Where \(\alpha\) is the transfer coefficient and k is the rate constant. At mixed potential, \(E_m\), the anodic and cathodic currents are equal, and making the assumption that all \(\alpha\)'s = \(\frac{1}{2}\):

\[
k_o [O_2] \exp\left[\frac{FE_m}{2RT}\right] = -k_{NO} [NO] \exp\left[\frac{FE_m}{2RT}\right] + k_{NO_2} [NO_2] \exp\left[\frac{-FE_m}{2RT}\right] \tag{3.15}
\]

\[
E_m = \frac{RT}{F} \ln \left(\frac{k_{NO_2} [NO_2]}{k_o [O_2] + k_{NO} [NO]}\right) \tag{3.16}
\]

Equation 3.16 predicts that for the limiting condition \(k_o [O_2] >> k_{NO} [NO]\), \(E_m\) should become independent of the concentration of NO. Although in our experiments we tested 3%O\textsubscript{2} and up to 1000 ppm NO and still observed an NO signal, so the derived equation may not be valid under the limiting condition. For NO concentrations in excess of equilibrium values, equations similar to (3.13-3.16) can also be set up.

3.4.3 Role of the filter

The sensor tests were done between 400-700\(^\circ\)C in O\textsubscript{2}. Thus, the reaction of interest on the zeolite filter is the equilibration between NO and NO\textsubscript{2} described in section 3.4.1.1.3. If the NO and NO\textsubscript{2} mixture is in the equilibrated state, the sensor signal should

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be close to the baseline since the driving force for electrochemical reactions is minimal. This indeed bears out experimentally, since the lowest signal for the 600 ppm NO\textsubscript{x} mixtures occurs when the NO:NO\textsubscript{2} ratio is close to 500:100. The equilibrium ratio of NO:NO\textsubscript{2} for 600 ppm NO in 3\%O\textsubscript{2} at 500°C is calculated to be 518:82 [11].

NO\textsubscript{x} reactions on the zeolite filter bed can be represented as:

\[ \text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_2 \] (3.17)

Analysis showed that in 3\%O\textsubscript{2} at 500°C, the PtY filter equilibrated the NO gas close to the thermodynamic value. This is also confirmed with the sensing data where with the filter and the sensor maintained at the same temperature, the signal to both NO and NO\textsubscript{2} were similar and small in magnitude.

3.4.4 Differential temperature measurements

If the PtY filter bed and the sensor are maintained at different temperatures, there is an increased driving force for the NO\textsubscript{x} to re-equilibrate at the electrodes. By controlling the temperature of the filter relative to that of the sensor, a ‘NO\textsubscript{2}’ or a ‘NO-like’ signal can be obtained. For example, when the filter bed is maintained at 400°C, the equilibrium shifts more in the direction of NO\textsubscript{2}, and the sensor output for all NO\textsubscript{x} compositions resembles a 'NO\textsubscript{2}-like' signal. Whereas, for the filter temperature at 700°C, the sensor provides a 'NO-like' signal.

The sensor signals for pure NO or NO\textsubscript{2} shown in Figures 3.4, 3.7 and 3.15 are the maximum possible signals. For gases passing through the filter, the maximum signal can be obtained only if the filter forms primarily NO or NO\textsubscript{2}. Thermodynamically, this can only happen at filter temperature extremes of 150°C or 900°C. Practically there is only a
certain range of temperatures that can be utilized. The PtY filter bed needs to be maintained below 700°C for physical stability of the material. Also we found the PtY filter will not oxidize CO below 150°C or fully equilibrate NOx below 400°C. Thus the filter needs to be maintained between 400-700°C. In addition, the sensor should be heated above 350°C for ionic conduction to occur and maintained below 600°C for a measurable NOx signal. Even with these restrictions, a wide range of operating conditions are possible for the filter and sensor temperature combinations to measure total NOx. Over time, long-term drifts have been observed in the sensor signal and are the subject of future studies.

3.4.5 Achieving selectivity towards CO

On the bare sensor electrode without the filter, the following electrochemical reaction is believed to occur for CO:

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (3.18)$$

With both NO and CO present, there was an enhanced signal (Figure 3.19) compared to NO and CO alone. PtY was also found to be a good catalyst for oxidation of CO and in the presence of PtY filter, there was no sensor response to CO, since it was all converted to CO2.

Sensor#2 (Figure 3.1b) demonstrated that it is possible to get rid of the air reference (Figure 3.16a). The layer of PtY placed directly onto one of the Pt electrodes (S2) leads to an equilibrium NOx mixture, with little driving force for the NOx to react electrochemically at the sensor. It acts as a pseudoreference towards NOx and CO. This idea has its origin in the work of Okamoto and coworkers, who demonstrated about 20
years ago that by using Pt/Al₂O₃ as a CO oxidation catalyst, a pseudoreference electrode could be created for CO gas sensing on YSZ [31]. The second bare Pt electrode (S₁) acted as the sensing electrode.

3.5 Conclusions

A total NOₓ sensing system was developed consisting of a YSZ mixed potential based sensor, a chromium oxide sensing electrode, a Pt air reference electrode and a microporous Pt zeolite Y catalytic filter bed. This system demonstrated the ability to detect NOₓ in the range of 200-1000 ppm independent of the CO concentration. These sensing behavior properties were due to the ability of the PtY filter bed to both fully equilibrate the NOₓ and oxidize CO above 400°C. By keeping the temperature of the filter and sensor at different temperatures, the magnitude of the signal could be increased. A direct application of PtY on Cr₂O₃ or Pt lead to the formation of a pseudoreference electrode, thus eliminating the need for an air reference. Development is underway to implement the pseudoreference total NOₓ/PtY filter sensor design into a package for testing in the engine exhaust set-up described in Chapter 2.

Acknowledgements

We would like to thank Dr. Ramachandra Rao for making the PtY powder and Professor Umit Ozkan for helpful discussions on the thermodynamic calculations.
Figure 3.1. A. Schematic of sensor type#1. B. Schematic of sensor type#2. S₁ and S₂ are the sensing electrodes. R is the Pt reference electrode.
Figure 3.2. Experimental set-up consisting of the sensor testing tube furnace, external catalytic chamber, chemiluminescence analyzer, and the gas mixing system. A picture of the catalyst filter bed is shown below.
Figure 3.3. (A) Experimental set-up for CO oxidation measurements of the catalytic bed using a gas chromatograph. (B) SEM images of Pt exchanged zeolite Y.
Figure 3.4. Transient response of the Cr$_2$O$_3$ sensing electrode on sensor#1a at 500°C for 100-1000 ppm NO (A) and 100-1000 ppm NO$_2$ (B) in 3%O$_2$. 

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Figure 3.5. Transient response of the Cr$_2$O$_3$ sensing electrode on sensor#1a at 500°C in 3% $O_2$ for mixtures of NO and NO$_2$ at a total NO$_x$ of 1000 ppm.
Figure 3.6. A. Sensitivity plots for the Cr$_2$O$_3$ electrode from the results of Figures 3.4 and 3.5. B. Comparison of the response of the Cr$_2$O$_3$ and Pt electrodes at 500°C in 3%O$_2$. 
Figure 3.7. A. Transient response of the Pt and Cr$_2$O$_3$ electrodes on sensor#1b for 100-1000 ppm NO in 3%O$_2$. B. Transient response of the Pt and Cr$_2$O$_3$ electrodes on sensor#1b for 100-1000 ppm NO$_2$ in 3% O$_2$. Both at 500°C.
Figure 3.8. A. Comparison of the response to 100-1000 ppm NO or NO₂ in 3% O₂ of the Cr₂O₃ and Pt electrodes on sensor#1b at 500°C. B. EMF vs. ln[NOₓ] plot for the Cr₂O₃ electrode on sensor#1b.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>% Conversion Observed</th>
<th>% Conversion Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>13.61 ± 0.80 (5 trials)</td>
<td>13.66</td>
</tr>
<tr>
<td>600</td>
<td>5.81 ± 1.62 (4 trials)</td>
<td>5.29</td>
</tr>
<tr>
<td>700</td>
<td>4.83 ± 1.24 (4 trials)</td>
<td>2.39</td>
</tr>
</tbody>
</table>

Table 3.1. Percent conversion of 600 ppm NO in 3% O₂ over the PtY zeolite bed at different temperatures.
Figure 3.9. A. Sensor#1b response at 500°C to 600 ppm NO or NO₂ in 3% O₂ with the test gas exposed directly to the sensor or first through the empty quartz tube ("blank") at 500°C. B and C. Sensor#1b response at 500°C to NO or NO₂ in 3% O₂ with the test gas exposed directly to the sensor or first through the quartz tube filled with zeolite NaY at 500°C. F = filtered region, NF = non-filtered region.
Figure 3.10. Sensor#1b response at 500°C for varying NO and NO$_2$ amounts in 3% O$_2$ with the test gas exposed directly to the sensor or through the PtY filled quartz tube at 500°C.
Figure 3.11. A. Comparison of response of sensor#1a at 500°C plotted in histogram form for 1000 ppm NO or NO₂ in 3% O₂ directly exposed to the sensor or through the PtY filter bed at 500°C. Inset shows plot of electrode signal for four ratios at a total NOₓ of 1000 ppm after passing through the PtY. B. NOₓ calibration curve of sensor#1b at 500°C with test gas passing through the PtY filter bed at 500°C.
Figure 3.12. Responses of sensor#1c with a Cr$_2$O$_3$ electrode to O$_2$ (A), NO (B), NO$_2$ (C) at varying temperatures.
Figure 3.13. A. Calibration curve of sensor#1c at 750°C for NO and NO₂ in 3% O₂. Data taken from Figures 3.12a and b. B. Calibration curve of sensor#1c at 500°C for NO and NO₂ in 3% O₂ passing through the PtY filter at 500°C.
Figure 3.14. Calibration curves for the Cr$_2$O$_3$ electrode on sensor#1b at 500°C for 400, 600, and 1000 ppm NO or NO$_2$ in 3% O$_2$ passing through the PtY filter at 400, 500, 600 and 700°C.
Figure 3.15. Calibration curves for the Cr$_2$O$_3$ electrode on sensor#1c at 400°C for 400, 600, 1000 ppm NO or NO$_2$ in 3% O$_2$ passing through the PtY filter at 400, 500, and 600°C. The response to NO and NO$_2$ without the filter is also shown for comparison.
Figure 3.16. A. Transient plot of the three sensor#2 electrode couples for 560 ppm NO\textsubscript{x}/3\% O\textsubscript{2} with PtY filter and pseudo reference electrode (S\textsubscript{1}: Pt electrode; S\textsubscript{2}: Pt electrode covered with PtY; R: reference electrode) B. Chemiluminescence analyzer response in the same time frame as sensor#2 to 560 ppm NO\textsubscript{x} direct or through the PtY filter.
Figure 3.17. Sensor response to 0-1000 ppm CO/ 3%O₂ for sensor#1a at 500°C.

<table>
<thead>
<tr>
<th>Zeolite Type</th>
<th>% Conversion of 7000ppm CO</th>
<th>% Conversion of 1000ppm CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td>NaY</td>
<td>17.4</td>
<td>32.9</td>
</tr>
<tr>
<td>PtY</td>
<td>88.9</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3.2. Percent conversion of CO to CO₂ at 500°C in 3% O₂ over NaY and PtY zeolites.
Figure 3.18. Sensor#1a response to CO for gases bypassing or passing through the PtY filter bed.
Figure 3.19. Bar graph showing absolute mixed potential response to CO with and without PtY filter in the presence of NO.
Figure 3.20. Equilibrium interconversion of NO and NO$_2$ at various temperatures in 20\% O$_2$ [15].
CHAPTER 4

Fundamental Studies on the Nature of Metal Oxide Electrodes in the Sensor Response for NO\(_x\) of a Cr\(_2\)O\(_3\) and La\(_{0.6}\)Sr\(_{0.4}\)Fe\(_{0.8}\)Co\(_{0.2}\)O\(_3\) Couple on YSZ

Chapters 2 and 3 detailed the development of various sensor designs for NO and NO\(_2\). The early models in chapter 2 were not selective and detected NO and NO\(_2\) as well as CO. The improved designs in chapter 3 led to the development of a total NO\(_x\) sensing system that could detect the total concentrations of NO and NO\(_2\) with selectivity against CO. The final sensor design proposal in chapter 3 utilized a planar orientation of the two sensing electrodes. One was a bare Pt electrode and the other was Pt coated with a layer of zeolite PtY creating a pseudoreference electrode. This design has the potential to be implemented onto a YSZ pellet similar to sensor type III in chapter 2. Chapter 4 explores the idea of creating a simpler pseudoreference by using perovskite material La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.2}\)Fe\(_{0.8}\)O\(_3\) (LSCFO) as an electrode. We found that LSCFO gave low sensitivity. Pairing the LSCFO with an electrode having a large sensitivity for NO\(_x\), such as Cr\(_2\)O\(_3\) shown in chapter 3, allows for a sizeable potential difference to be measured between the two electrodes. The idea of using two electrodes with different sensitivities has been reported before in the literature, but with little understanding of the processes that lead to the electrode behavior. In this chapter, we investigate the fundamental reasons for the difference in sensitivity to NO\(_x\) between the LSCFO and Cr\(_2\)O\(_3\) electrodes.
4.1 Introduction

A discussed in Chapter 1 there has been a move to use metal oxide electrodes instead of pure metals such as Pt and Au for better sensor performance and cheaper cost. In this chapter we have chosen two electrode materials, \( \text{Cr}_2\text{O}_3 \) and \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 \) that gave different sensitivities to NO and NO\(_2\). We decided to investigate the underlying properties of these materials to develop an understanding of their different sensing characteristics.

4.1.1 Lanthanum oxide perovskite compounds in the literature

A survey of the literature found that \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 \) is often referred to as LSCF [1, 2], LSFC [3], LSCFO [4], or LSCF6428 [5, 6] depending on the authors. In addition the oxygen coefficient is represented as stoichiometric i.e. \( \text{O}_3 \) or non-stoichiometric i.e. \( \text{O}_{3-\delta} \) depending on the temperature and oxygen pressure. We will refer to the compound as LSCFO in this chapter. LSCFO has the perovskite structure of the form \( \text{ABO}_3 \) with \text{A} typically being a lanthanide or alkaline earth metal and \text{B} a transition metal [4].

Lanthanum oxide based perovskites are mixed ionic electronic conductors (MIECs) and have seen increasing application due to their conducting properties and for their catalytic abilities. Many variations of the LSCFO stoichiometry have been studied including using other metals at the \text{B} site such as \text{Cr} [7], \text{Pd} [8], \text{Ni} [9] and \text{Mn} [10, 11]. They have been touted as cheap replacements for the catalysts in the three-way catalytic converters since the 1970's and there has been considerable research in this area [8].
Other groups have used them as electrodes on YSZ or doped CeO$_2$ electrolytes for electrochemical NO$_x$ reduction to the elements in exhaust gas purification [1, 12, 13]. They have also been used as fuel cell (SOFC type) electrode materials for oxygen reduction at the cathode or hydrocarbon activation at the anode [3, 5, 6, 14-23] [22, 24-31]. There is also a need for MIECs in dense membranes for separating O$_2$ from air mixtures [32-35] and as catalytic membranes for the partial oxidation of hydrocarbons to produce syngas and upgraded compounds [36] [37-41].

The area of gas sensors has also seen the use of lanthanum oxide perovskites as sensing electrodes. Table 4.1 lists some of the different oxides that have been used for various types of sensors for NO$_x$, CO and HCs. Miura screened assorted oxides for NO$_x$ sensing and found that electrodes on YSZ made of LaCrO$_3$, LaFeO$_3$, LaCoO$_3$, LaNiO$_3$ coated on a porous Pt layer gave low signals for 200 ppm NO or NO$_2$ at 600°C [7]. It was suggested that the perovskites may be too active for heterogeneous NO$_x$ equilibration before the electrochemical reactions can occur, although this was not supported by any catalytic data.

4.1.2 Cr$_2$O$_3$ properties and uses in the literature

We have utilized Cr$_2$O$_3$ as a sensing electrode in this chapter (as well as chapter 3) and found that it gave a higher sensitivity to NO$_x$ than the LSCFO at 500°C. Cr$_2$O$_3$, also called chromia [63] or eskolaite [64], crystallizes in the corundum structure [63] and is usually stated to be a pure electronic conductor [63] [65] but has been referred to as a MIEC under certain conditions [66]. It is used as a protective layer for various alloys [63]
and studied as an electrode material for electrochromic windows and possible use in solar energy applications [67]. It has also been utilized as an electrode or sensing material for gas sensors. Table 1.2 lists various sensors that have used or screened Cr$_2$O$_3$ as a sensing electrode or material and shows that above 600°C Cr$_2$O$_3$ does not perform well having a low sensitivity for NO$_x$, HC, or CO. In this study we are primarily focused on developing an understanding of the difference in sensitivities to NO$_x$ for the LSCFO and Cr$_2$O$_3$ electrodes, rather than the absolute sensitivity of a given electrode. Maximizing the electrode sensitivity towards NO$_x$ will be the subject of future studies in this group.

4.2 Experimental

4.2.1 Sensor fabrication

Sensor fabrication was done in an identical manner as the previous chapters. The LSCFO or Cr$_2$O$_3$ electrode powder was mixed with terpineol in a 50/50 wt% paste and painted on top of a Pt wire wrapped around the YSZ tube (sensors#4.2-4.4) or a Pt paste layer (only the Cr$_2$O$_3$ electrode in sensor#4.1) and heated to 750°C with a 6°C/min heating and cooling rate. The sensor designs and optical images of typical electrodes are shown in Figures 4.1 and 4.2, respectively.

4.2.2 Surface area measurements

Single point surface area measurements of the powders were done on a Micromeritics Pulse Chemisorbed 2700 instrument. A typical experiment involved placing the LSCFO or Cr$_2$O$_3$ into a U-shaped quartz holder and outgassing for 2 hours at 400°C under a flow of N$_2$. When testing, the gas flow was switched to a 30%N$_2$/70%He mixture. For the adsorption cycle, the sample was cooled to liquid nitrogen temperature.
and the total surface area counts were recorded, which was then divided by the sample weight to obtain the specific surface area. For the desorption cycle, the liquid nitrogen flask was removed and replaced with a beaker of room temperature water. The total surface area count was recorded and converted to specific surface area. Ideally, the adsorption and desorption areas should be the same but there was a significant variation in the adsorption areas, thus the desorption values were used throughout. Multiple readings were taken for each sample and the desorption values were similar. For verification of instrument performance, an alumina standard with a specific surface area of 10 m$^2$/g was periodically tested.

### 4.2.3 NO$_x$ catalytic activity and pressure swing adsorption measurements

The heterogeneous catalysis and pressure swing adsorption measurements were done in the same set-up as the zeolite catalysis measurements in chapter 3 (refer to section 3.2.2.1 and 3.2.2.2) using a heated fixed bed quartz reactor and a NO$_x$ chemiluminescence analyzer. The pressure swing adsorption experiments are described in section 4.3.4.

### 4.2.4 SEM analysis

SEM images were taken with Au coated samples using a Philips XL-30 ESEM at the Campus Electron Optics Facility (CEOF) at The Ohio State University. EDX analysis of the powders was done using carbon coated samples at the Microscopic and Chemical Analysis Research Center (MARC) at The Ohio State University.
4.2.5 Elemental analysis
The LSCFO sample was submitted to the Microscopic and Chemical Analysis Research Center (MARC) at The Ohio State University for inductively coupled plasma optical emission (ICP-OES) analysis.

4.2.6 Electrical measurements (impedence/polarization)
Current voltage polarization plots were obtained using a Gamry instruments potentiostat with software control in Tafel mode. A DC voltage was scanned from negative to positive in the range of +/- 500 mV and the resulting current of the electrode/electrolyte system was measured.

Impedance measurements were performed with a Solartron SI 1260 impedance/gain-phase analyzer using Zplot and Zview software. A 10 mV AC signal was applied to the sample with a varied frequency range from $10^6$ Hz to 0.1 Hz.

Both types of electrical measurements were done using an actual sensor device and a symmetrical electrode YSZ cell in 21%O$_2$/N$_2$ between 500-700°C.

4.3 Results

4.3.1 Sensor tests for NO$_x$ response
Four sensors were tested using LSCFO and Cr$_2$O$_3$ electrodes. The general trend observed for all four sensors was that the Cr$_2$O$_3$ electrode had a larger sensitivity for NO$_x$ than the LSCFO electrode at 500°C in 3%O$_2$ or 21%O$_2$. The results of these tests are presented next.
4.3.1.1 21% O₂/N₂ background at 500°C

4.3.1.1.1 Sensor#4.1 “blank” response

Sensor#4.1 (Figure 4.1a) was first tested with only the Pt paste electrodes and Pt lead wires at E1 and E3 and only a Pt lead wire (no Pt paste) in the E2 position for the response to NO, NO₂ and CO. It was observed that there was no useful signal for the Pt wire alone in the E2 position indicating a short circuit from the poor contact of the wire and the YSZ surface. Thus only the results for E1 and E3 are considered for the “blank” response (no oxide layer). Figure 4.3 shows the sensor#4.1 response to varying concentrations of NO (200, 400, 600, and 800 ppm) and NO₂ (200, 400, 600, 800 ppm) at 500°C in a 21%O₂/N₂ background. The electrode transient responses for E1/Pt_ref, E3/Pt_ref, and E1/E3 are plotted. It can be seen that the planar combination of E1 and E3 gives a small signal for the changing NOₓ concentrations. This would be expected for two identical Pt electrodes as discussed elsewhere [68]. The small signal change observed for NO₂ in the planar signal is caused by some asymmetry in the two Pt electrodes due to the Pt ink painting procedure. This asymmetry can be observed by monitoring each Pt sensing electrode to the Pt reference also shown in Figure 4.3, which plots the three signals all at the same time. It can be seen that both E1/Pt_ref and E3/Pt_ref have a similar signal for NO but a slightly different signal for NO₂ resulting in the small NO₂ signal in the planar E1/E3 configuration.

The "blank" sensor was also tested for varying concentrations of CO (200, 400, 600, 800 ppm). It was observed that the response to CO was smaller than that of NO. Figure 4.4 shows a comparison of the sensitivity plots for NO, NO₂ and CO of the planar
and air reference signals. The sensitivity plot calibration curves are all plotted on a linear scale. The values displayed were taken from the points immediately before changing to the next gas concentration. In Figure 4.4A it is observed that NO and NO$_2$ change in opposite directions in accord with the mixed potential behavior. In Figure 4.4B it can be seen that the two Pt electrodes E1/Pt$_{\text{ref}}$ and E3/Pt$_{\text{ref}}$ do not have the same response for CO. Thus, there is a small net signal for the planar configuration E1/E3.

It can be seen from the above tests with just the E1 and E3 Pt electrodes alone that the overall sensor signal is controlled by both electrodes as we discussed in earlier chapters. A maximum signal can be achieved if one of the electrodes has no response for the gas i.e. NO$_x$ or CO and the other electrode has a large response. The use of a pseudo reference electrode with respect to NO$_x$ or CO would be beneficial to enhancing the signal as was shown in chapter 3. In our previous paper we created an asymmetry between two Pt electrodes with a zeolite coating onto one of them, which acted as a chemical filter [68].

**4.3.1.1.2 Sensor#4.1 response with Cr$_2$O$_3$ at E3 and LSCFO at E2**

After testing the sensor#4.1 response with just Pt paste or Pt wire, the Cr$_2$O$_3$ and LSCFO electrodes were prepared as described above. In the case of E3, with the Cr$_2$O$_3$ on top of the Pt paste, the signal response of the E3/Pt$_{\text{ref}}$ couple increased to NO, NO$_2$ and CO as compared with the Pt paste only as shown in Figure 4.5. It is possible that the Cr$_2$O$_3$ has a different electrochemical catalytic activity than Pt, or enhances adsorption at the triple point boundaries of the electrode. The performance of E1, the still bare Pt electrode, remained relatively the same with the signal response to NO, NO$_2$ and CO now
being smaller than that of E3. The addition of the Cr$_2$O$_3$ has created an asymmetry between the two Pt electrodes E1 and E3.

With the LSFCO on the Pt wire for E2 there was now a complete circuit due to the presence of the oxide and the E2 electrode response could be measured. It was observed that the signal response for E2 to NO, NO$_2$, and CO was relatively low with respect to the signal response of E1 and E3. This observation is in agreement with some other lanthanum based perovskite type oxides tested before [7, 11]. Figure 4.6A and B compares the signal responses of the three couples E1/Pt_ref, E2/Pt_ref and E3/Pt_Ref to changing NO, NO$_2$, and CO concentrations. Note in Figure 4.6A that the data for E3 (Cr$_2$O$_3$ on Pt paste) was also shown in Figure 4.5 and represented as E3_Cr where it was compared against the original Pt paste electrode.

The sensor transients for the calibration data in Figure 4.6 to NO, NO$_2$, and CO are shown for the three couples E1/Pt_ref, E2/Pt_ref and E3/Pt_Ref in Figure 4.7. The gas concentrations were changed at 20 minute intervals from increasing concentration levels of 200, 400, 600, and 800 ppm and finally the gas was turned off after 800 ppm to just the 21% O$_2$/N$_2$ baseline. Although the Cr$_2$O$_3$ + Pt paste electrode E3 had the largest response magnitude at each concentration on sensor#4.1 it also had the slowest response time. While the LSCFO electrode at E2, with the smallest response magnitude, had the quickest response time. The t$_{90}$ response times from 0-200 ppm NO for the LSCFO were 4 minutes and 5 minutes for the Cr$_2$O$_3$. The t$_{90}$ recovery times for 800-0 ppm NO for the LSCFO were 5 minutes and 44 minutes for the Cr$_2$O$_3$. The t$_{90}$ response time for 0-200 ppm NO$_2$ was 18 minutes for LSCFO and the Cr$_2$O$_3$ signal did not reach a stable value in the 20 minute window. The t$_{90}$ recovery times for 800-0 ppm NO$_2$ were 7.5 minutes for
LSCFO and 74 minutes for Cr$_2$O$_3$. The largest response for LSCFO was 8.3 mV to 800 ppm NO$_2$ and 2 mV for 800 ppm NO as plotted in Figure 4.6a. In practical combustion situations there should not be more than 200 ppm NO$_2$ present as described in Chapter 1 since typically only 5% of the existing total NO$_x$ is NO$_2$. The magnitude of response was only 2 mV to 200 ppm NO$_2$, thus the LSCFO electrode properties in this test could serve as a possible pseudo reference electrode.

We found that on some of our sensors the electrode signals to NO and NO$_2$ actually increased after aging. This was observed for both the Cr$_2$O$_3$ and LSCFO electrodes when testing over a period of two weeks. Figure 4.8 shows an example of the signal increase for the LSCFO and Cr$_2$O$_3$ electrodes on sensor#4.1 to NO$_x$ from the first and third day of testing (the data previously shown in Figures 4.5-4.7 was from the third day of testing). The LSCFO baseline (21% O$_2$/N$_2$) shifted from -0.06 mV on day#1 to -0.33 mV on day#3 (values taken before NO testing on either day). The change in voltage from the baseline to 800 ppm NO was -0.69 mV on day#1 and -1.63 mV on day#3 resulting in an increase of 136%. Similarly, the change in voltage from the baseline to 800 ppm NO$_2$ (values taken at the end of the 20 minutes test period) was 4.32 mV on day#1 and 8.51 mV on day#3 resulting in an increase of 97%. The Cr$_2$O$_3$ baseline (21% O$_2$/N$_2$) shifted from -0.78 mV on day#1 to -1.98 mV on day#3 (values taken before NO testing on either day). The change in voltage from the baseline to 800 ppm NO was -12.24 mV on day#1 and -27.91 mV on day#3 resulting in an increase of 128%. Similarly, the change in voltage from the baseline to 800 ppm NO$_2$ (values taken at the end of the 20 minutes test period) was 49.42 mV on day#1 and 76.22 mV on day#3 resulting in an increase of 54%. Zhuiykov observed a 20% increase in signal for a ZnFe$_2$O$_4$ spinel
electrode on YSZ at 700°C to 100 ppm NO$_2$/21%O$_2$ after a period of 20 days. The sensor was further tested up to 120 days where the signal reached a stable level although it had increased 71% from day 1 [69, 70]. In the same paper Zhuiykov also found that a ZnCr$_2$O$_4$ electrode had a decrease in signal (no value given) to NO$_2$ with aging at 700°C in air [70]. No explanation was given about the reasons for the signal changes but it appears that a heat treatment step for better electrode stability may be useful.

4.3.1.2 3% O$_2$/N$_2$ baseline

We fabricated new sensors based on Figure 4.1B to test Cr$_2$O$_3$ and LSCFO in an environment of 3%O$_2$, which would be more amenable to a real combustion environment. A similar result was observed for sensors#4.2-#4.4 as compared to sensor#4.1 in that the Cr$_2$O$_3$ electrode gave a larger signal to NO$_x$ than the LSCFO electrode. Some variation in the absolute signal magnitude was observed from sensor to sensor but the overall trend remained. For sensors#4.2-4.4 the Cr$_2$O$_3$ electrode is placed on a Pt wire current collector instead of Pt paste in sensor#4.1 and there does not appear to be much difference in performance. Figure 4.9 compares the response of sensors#4.2-#4.4 to 600 ppm NO or NO$_2$ in 3% O$_2$ at a 100 cm$^3$/min flow rate. Sensor#4.4 was tested above 500°C and it was observed that the NO$_x$ response magnitude also decreased with increasing temperature with almost no observable signal at 700°C. At 500°C the signals from the 3% O$_2$ baseline were -8.2 mV (NO) and 54.4 mV (NO$_2$) for Cr$_2$O$_3$ and -0.6 mV (NO) and 17 mV (NO$_2$) for LSCFO. At 600°C the signals from the 3% O$_2$ baseline were -0.7 mV (NO) and 7.7 mV (NO$_2$) for Cr$_2$O$_3$ and -0.1 mV (NO) and 4.8 mV (NO$_2$) for LSCFO. At 700°C the signals from the 3% O$_2$ baseline were -0.2 mV (NO) and 0.7 mV (NO$_2$) for Cr$_2$O$_3$ and
less than -0.1 mV (NO) and 0.8 mV (NO\textsubscript{2}) for LSCFO. The small shifts at 700°C could be due primarily to a small change in O\textsubscript{2} when introducing NO\textsubscript{x} or the by O\textsubscript{2} consumption during the equilibration reaction as discussed in chapter 3 (section 3.3.3.2).

In sensors #4.1, #4.2, #4.4 the placement of the LSCFO electrode was closest to the tip of the closed end YSZ tube and the Cr\textsubscript{2}O\textsubscript{3} was farther from the tip as shown in Figure 4.1. In sensor #4.3 the electrode placement order was reversed with the Cr\textsubscript{2}O\textsubscript{3} being closest to the tip and the LSCFO farther from the tip. Regardless of the electrode order the same trend in different NO\textsubscript{x} response magnitudes, as exhibited in Figure 4.9, was observed suggesting different chemical and/or electrochemical properties between the LSCFO and Cr\textsubscript{2}O\textsubscript{3}. In the next sections we will attempt to identify the reasons for the difference in response of the two electrodes to NO\textsubscript{x}.

Figure 4.10 shows a schematic of the three sensor electrode reaction zones that can have an influence on the sensor signal as discussed in the literature [7, 47]. We will use this model as a guide to investigate the materials ability to chemically/catalytically react with NO\textsubscript{x}, compare the NO\textsubscript{x} adsorption ability of the two oxides, and then look at the electrical properties of the two electrodes.

### 4.3.2 Materials characterization

The LSCFO powder was obtained from Superconductive Components Inc. in Columbus, OH. The powder was quoted on the bottle as having a stoichiometry of La\textsubscript{0.6}Sr\textsubscript{0.4}Fe\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{x}, which was verified by ICP elemental analysis within experimental error using fresh LSCFO powder. EDX spectroscopy on carbon coated LSCFO also indicated the presence of the expected elements (Figure 4.11). An XRD was taken of the
fresh LSCFO and looked similar to a known JCPDS pattern of a lanthanum oxide perovskite with a related stoichiometry (La_{0.6}Sr_{0.4}Fe_{0.2}Co_{0.8}O_x) [71] shown in Figure 4.12. The Cr_2O_3 powder (99% pure - metals basis) was purchased from Alfa Aesar. The bottle label stated that it was 325 mesh (45µm) agglomerated powder and the expected elements were observed by EDX spectroscopy (Figure 4.13). SEM images were taken of the fresh and heated LSCFO and Cr_2O_3 powders by themselves and deposited on YSZ. The fresh LSCFO powder had a particle size of around 100-200 nm and a spherical shape as shown in Figure 4.14 and Figure 4.15. Single point nitrogen desorption measurements gave a specific surface area of 4.2m^2/g for the fresh LSCFO powder. If we assume a density of 6.5g/cm^3 for LSCFO, similar to other perovskites of this composition [71], then the calculated specific surface areas for 100 nm and 200 nm diameter spheres are 9.7 m^2/g and 4.6m^2/g respectively. Thus, the average LSCFO particle size of the fresh powder is probably closer to 200 nm. It was found that after heat treating the fresh LSCFO powder + terpineol on the YSZ based sensor at 750°C for 2hrs with a 6°C/min heating and cooling rate that some grain growth occurred as shown in Figure 4.16. As mentioned earlier LSCFO does not bond very well to the YSZ when heat treated at only 750°C. Due to the grain growth some of the LSCFO particles stuck to each other when the electrode material was scraped off the electrolyte. The LSCFO also left a light black mark where it was located suggesting some physical diffusion into the surface layer of the YSZ. There have been reports of lanthanum oxide perovskites reacting with YSZ to form non-conducting phases at temperatures above 1100°C for 120 hours [19, 72]. In our case we heat treated the electrodes to only 750°C for 2 hours and our sensing test were done
typically at 500°C with occasional testing up to 700°C. Therefore no significant chemical reactivity between YSZ and LSCFO is expected to occur under our conditions.

The fresh Cr$_2$O$_3$ powder did not have a uniform size distribution. Particles with size in the range of 100 nm were also observed as shown in Figure 4.17, however there was evidence of larger agglomerated porous structures in other regions of the sample observed in Figure 4.18. Single point nitrogen desorption measurements on the fresh Cr$_2$O$_3$ powder gave a specific surface area of 45.9 m$^2$/g. The fresh Cr$_2$O$_3$ powder was heated to 750°C for 2 hrs with a 6°C/min heating and cooling rate to observe any possible morphological changes. The particle size distribution became more uniform, with some particles having a needle like structure. Multiple heat treated Cr$_2$O$_3$ samples were investigated and no evidence of the large porous agglomerations could be found as shown in Figure 4.19. In addition nitrogen desorption measurements were done on heat treated Cr$_2$O$_3$ powder mixed with terpineol (the same paste used for the sensor electrode) giving a reduced specific surface area of 21.5 m$^2$/g. Cr$_2$O$_3$ has a density of 5.22 g/cm$^3$ then the calculated specific surface areas for 100 nm and 200 nm diameter spheres are 11.5 m$^2$/g and 5.75 m$^2$/g respectively which suggests that some mesoporosity is still present in the Cr$_2$O$_3$ heated sample. Similar to the LSCFO when the Cr$_2$O$_3$ was scraped from the YSZ a light green color was left behind suggesting some physical diffusion into the surface layer. The color in both cases could be removed by sanding of the YSZ surface. The exact surface areas of the two electrode powders on the YSZ surface may be different than those determined from the heated powders alone. However, the results suggest that the Cr$_2$O$_3$ layer is more porous than the LSCFO layer.
In Figure 4.2 a typical optical image of the \( \text{Cr}_2\text{O}_3 \) and LSCFO electrodes was shown. Normally the electrode pastes were painted on about half of the circumference of the YSZ tube. After scraping off the electrode powders a typical weight was between 2-3 mg of material.

4.3.3 \( \text{NO}_x \) equilibration chemistry on the \( \text{Cr}_2\text{O}_3 \) and LSCFO powders

The catalytic ability to equilibrate the \( \text{NO} + \text{O}_2 \leftrightarrow \text{NO}_2 \) reaction was investigated for the LSCFO and \( \text{Cr}_2\text{O}_3 \) powders in the same manner as shown in Chapter 3 (Figure 3.2) utilizing a standard quartz flow reactor and chemiluminescence analyzer. We first investigated the conversion ability of 5 mg of the two powders towards 600 ppm NO and 600 ppm \( \text{NO}_2 \) in 3% \( \text{O}_2 \) at temperatures from 200-700°C in 100°C increments for a gas flow rate of 200 cm\(^3\)/min. Fresh powders were added to the flow reactor and tested for \( \text{NO}_x \) conversion starting from 200°C and progressing to 700°C (note the \( \text{Cr}_2\text{O}_3 \) powder had a larger volume than the LSCFO for the same weight due to its lower density and higher surface area). The powders were again tested for \( \text{NO}_x \) conversion a second time in the same manner. In this way, the powders underwent a heat treatment similar to that of the sensor. Using the single point surface area measurements for the heated powders the total surface area of 5 mg of \( \text{Cr}_2\text{O}_3 \) (21.5 m\(^2\)/g) is 0.108 m\(^2\) and for 5 mg LSCFO (4.2 m\(^2\)/g) it is 0.021 m\(^2\).

We observed that the \( \text{NO}_2 \) conversion at 500°C for the second test of \( \text{Cr}_2\text{O}_3 \) was about 11% less than the first test (87% to 76%) possibly due to the decrease in the surface area after heating as discussed in the earlier section. A similar result for \( \text{NO}_2 \) conversion...
over Cr$_2$O$_3$ was observed at 400°C (26% to 7%). For LSCFO the conversion for NO$_2$ at 400°C and 500°C did not change after the heat treatment.

In the case of NO, over Cr$_2$O$_3$ there was no decrease in conversion at 500°C and only a 0.5% decrease at 400°C after the heat treatment cycle. For LSCFO there was a 2% decrease in NO conversion at 500°C (11% to 9%) and a 12.5% decrease at 400°C (22% to 9.5%).

Figures 4.20-4.21 compare the NO$_2$ or NO conversion for the Cr$_2$O$_3$ and LSCFO of the post heat treatment, the calculated conversion using thermodynamic data, and the empty reactor conversion over the range of temperature tested. At the sensing temperature of 500°C, the Cr$_2$O$_3$ shows a higher conversion for NO$_2$ than the LSCFO (76% to 30%) and a similar conversion for NO (10% to 9%). It can be seen from the plots that both catalysts bring the NO$_2$ close to equilibrium at 600°C and above and the NO close to equilibrium at 500°C and above. At lower temperatures the catalysts are not activated to fully equilibrate the NO$_x$ gases. Even though only 5 mg of electrode material is tested it is still enough to have a higher conversion than that of the empty quartz reactor.

The Cr$_2$O$_3$ had a higher sensor signal for NO and NO$_2$ than LSCFO. The results for conversion measurements show that for NO$_2$, the Cr$_2$O$_3$ has a higher conversion than LSCFO, which does not correlate directly with the sensor response. In addition the equilibration of NO for each electrode is comparable. As stated earlier, only 2-3 mg of electrode material is actually used for the sensor electrodes. On the actual sensor the gas
flow is across the electrode surface and not directly through a bed of the powder, which will have a different contact time than the catalytic flow reactor.

When the amount of powder was increased, the percent conversion at the sensing temperature of 500°C generally increased for the two materials as shown in Table 4.3. The table shows that the conversion for LSCFO and the Cr₂O₃ for 100 mg becomes comparable for both gases.

4.3.4 Adsorption measurements

The previous section compared the catalytic ability of the two oxides to equilibrate NOₓ. In this section, we utilized the pressure swing adsorption (PSA) technique to compare the ability of the Cr₂O₃ and LSCFO to adsorb NO or NO₂. PSA has been used before to compare the adsorption of NO and NO₂ for different NOₓ reduction catalysts for zeolite and metal oxide samples [73-75]. The PSA method is relatively simple and could give some insight into the electrode properties and involves the same set-up as in the catalysis measurements in section 4.3.3. First the response time of the system to 600 ppm NO or NO₂ is measured without the catalyst. The NOₓ gas is turned on and the time it takes for the chemiluminescent analyzer to read 600 ppm is recorded. Similarly the NOₓ gas is turned off and the time it takes for the analyzer signal to return to the baseline is again recorded. The experiment it then repeated with the material of interest (here Cr₂O₃ or LSCFO) placed in the bed. If there is any adsorption of NO or NO₂ onto the oxide then the time it takes for the signal to reach a reading of 600 ppm (adsorption) or go back to a reading near zero (desorption) will be longer. The two transient curves can be compared and the difference in the areas for the adsorption and
desorption steps can be obtained. Figure 4.22 shows a schematic of a typical experiment and two types of adsorption can typically be observed, reversible (physisorption) and irreversible (chemisorption) adsorption. This will be evident if the areas of A and D are not equal in early experiments and become equal after subsequent runs. Eventually the amount of gas adsorbed is equal to the amount desorbed but in some cases there is an initial point of irreversible adsorption, as \( A = a_{\text{reversible}} + a_{\text{irreversible}} \), and once all of the irreversible sites are filled then only reversible adsorption occurs. The adsorption transients of different materials can be compared in time as breakthrough curves.

Even though only 3 mg of electrode powder are typically used on the sensor 100 mg of \( \text{Cr}_2\text{O}_3 \) and LSCFO were used for the PSA tests to increase the amount of total adsorption. Since the \( \text{Cr}_2\text{O}_3 \) had a much larger volume than the LSCFO it was first pressed into a pellet by hand and then broken up into pieces to minimize the pressure drop in the reactor. Otherwise we found the \( \text{Cr}_2\text{O}_3 \) could physically block the flow of gas. By compacting the \( \text{Cr}_2\text{O}_3 \) powder the surface area is reduced but it still occupied a larger volume in the quartz tube than the LSCFO. The results could then be normalized to the amount of \( \text{NO}_x \) adsorbed per weight or surface area of material. The PSA experiments were done at 500°C under similar conditions as the sensing tests by first flowing 3% \( \text{O}_2/\text{N}_2 \) through the empty quartz reactor or with catalyst then adding 600 ppm NO or \( \text{NO}_2 \) to the gas flow. The adsorption time was the time from when the gas valve was opened to the time the reading on the analyzer reached 600 ppm. The desorption time was determined from when the gas valve for \( \text{NO}_x \) was closed and the analyzer signal reached the baseline value.
Figure 4.23 shows the results for the NO PSA experiments at 500°C. It compares the adsorption and desorption curves for both 100 mg of the Cr₂O₃ and LSCFO. Figure 4.24 shows enlarged images of the adsorption and desorption regions from Figure 4.23. The spikes and wavy regions are due to the gas mixing system. Subtracting the two curve regions for adsorption and desorption of the oxides from the empty reactor response, integrating the result over the adsorption/desorption time, and knowing the concentration (600 ppm) and powder weight (100 mg) the amount of NO adsorbed or desorbed on the oxides can be calculated. Under these testing conditions we found that the Cr₂O₃ did not have any significant adsorption of NO within the time resolution of the instrument as shown in Figure 4.24. Whereas the LSCFO had an adsorption of 88.4*10⁻³ cm³ (1.39 µmols) NOₓ/g and a desorption of 90.5*10⁻³ cm³ (1.43 µmols) NOₓ/g. Here NOₓ is the sum of NO + NO₂. Upon doing successive experiments we did not find any significant changes in the adsorption amount on LSCFO suggesting under these testing conditions irreversible adsorption did not occur to a measurable extent.

When passing 600 ppm NO over the oxides, the amount of NO remaining was measured. For the Cr₂O₃, there was 518 ppm of NO remaining (13.7% conversion) and for LSCFO there was 520 ppm remaining (13.3% conversion). Thus both oxides completely equilibrated the NO as expected in Table 4.3 (13.7% conversion at 500°C/3% O₂). Figure 4.25 overlaps the LSCFO PSA transients for NOₓ (NO + NO₂) and NO and it can be seen during the adsorption step that the incoming NO is oxidized to NO₂. During desorption, when the NO is turned off, the NO curve overlaps well with the NOₓ (NO + NO₂) curve suggesting that the primary adsorbed species was NO. We further verified
this by flowing 600ppm NO/N\textsubscript{2} in the absence of O\textsubscript{2} and still observed a similar NO adsorption/desorption profile on LSCFO as that in Figures 4.23 and 4.24.

Figure 4.26 shows the results for the NO\textsubscript{2} PSA experiments at 500°C. The empty reactor showed some sign of tailing during the desorption step as compared to that for NO, which suggests it takes longer to flush NO\textsubscript{2} from the system possibly due to adsorption onto the quartz and stainless steel tubing. Similar to the NO experiment no adsorption of NO\textsubscript{x} was observed on the Cr\textsubscript{2}O\textsubscript{3} when flowing NO\textsubscript{2} but there was some adsorption on the LSCFO. The total amount of NO\textsubscript{x} adsorbed and desorbed when flowing NO\textsubscript{2} was 52.9*10\textsuperscript{-3} cm\textsuperscript{3} (0.83 \textmu mols) NO\textsubscript{x}/g and 35.1*10\textsuperscript{-3} cm\textsuperscript{3} (0.55 \textmu mols) NO\textsubscript{x}/g respectively. The total amount adsorbed is less than that when flowing NO, which could be due to the catalyst being successively tested. We found with multiple tests for NO\textsubscript{2} that the desorption curves overlapped very closely but their was some variation in the adsorption curves suggesting some irreversible adsorption, which may be indicated by the difference in the total amount of NO\textsubscript{x} adsorbed and desorbed. Since the desorption transient was reproducible, 35.1*10\textsuperscript{-3} cm\textsuperscript{3} NO\textsubscript{x}/g is most likely the amount of reversible adsorption. Figure 4.27 overlaps the NO\textsubscript{2} PSA transients for NO\textsubscript{x} and NO and it can be seen during the adsorption step that the incoming NO\textsubscript{2} is reduced to NO. For the NO\textsubscript{2} experiment during desorption the NO curve overlapped well with the NO\textsubscript{x} curve and both had a similar appearance to those in Figure 4.25 for the NO experiment.

The results of the PSA experiments show that under these operating conditions in a fixed bed reactor at 500°C with a 3% O\textsubscript{2}/N\textsubscript{2} background LSCFO adsorbs more NO\textsubscript{x} than the Cr\textsubscript{2}O\textsubscript{3} on a weight basis. Since the NO and NO\textsubscript{x} desorption curves overlap this suggest that NO is the species that adsorbs on LSCFO when flowing NO or NO\textsubscript{2} through
the bed. This may be expected since the experiments are done at 500°C where NO is the primary NO\textsubscript{x} species.

### 4.3.5 Electrical measurements

#### 4.3.5.1 Sensor electrode response times to O\textsubscript{2} transients

We investigated the electrical properties of the sensor electrodes. The response of sensor\#4.1 and sensor\#4.4 was investigated to changing O\textsubscript{2} concentrations from 3-21%. It is clear that the response time of the Cr\textsubscript{2}O\textsubscript{3} is slower than the LSCFO electrode for sensor\#4.1 as shown in Figure 4.28. The t\textsubscript{90} response time for a step change from 21% O\textsubscript{2} to 15% O\textsubscript{2} for LSCFO was 1 minute. The Cr\textsubscript{2}O\textsubscript{3} did not reach a stable value in the 16 minutes allotted for the 21% to 15% O\textsubscript{2} step however the t\textsubscript{90} response time was 9.5 minutes. In 21% O\textsubscript{2} the LSCFO had a baseline of 0.06 mV and the Cr\textsubscript{2}O\textsubscript{3} baseline was offset from 0 at -5.07 mV suggesting a slow equilibrium process for the O\textsubscript{2} reaction \[10, 76\]. The t\textsubscript{90} recovery time from 5% O\textsubscript{2} to 21% O\textsubscript{2} for LSCFO was 0.66 minutes. The Cr\textsubscript{2}O\textsubscript{3} signal was not stable at the starting point of 5%O\textsubscript{2} but reached a stable value of -5.93 mV in 21% O\textsubscript{2} after 40 minutes giving a t\textsubscript{90} recovery time of 6.42 minutes. The slope of the LSCFO electrode was Nernstian at 16.85 mV/decade matching with the calculated value of 16.65 mV/decade. Taking the voltages values right before the change in increasing O\textsubscript{2} levels the slope of the Cr\textsubscript{2}O\textsubscript{3} response was 15.44 mV/decade. As can be seen in Figure 4.28 the voltage values of Cr\textsubscript{2}O\textsubscript{3} did not stabilize in the time frame of the test as did those for LSCFO. By waiting for a longer time period the Cr\textsubscript{2}O\textsubscript{3} electrode response slope to O\textsubscript{2} would likely approach the Nernst value although the absolute voltages would be shifted.
Sensor#4.4 was tested for response to changing O₂ from 21% to 3%. In addition to the Cr₂O₃ and LSCFO electrodes a Pt electrode was placed on the sensor tip as well for comparison. The sensor was tested at 400, 500, 600, and 700°C as shown in Figure 4.29 and the response times were compared. At 400°C, the response of the Pt electrode was very sluggish upon changing from 21% to 3% O₂. With 21% O₂ on both sides the Pt baseline was -32 mV suggesting non-equilibrium of the O₂ reaction. The LSCFO and Cr₂O₃ electrode had a faster response time than Pt and the signals were close to zero in 21% O₂ with the Cr₂O₃ having an offset of 3 mV. Both did not reach the theoretical value of -28.2 mV in 3%O₂ with LSCFO having a voltage of -24.5 and Cr₂O₃ at -16.9 mV. This result does suggest that the LSCFO has better faster electrode kinetics than the Cr₂O₃ at 400°C. As the sensor temperature increased, the response time decreased for all of the electrodes and the transients overlapped very well at 700°C as can be seen in Figure 4.29. The Nernstian values at 500, 600 and 700°C for 3%O₂ are -32.4 mV, -36.6 mV, and -40.8 mV respectively. At 500°C the 3% O₂ values were -32.0 mV for LSCFO, -29.8 mV for Cr₂O₃, and -31.7 mV for Pt and the 21%O₂ values were -0.1 mV for LSCFO, -0.2 mV for Cr₂O₃, and -3.92 mV for Pt. At 500°C the LSCFO matched the Nernstian values as in sensor#4.1 however the other electrodes were shifted at 3 or 21%O₂ by around 3 mV. At 600°C and 700°C the LSCFO was gave the Nernstian values while the Cr₂O₃ and Pt still had a 2 mV offset at 3%O₂ with a value near -34.5 mV. At 700°C the Pt and Cr₂O₃ electrodes had a 1 mV offset from the Nernst value for 3%O₂ (-39.8 mV each) and had nearly the same response at LSCFO suggesting this was a sufficient temperature where the electrode kinetics were more comparable for the three materials.
4.3.5.2 Current-voltage polarization curves

The oxygen transients showed that the Cr$_2$O$_3$ electrode had a slower response time than the LSCFO electrode at 500°C. Electrode current voltage polarization curves were studied in an attempt to determine if there was a difference in the O$_2$ reduction ability between the two oxide electrodes. By knowing which electrode is connected to the positive/negative terminal, the direction of current can be determined when a positive or negative voltage is applied. Thus, it is possible to distinguish at which electrode O$_2$ reduction is occurring and O$_2^-$ anion oxidation. At any given point, the total current is a sum of both the reduction and oxidation currents. Polarization curves were obtained using a Gamry potentiostat in Tafel mode with a 1 mV/second scan rate from +/- 500 mV or +/- 250 mV relative to the open circuit voltage and a 2 second sample period for all tests. The tests were done with the actual sensor#4.4 and two planar symmetric cells of LSCFO and Cr$_2$O$_3$ in 21% O$_2$/N$_2$ between 500-700°C. For the planar cells, a 100 cm$^3$/min total flow rate was exposed to both electrodes. For sensor#4.4 a 100 cm$^3$/min flow rate was used on the LSCFO, Cr$_2$O$_3$ "sensing" side and static 21% O$_2$/N$_2$ on the Pt "reference" side. At each temperature 3 measurement combinations were made: Pt$_{ref}$/LSCFO, Pt$_{ref}$/Cr$_2$O$_3$, LSCFO/Cr$_2$O$_3$.

First, the planar cells were tested consisting of a 10 mm diameter YSZ pellet with either two Cr$_2$O$_3$ or LSCFO electrodes covering the whole of either side. In both cases the electrode areas were 0.79 cm$^2$. A small amount of Pt paste was put onto the YSZ to connect the Pt wire and the oxides were painted onto the Pt. The tests were done at 600°C and 700°C for the two symmetrical devices and the results are shown in Figure 4.30. It is clear that the current density at a given potential on the LSCFO electrode system is much
greater than the Cr$_2$O$_3$ system. At 700°C the current density increased as compared to 600°C.

Polarization curves were measured on the actual sensor#4.4. The electrode areas on sensor#4.4 were not identical as in the symmetrical cells but a correlation could still be made with the observed cell current. Figures 4.31-4.33 show the polarization curves from -250 mV to +250 mV in air between the Pt reference electrode and the Cr$_2$O$_3$ or LSCFO electrode at 500, 600, and 700°C. The most noticeable results are that the total current of the Pt$_{ref}$/LSCFO couple is far greater than that of the Pt$_{ref}$/Cr$_2$O$_3$ couple and as the temperature is increased, the total current increases similar to the symmetrical cells in Figure 4.30. These, results are in agreement with the observations on the symmetrical cells where the total current was larger with the LSCFO electrode. We observed at 500°C that for both electrode systems when the voltage scan reached zero, i.e. potentiometric mode, that the current was greater than zero. This could be caused by some induced polarization from starting the scan at -250 mV. The polarization went away at 600 and 700°C as can be seen from Figures 4.32 and 4.33.

Figure 4.34 compares the polarization curves between the planar couple of the LSCFO and Cr$_2$O$_3$ at 500, 600, and 700°C. It clearly shows there is some asymmetry in the O$_2$ reduction ability between the two oxides, which could influence the mixed potential signal.

4.3.5.3 Impedance spectroscopy

Since the polarization measurements showed that the Pt$_{ref}$/LSCFO couple gave a higher current than the Pt$_{ref}$/Cr$_2$O$_3$ couple this suggests that there is less resistance to
charge transfer at LSCFO as compared to the Cr$_2$O$_3$ electrode. This process should be reflected in the electrode/electrolyte interfacial resistance, which can be measured by impedance spectroscopy [77]. Impedance spectra were obtained at 500, 600 and 700$^\circ$C in air of the Pt$_{ref}$/LSCFO, Pt$_{ref}$/Cr$_2$O$_3$ and LSCFO/Cr$_2$O$_3$ couples as shown in the Nyquist plots in Figures 4.35-4.38. The plots show the resistance on the x axis (real portion) and the reactance on the y axis (imaginary portion). These two parameters were measured as a function of the frequency of a 10mV AC signal applied to the system. The frequency was scanned from $10^6$ Hz to 0.1 Hz as indicated by the labels on the graphs. Several observations can be deduced from these plots. First, it is clear that the frequency response of the Pt$_{ref}$/LSCFO couple is different than the Pt$_{ref}$/Cr$_2$O$_3$ over the same range at all temperatures. Typically, impedance spectra can be divided into three regions dependant on the frequency for these types of electrode/electrolyte systems that indicate a measure of bulk electrolyte resistance, grain boundary resistance, and electrode/electrolyte interfacial resistance [28]. The three conduction regions can be observed from highest to lowest frequency, respectively.

In our system, sensor#4.4, the Cr$_2$O$_3$ electrode is placed closer to the Pt air reference than the LSCFO but this would only affect the bulk resistance parameter and not the electrode polarization. At 500$^\circ$C, we observe the bulk resistance of the Pt$_{ref}$/LSCFO couple to be on the order of 12,500 $\Omega$ and the interfacial resistance at a frequency of 0.1 Hz is far less than that of the Pt$_{ref}$/Cr$_2$O$_3$ electrode. For the Pt$_{ref}$/Cr$_2$O$_3$ couple the two semicircles related to the bulk resistance were not observed and it is possible a higher frequency is needed to observe this region or they are convoluted with the interfacial resistance region. We obtained the impedance spectra of the symmetrical
Cr$_2$O$_3$ cell in air at 500°C and observed a semicircle for the bulk resistance at high frequencies indicating the frequency response of the Pt$_{\text{ref}}$/Cr$_2$O$_3$ couple may have shifted out of the range of our instrument. At higher temperatures, for both couples the resistance decreases significantly which correlates with the faster response time of the sensor. Table 4.3 shows the interfacial resistance at 0.1 Hz of the Pt$_{\text{ref}}$/Cr$_2$O$_3$ and Pt$_{\text{ref}}$/LSCFO couple over the range of 500-700°C. The trend remains that Cr$_2$O$_3$ couple always has a higher electrode/electrolyte interfacial resistance than the LSCFO couple. This supports the observations with the polarization measurements.

4.4 Discussion

4.4.1 Sensor response

There have been numerous papers in the literature about sensors for various combustion gases using solid electrolytes and metal oxide electrodes [51, 59, 78]. Very few of the papers have offered a detailed explanation about the mechanism of sensor response. Many of the studies simply screened various metal oxides for their response magnitude to NO$_x$ or CO [7, 55], and chose to further test the oxide with the largest signal offering no explanation for the performance characteristics. In our lab we have tried to test the reproducibility of the same oxide material on different sensors fabricated in the same manner. As shown in Figure 4.9, there was still a significant variation in the response to 600 ppm NO or NO$_2$ for the different sensors. For example, there was a variation of signal response to 600 ppm NO$_2$/3% O$_2$ from 78 mV on sensor#4.2 to 53 mV on sensor#4.4 for the Cr$_2$O$_3$ electrode and 9 mV on sensor#4.2 to 23 mV on sensor#4.3 for the LSCFO electrode. This suggests that the microstructure, interface formation, and
thickness of the electrodes play an important role. Each of these factors can affect the TPB, catalytic activity and adsorption properties ultimately affecting the observed sensor signal as shown in the schematic of Figure 4.10. Mukundan et al. used very controlled sputter deposition of Pt and Au electrodes on two samples and they found that there was still a small difference in the O$_2$ polarization curves between the two Pt or two Au electrodes and suggested that the difference was due to surface area and morphological variations [79]. Brosha made multiple YSZ based sensors for CO and hydrocarbons using LaMnO$_3$ and TbYSZ oxide electrodes and found variations in device response [11]. They attributed the variations to random formation of the triple point boundary of the oxides, which can affect the O$_2$ reduction over-potentials.

In the literature researchers use various methods to collect current on the oxide electrode typically using either Pt or Au in the form of wire wraps [76], sputtered metallic pads [11, 47], fired metallic pastes [7, 55], or metallic meshes [80] all placed on top of the oxide layer or underneath. The current collection method and metal type has been shown to have a significant affect on the sensor signal [11, 61]. Brosha observed that a LaMnO$_3$ electrode on YSZ covered with a Pt pad current collector could serve as a pseudo reference since it gave a low signal for CO [11]. They attributed the low signal to be due in part to the CO oxidation activity of the Pt pad. The group states that they are trying to develop devices without using noble metal collectors on the oxide electrode. They filed a patent application in December 2002 using a sintered La$_{0.8}$Sr$_{0.2}$CrO$_3$ electrode buried in YSZ powder that was subsequently sintered [81]. This process was an attempt to maintain a controlled surface area of the electrode and triple point boundary region. A small Pt wire was still connected to the oxide electrode with Pt paint however.
The reference electrode was a lone Pt wire buried in the YSZ (similar to the oxide electrode) when it was sintered. The catalytic activity of the current collector is also evident from the work of Lu et al., who did a study on the position and type of the Pt metal on a WO₃ electrode on YSZ for NOₓ sensing [61]. Three sensor designs were used: the first had the WO₃ layer placed directly on the YSZ with only a Pt wire wrapped around the oxide (device A), the second used a Pt mesh placed on top of the WO₃ layer (device B), and the third design had a layer of Pt paste directly on the YSZ with the WO₃ coated on top (device C). The order of sensitivity for NOₓ at 600°C from highest to lowest was: A > B > C. The explanation for these results was that in device A, the Pt wire had little catalytic effect on the NOₓ, whereas the Pt mesh in device B and the Pt paste layer in device C catalyzed NO and NO₂ towards equilibrium at 600°C. Due to the electrode morphology variations and current collection methods one should be wary of the tabulated response values in the literature for absolute signal magnitudes of a given oxide [7, 76, 82] presented without standard deviations for the responses or reproducibility trends. In our study described here, we wrapped a Pt wire around the YSZ tube first and then painted a layer of oxide on top (also see chapter 3) except in the case of sensor#4.1 where a Pt paste collector was used underneath the Cr₂O₃ electrode. The Pt paste/Cr₂O₃ did not show a significant difference in sensitivity towards NOₓ compared to the Pt wire/Cr₂O₃ as shown in Figure 4.9 with the signal for NO₂ in the range of the Pt wire sensors (#4.2-#4.4) but giving a higher signal to NO.

It is reasonable to expect the NOₓ signal variation of the Cr₂O₃ and LSCFO electrodes is due to the same processes happening during preparation. We also found a much higher variation in signal response for all gases when using different Pt electrodes.
on multiple sensors. The changing morphology and catalytic activity over time could affect the sensor signal stability as in the case of the responses shown in Figure 4.8. Little explanation is given for the change in signal versus time in the literature. It is possible that the NO$_x$ equilibration ability of the electrode materials decreases with time allowing more NO$_x$ to reach the TPB. We observed in our catalytic measurements in section 4.3.3. that after a heat treatment the NO$_x$ conversion ability of the two powders decreased. Even though the conversion does not seem to be the main reason for the difference in sensitivity between the LSCFO and Cr$_2$O$_3$ it may be a reason for the increase in signal.

Furthermore, it is possible that the O$_2$ kinetics of the electrode become slower with aging, which can affect the O$_2$ polarization curve giving a larger mixed potential as will be discussed in section 4.4.5.

4.4.2 Electrode morphology

We found in all cases that the Cr$_2$O$_3$ electrode gave a higher signal for NO$_x$ than did LSCFO. The powder morphology was investigated separately and on the sensor. We found in the single point surface area measurements that the Cr$_2$O$_3$ had a higher surface area than the LSCFO whether it was fresh out of the bottle or heat treated similar to the sensor preparation. The heat treated powders on the sensors showed similar particle sizes in the range of 200 nm and larger but it is obvious that some grain growth had occurred. Even though the surface areas of the two powders on the YSZ electrolyte are probably different than the free powders the trend probably remains. The SEM images on a 1µm scale of the electrode powders on YSZ in Figure 4.16 (LSCFO - middle image) and Figure 4.19 (Cr$_2$O$_3$ top image) show that the Cr$_2$O$_3$ appears to be more porous.
4.4.3 Electrode catalytic activity

Based on the higher surface area, we might expect that the Cr$_2$O$_3$ has a higher catalytic activity than the LSCFO. We first tested 5 mg of the two oxides, which was close to the amount used on the sensor (2-3 mg). Figure 4.20 and Figure 4.21 showed the conversion over a range of temperatures from 200-700°C. It is evident that at the sensing temperature of 500°C Cr$_2$O$_3$ showed a higher conversion of NO$_2$ than the LSCFO (76% to 30%) but that both oxides had a similar conversion of NO (10% to 9%). These results do not agree with the sensing response if based solely on catalytic activity. The Cr$_2$O$_3$ and LSFCO should have nearly the same signal for NO and LSCFO a higher signal for NO$_2$ (as more un-equilibrated NO$_2$ would get to the triple points, refer to Figure 4.10). At higher temperatures both oxides fully equilibrated NO and NO$_2$ and the sensor response decreased significantly with no signal above 650°C typical of mixed potential sensors. We also found that using 100 mg of both oxides completely equilibrated the two NO$_x$ gases. This suggests that the high activity of the 5 mg of Cr$_2$O$_3$ is due mainly to its higher surface area and as the amount of LSCFO is increased, the same trend results. In addition, the metal ions in LSCFO could also be important for its catalytic activity. Since the amount of oxide on the sensor is less than in the catalytic measurements, the gas flow dynamics are different, and the electrode thickness is much less than the catalytic bed thickness, it may be difficult to make a direct comparison. Finally, the Cr$_2$O$_3$ electrode appears more porous than the LSCFO and the NO$_x$ diffusion may be easier to the triple points than in the catalytic bed where the particles are packed closer together favoring reaction.
A few groups in the literature have tried to correlate the potentiometric sensor response to the heterogeneous catalytic activity of the electrode material towards the gas of interest [10, 42, 83, 84]. For a specific example, recently Miura *et al.* have screened four oxide materials, ZnFe$_2$O$_4$, NiCr$_2$O$_4$, ZnCr$_2$O$_4$, and CrMn$_2$O$_4$ for their sensitivity to NO or NO$_2$ at 700°C. They found the order of sensitivity to 200 ppm NO or NO$_2$ in 21%O$_2$ was ZnFe$_2$O$_4$ > NiCr$_2$O$_4$ > ZnCr$_2$O$_4$ > CrMn$_2$O$_4$. They did catalytic conversion measurements of NO$_2$ to NO over a range of temperatures (200-700°C). At 700°C all the oxides fully equilibrated the NO$_2$ but at lower temperatures (below 550°C) the activity was reduced in the order ZnCr$_2$O$_4$ > NiCr$_2$O$_4$ = CrMn$_2$O$_4$ > ZnFe$_2$O$_4$. The conclusion was that since the ZnFe$_2$O$_4$ had the lowest activity at lower temperatures this may be the reason for the higher signal. Interestingly the ZnCr$_2$O$_4$ had the highest NO$_2$ conversion but still gave a larger signal than the CrMn$_2$O$_4$ electrode and the catalytic activity of NiCr$_2$O$_4$ and CrMn$_2$O$_4$ were the same but the NiCr$_2$O$_4$ gave a larger signal and no explanation was given as to why. Since the ZnFe$_2$O$_4$ gave the largest signal it was the focus of the paper. Miura subsequently used O$_2$ and NO$_2$ desorption measurements (via TPD) and found the total amount of O$_2$ and NO$_2$ adsorbed on ZnFe$_2$O$_4$ was greater than the other oxides while it had a lower catalytic activity. A correlation between all four oxides and the sensor signal was not given. Numerous sensor papers have been published and relatively few have utilized catalytic activity to explain sensor performance but those conclusions based on catalysis alone have likely been coincidental. It is highly probable that many of the sensor systems in the literature if tested would not show a direct correlation with catalytic activity and other electrode properties must be investigated. In
fact, no paper could be found where a group systematically investigated all three of the reaction zones shown in Figure 4.10 with respect to the sensor response.

### 4.4.4 Adsorption properties

Since the catalytic NO\textsubscript{x} conversions did not match with the sensor signals, we investigated the ability of the two oxides to adsorb NO\textsubscript{x}. The pressure swing adsorption technique was chosen as it has been successfully used in the field of catalysis. We found that the LSCFO adsorbed more NO\textsubscript{x} when flowing NO (1.39 \(\mu\)mols NO\textsubscript{x}/g) or NO\textsubscript{2} (0.83 \(\mu\)mols NO\textsubscript{x}/g) than the Cr\textsubscript{2}O\textsubscript{3}. The amount of NO\textsubscript{x} on the Cr\textsubscript{2}O\textsubscript{3} could not be evaluated under the time resolution of the instrument but would be much smaller than the LSCFO.

The testing temperature of our experiments at 500\textdegree C was higher than similar PSA experiments in the catalyst literature at 25\textdegree C using MFI and faujisite zeolites [73] and nickel-copper manganites [75] and at 400\textdegree C using ZSM-5 zeolites. Zhang found that the amounts of reversible and irreversible adsorption decreased with increasing temperature (250K to 375K) on Cu-MFI zeolites [73]. Ogura observed that as the NO\textsubscript{x} concentration was increased (100 to 1000 ppm), the amount of NO\textsubscript{x} adsorbed was higher on ZSM-5 zeolites at 400\textdegree C [85]. For comparison, the amounts of NO\textsubscript{x} adsorbed on 100 mg LSCFO in 600 ppm NO or NO\textsubscript{2} + 3\% O\textsubscript{2}/N\textsubscript{2}, at 500\textdegree C for a 200 cm\textsuperscript{3}/min flow rate were less (1.39 \(\mu\)mols NO\textsubscript{x}/g from NO and 0.83 \(\mu\)mols NO\textsubscript{x}/g from NO\textsubscript{2}) than that at 400\textdegree C for 100 mg of Ir/In/H-ZSM-5 catalyst exposed to 100 ppm NO or NO\textsubscript{2} + 10\%O\textsubscript{2}/He at a flow rate of 100 cm\textsuperscript{3}/min (12 \(\mu\)mols NO\textsubscript{x}/g from NO and 8 \(\mu\)mols NO\textsubscript{x}/g from NO\textsubscript{2}) [74]. At 25\textdegree C Drouet found an average reversible adsorption on several nickel-copper manganites...
of 64 µmols NO/g for 900 ppm NO/Ar with a 60 cm$^3$/min flow rate [75]. Also at 25°C, Zhang found a reversible adsorption of 190µmols NO/g on Cu-MFI zeolite for 997 ppm NO/He at 100 cm$^3$/min [73]. Based on the testing parameters we used, the lower amount of adsorption of NO$_x$ on LSCFO would be expected due to the higher temperatures and faster flow rate giving a decreased contact time. The results of the adsorption measurements alone may correlate with the sensor measurement. As no significant NO$_x$ was adsorbed on the 100 mg Cr$_2$O$_3$ bed it suggests the gas molecules can easily flow through the highly porous 2 mg electrode layer and reach the triple point reaction zone. However, the catalyst measurements suggest that the Cr$_2$O$_3$ is simply acting as a high surface area material with no specific adsorption at 500°C and there is probably some conversion towards equilibrium before the triple points but not enough to cause a small signal.

In the case of LSCFO, which has a lower specific surface area than Cr$_2$O$_3$, the NO$_x$ adsorption could be enhanced by the presence of the various metal ions in its structure. It was observed by Zhang [73] that different metal ions exchanged into an MFI type zeolite, including Cr, La, Sr, Fe, and Co had different NO adsorption properties. With the order of reversible adsorption being Sr > Co > Fe > Cr > La and the order of irreversible adsorption being Co > Fe > Cr > La > Sr. Co was found to have about six times as much irreversible adsorption than the next closest metal ion. It was suggested that in the MFI and FAU type zeolites a [Co-(NO)$_2$]$^{2+}$ complex was formed.

Even though the LSCFO adsorbed more NO$_x$ in the PSA tests similar to the Cr$_2$O$_3$ the layer is thinner on the sensor than that used in adsorption and probably porous enough to let the gases to get to the triple points without much catalytic conversion. In addition,
during the sensing tests the NO\textsubscript{x} gas is constantly exposed to the electrode materials so the slower NO\textsubscript{x} breakthrough on the LSCFO during the PSA experiments may not have much significance.

Often when testing a new sensor, the very first time it is exposed to a step pulse of NO or NO\textsubscript{2} the sensor transient does not take a smooth step profile as observed in Figure 4.7. The step may have spikes, a sluggish response, or give a lower magnitude but upon a second or third NO\textsubscript{x} pulse the step profile becomes smooth. This suggests a possible initial irreversible adsorption step even at high temperatures on the electrode materials under the sensing conditions.

As discussed above, the Miura group tried to correlate the response of a NO\textsubscript{x} sensor on four oxides. They did a temperature programmed desorption experiment and found the ZnFe\textsubscript{2}O\textsubscript{4} had the strongest NO\textsubscript{2} adsorption but the lowest catalytic conversion for NO\textsubscript{2}. It also gave the highest signal to NO\textsubscript{2} as compared to the other oxides. They suggested this could cause a larger triple point adsorption. In our case the LSCFO had a higher adsorption than the Cr\textsubscript{2}O\textsubscript{3}, a lower catalytic activity, but also gave a lower signal. Thus, another parameter must be influencing the electrode signal and we decided to look at the electrical properties of the two materials.

### 4.4.5 Electrical measurements

Our polarization results can be compared with that obtained by Miura et al. [7] using a YSZ tube with a Pt air reference and two sensing electrodes, either Pt or Pt covered with a CdCr\textsubscript{2}O\textsubscript{4} layer. A polarization test was done in air at 500°C for the two electrode couples. They observed an exponential increase in current as a voltage was
applied to the device over a +/- 400 mV range. There was hardly any difference observed in the current levels in O$_2$ for the Pt or Pt + CdCr$_2$O$_4$ but there was a difference in response to 200 ppm NO$_x$ and this was reflected in the polarization curves of 21% O$_2$ + NO$_x$. No correlation was made with the O$_2$ reduction ability of the two oxides and little insight into the mechanism was given. However, the total current for the Pt$_{ref}$/Pt system at +/- 200 mV was +3 µA/-3 µA. At +/- 200 mV on our system, we obtained a current of +7.2 µA/-4.8 µA for the Pt$_{ref}$/LSCFO and +.75 µA/-.3 µA for the Pt$_{ref}$/Cr$_2$O$_3$.

Several groups have used two [7, 47, 86] or three [79, 87-94] electrode systems in the literature to study the current/overpotential behavior of different electrodes on YSZ. The current versus potential diagrams are plotted in several manners with the most common being log current verses potential although we used a linear scale for the current. In all cases similar behavior is observed and the shape of the polarization curve can be divided into several regions. Concerning the shape of the polarization curves in our study, shown in Figures 4.30-4.34, there are two regions observed for both electrodes consistent with the literature based on the Butler-Volmer equation. At low applied potential (low overpotential) there is a linear region that has ohmic behavior and at higher overpotentials an exponential characteristic is exhibited, which is indicative of Tafel behavior. In the case of our sensors, the voltages observed for NO$_x$ are generally below 75 mV, which corresponds to the ohmic region (linear portion) of the O$_2$ polarization curves. We additionally tested the Pt$_{ref}$/Cr$_2$O$_3$ and Pt$_{ref}$/LSCFO couple on sensor#4.4 at overpotentials up to +/- 1 V (compared to +/-250 mV shown in Figures 4.31-4.34). We found a limiting current behavior on the Pt$_{ref}$/Cr$_2$O$_3$ couple while the Pt$_{ref}$/LSCFO couple continued to exhibit Tafel behavior. Tsiakaras et al. observed symmetric polarization
curves for the cathodic and anodic reactions of O\textsubscript{2} reduction and O\textsuperscript{2-} anion oxidation of LSCFO on YSZ at 800°C consistent with our results at lower temperatures [93].

The electrical conductivity of oxides is usually determined by pressing a pellet and using metallic electrodes. Many factors can influence the measured conductivity at a certain temperature and in a given atmosphere including the sample density/porosity, purity, and type of electrode. Thus, the reported values for conductivity of a sample can vary widely throughout the literature. Using the four point AC technique, for Cr\textsubscript{2}O\textsubscript{3} an electrical conductivity of 3.98*10\textsuperscript{-3} S/cm at 550°C for a porous sample using Au electrodes was obtained at p\textsubscript{O2} = 1 atm [95]. In the same reference using Pt electrodes an electrical conductivity of 3.24*10\textsuperscript{-3} S/cm was obtained at 500°C and p\textsubscript{O2} = 10\textsuperscript{-4} atm for a porous Cr\textsubscript{2}O\textsubscript{3} pellet and 32.4*10\textsuperscript{-3} S/cm at 500°C and p\textsubscript{O2} = 10\textsuperscript{-14} atm and for a compact Cr\textsubscript{2}O\textsubscript{3} pellet. A conductivity of 1*10\textsuperscript{-5} S/cm in air at 500°C was obtained for a thermally grown Cr\textsubscript{2}O\textsubscript{3} scale [96]. In the case of La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3}, Kostogloudis obtained a total conductivity (electronic + ionic) of 468 S/cm at 500°C in air for a dense bar [21]. He found that above 500°C the total conductivity decreased and states that the ionic conductivity is smaller than the electronic conductivity by about two orders of magnitude. Chen et al, using Ce\textsubscript{0.85}Sm\textsubscript{0.15}O\textsubscript{2} blocking electrodes on a dense LSCFO disk with Pt current collectors, found an ionic conductivity of 1*10\textsuperscript{-3} S/cm at 500°C and stated that it was comparable to YSZ [15]. Although our Cr\textsubscript{2}O\textsubscript{3} and LSCFO sensor electrodes are likely more porous than the typical samples used for electrical studies in the literature the inherent conduction properties of the materials will remain.
A study was done by Jiang et al concerned with the deposition of Cr species on a Sr doped LaMnO$_3$ electrode from metallic interconnects in fuel cell applications. Cr vapor can deposit as Cr$_2$O$_3$, which can react to form (Cr,Mn)$_3$O$_4$ spinels at the triple phase boundary reducing the cell performance significantly [97]. They also gave reference to studies that found Cr$_2$O$_3$ and Sr doped LaCrO$_3$ had a low O$_2$ reduction ability compared to Pt or LaMnO$_3$ electrodes. Matsuzaki also studied Cr poisoning of a LSCFO SOFC cathode [98].

These results suggest that the higher current observed in the polarization tests for LSCFO is due to its good O$_2$ reduction ability and its mixed conducting property allowing a high throughput of O$^{2-}$ ions across the interface [30]. It is well known that mixed conducting lanthanum oxide perovskites can convert O$_2$ to O$^{2-}$ at the TPB of the oxide/electrolyte/gas and at the double phase boundary of the oxide/gas resulting in a high transport of O$_2$ species. On the contrary the Cr$_2$O$_3$ can only convert O$_2$ gas at the TPB similar to that of other electronic conductors such as Pt resulting in a lower rate of charge transfer than LSCFO.

Several groups have used impedance spectroscopy to determine the electrical properties of a sensor or electrode/electrolyte system. Grilli compared the sensor impedance in air or exposed to NO$_2$ at 450°C for a two terminal system of (Pt)LaFeO$_3$/YSZ/Pt [51]. They observed an arc at high frequencies due to the bulk impedance and a spike at low frequencies due to the electrode/electrolyte interface similar to the Pt$_{rev}$/LSCFO and Pt$_{rev}$/Cr$_2$O$_3$ system in our study. The impedance of the sensor decreased upon exposure to NO$_2$. The explanation given was that the O$^{2-}$ produced by NO$_2$ decomposition decreased the voltage barrier. No explanation was given as to
which electrode was responsible for the NO2 signal as they did not use an air reference. In addition, no mention was made about the O2 redox properties of the electrodes. Huang examined a Bi2O3-Y2O3-CeO2 electrolyte system with LSCFO and Ag electrodes [28]. They found a significantly lower electrode interfacial resistance at low frequencies for LSCFO than Ag in air at temperatures between 300-600°C. They concluded that the LSCFO was a good oxygen electrode based on its conduction properties. In our system we measured the impedance of a two terminal system consisting of a common Pt reference electrode and a LSCFO or Cr2O3 electrode. It is recognized that in these measurements that the overall impedance is the sum of both electrodes in the couple and exact numbers for each electrode cannot be determined. Although, since the two couples use a common Pt reference any difference in the impedance measurement is due to the different behavior of the two oxides. This was reflected in Table 4.3, which shows that at a frequency of 0.1 Hz at each temperature the Pt_ref/Cr2O3 couple had a larger total interfacial resistance than the Pt_ref/LSCFO couple.

It appears that in the case of LSCFO and Cr2O3 that the electrical properties play the most important role in the sensor response magnitude between the two electrodes. Mixed potential sensor models in the literature have been derived for Au, Pt, and oxide electrode systems [79, 83, 86, 99, 100]. As discussed in chapter 1, existing models greatly simplify the parameters of the system and no predictive calculations for solid-state gas sensors have been determined. Considering only a two gas system consisting of O2 and test gases such as NO, NO2, or CO all of the catalytic and electrocatalytic parameters of the O2 and sensing gas reactions would have to be known, which is impossible a priori [99]. The current-potential characteristics of an electrochemical reaction can be
approximated by the Butler-Volmer equation, which was discussed briefly in chapters 1 and 3. Here we discuss the equation and its relation to the sensor signal in more detail. To review, the equation takes the general form as shown below:

\[ i_{\text{net}} = i^0 \exp \left( \frac{\alpha n F \eta}{RT} \right) - i^0 \exp \left( \frac{-(1-\alpha)n F \eta}{RT} \right) \]  \hspace{1cm} (4.1)

\( I_{\text{net}} \) is the total current for the oxidation (anodic) and reduction (cathodic) portions of the reaction, which are the first and second terms on the right side of the equation, respectively. The transfer coefficient \( \alpha \), is a measure of the symmetry of the oxidation and reduction reactions, \( n \), \( F \), \( R \), and \( T \) have their usual meanings. The remaining two terms \( i^0 \), the exchange current, and \( \eta \), the overpotential, are important in determining the mixed potential.

The overpotential, \( \eta \), is the difference between the reversible potential of the reaction and the actual potential (the mixed potential), thus, \( \eta = E_{\text{mix}} - E_{\text{rev}} \). The reversible potential is also known as the equilibrium potential, or cell potential and is related to the free energy change by:

\[ \Delta G = -nFE_{\text{rev}} \]  \hspace{1cm} (4.2)

The electrochemical half-cell reactions that are of interest to us are:

\[ \text{NO} + O^{2-} \rightarrow \text{NO}_2 + 4e^- \hspace{1cm} (4.3) \]
\[ O_2 + 4e^- \rightarrow O^{2-} \hspace{1cm} (4.4) \]
\[ \text{NO}_2 + 4e^- \rightarrow \text{NO} + O^{2-} \hspace{1cm} (4.5) \]
\[ O^{2-} \rightarrow O_2 + 4e^- \hspace{1cm} (4.6) \]
and throughout this discussion we will consider only the reaction of NO oxidation and O\textsubscript{2} reduction (eqs. 4.3 and 4.4) on the air reference type sensor while similar derivations can be made for NO\textsubscript{2} reduction. When the gas species are in their standard states (1 atm) for the electrochemical reactions the standard cell potential is also related to the free energy by

\[ \Delta G^o = -nF E^o \]  

(4.7)

In solid-state sensor systems using YSZ the O\textsubscript{2} reduction reaction at 1 atm is convenient to use as the reference electrode as compared to the standard hydrogen electrode (SHE) in liquid systems [99].

If we consider a YSZ tubular system with a 1 atm reference on one side and pure NO at 1 atm on the other side then the two half-cell reactions 4.3 and 4.4 above would combine to give an overall cell reaction of:

\[ \text{NO + O}_2 \rightarrow \text{NO}_2 \]  

(4.8)

The calculated standard potential for NO oxidation (based on thermodynamics and eq. 4.7) at the sensing temperature of 500°C is -2.79 mV and it is 0 mV for O\textsubscript{2} since it is defined as the reference. In reality during the sensing measurements the tests are not done under standard conditions. We typically used an air reference at 0.21 atm and a sensing gas with 0.03 atm (3%) O\textsubscript{2} and 100-1000 ppm NO\textsubscript{x}. Under nonstandard conditions at equilibrium the reversible potential is related to the standard potential by the Nernst equation:

\[ E_{rev} = E^o + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Re d}]} \]  

(4.9)
This equation can be used for the cell reaction or the half-cell reactions. For the normal oxygen sensor without NO\textsubscript{x} present \(E^0\) is zero and equation 4.9 can be used to calculate the reversible potentials using a 0.21 atm reference, which is -32.4mV for 3%O\textsubscript{2}. However we cannot use the Nernst equations in the presence of NO\textsubscript{x} because there is a mixed potential due to non-equilibrium conditions on the sensing electrode since there are two simultaneous electrode reactions (eqs 4.3 and 4.4). The observed sensor mixed potential is the potential difference between the equilibrium potential on the 21% air reference electrode and the mixed potential on the sensing electrode. The mixed potential on the sensing electrode is determined by kinetic factors and not thermodynamic factors as given by the Nernst equation.

At the reversible potential of an electrochemical reaction the system is at equilibrium and no net current it observed. In other words when the overpotential is zero the system is at the reversible potential. In the Butler-Volmer equation when \(\eta=0\) then \(i_{\text{net}}\) becomes zero however this does not mean \(i^0\), the exchange current is zero. At equilibrium the forward and backward reactions are still occurring with a non-zero current \(i^0\). In addition the Butler-Volmer equation can be reduced to the low overpotential linear form since \(e^x = 1 + x\) and be expressed as:

\[
\begin{align*}
    i_{\text{net}} &= i^0 \left[ \frac{nF\eta}{RT} \right] 
\end{align*}
\]  (4.10)

As discussed above the mixed potential sensor signal occurs as high overpotentials for NO in the Tafel region and at low overpotentials for O\textsubscript{2} (linear
approximation region). The current potential expressions for the two reactions based on the two forms of the Butler-Volmer equation are:

\[
i_{O_2} = -i^{\circ}_{O_2} \left[ \frac{4F(E_{mix} - E_{O_2}^{rev})}{RT} \right] \quad (4.11)
\]

\[
i_{NO} = i^{\circ}_{NO} \exp \left[ \frac{4\alpha F(E_{mix} - E_{NO}^{rev})}{RT} \right] \quad (4.12)
\]

Considering the two half-cell reactions the reversible potential for each can be given as:

\[
E_{O_2}^{rev} = E_{O_2}^{\circ} + \frac{RT}{nF} \ln \frac{[O^{2-}]}{[O_2]} \quad (4.13)
\]

\[
E_{NO}^{rev} = E_{NO}^{\circ} - \frac{RT}{nF} \ln \frac{[NO][O^{2-}]}{[NO_2]} \quad (4.14)
\]

In addition the exchange current also depends on the concentration of the gases since it is a function of the rate of reaction.

\[
i^{\circ}_{O_2} = nFAk_{O_2}^{\circ}[O_2]^y \quad \rightarrow \quad i^{\circ}_{O_2} = C_1[O_2]^y \quad (4.15)
\]

\[
i^{\circ}_{NO} = nFAk_{NO}^{\circ}[NO]^x \quad \rightarrow \quad i^{\circ}_{NO} = C_2[NO]^x \quad (4.16)
\]

where A is the electrode area, \(k_{O_2}^{\circ}\) and \(k_{NO}^{\circ}\) are the standard rate constants, x and y are constants, [NO] and [O_2] are the gas concentrations, and n and F have their usual meanings.
By definition, at the observed mixed potential, the net current is zero requiring the rates of all reducing and oxidizing electrochemical reactions to be equal. This can be observed by looking at the point where the polarization curves have equal oxidation and reduction currents, \(i_{O_2} = i_{NO}\) (refer to Figure 1.21). We can equate the currents in equations 4.11 and 4.12, substitute the exchange current expressions and solve for \(E_{mix}\) as has been done in the literature [48, 100]. The resulting expression is:

\[
E_{mix} = E_{NO}^{rev} + \frac{RT}{4\alpha F} \left[ \ln \frac{C_1}{C_2} + \ln \frac{4F}{RT} (E_{mix} - E_{O_2}^{rev}) + y \ln[O_2] - x \ln[NO] \right]
\] (4.17)

In a constant background oxygen level (3% in our tests) the mixed potential varies logarithmically with changing NO levels. The literature will typically use a form of this expression to explain the log dependence of the sensor signal. In addition \(E_{NO}^{rev}\) shifts when changing the concentration of NO also causing a change in \(E_{mix}\).

Early models considered the sensing gas reaction to be more important in determining the electrode potential. However, it is now agreed that since \(O_2\) is in excess in the sensing environment (1-10%) compared to the sensing gas concentration (100-1000 ppm) that consideration must be given to the \(O_2\) reaction also [79, 83]. Using \(NO_x\) as an example, theoretically the observed mixed potential will be in between the equilibrium (reversible) potential of the \(O_2\) reaction and the equilibrium (reversible) potential of the NO/NO\(_2\) reaction. It is easy to determine the equilibrium potential of the \(O_2\) reaction, which is just the voltage in the case of the \(O_2\) sensor in the absence of test gas as shown above. We found that both the \(Cr_2O_3\) and LSCFO electrode brought \(O_2\) to equilibrium (although at different rates) because they both gave a Nernstian response. The
polarization curves for O\textsubscript{2} were obtained but it is not possible to obtain the polarization curves for NO or NO\textsubscript{2} alone. This would require testing the NO\textsubscript{x} in the absence of O\textsubscript{2}. It has been suggested that if the polarization curve for the sensing gas could be obtained in the absence of O\textsubscript{2} it would be different than the one in O\textsubscript{2} due to different catalytic rates on the electrode [79].

We can draw a model diagram of the polarization curves for the O\textsubscript{2} and NO\textsubscript{x} reactions based on the literature to explain why the LSCFO and \textit{Cr}_2O_3 electrodes give a different response. Considering the reaction for NO, the model in Figure 4.39 shows ideal polarization curves plotted on a linear current versus potential plot for the O\textsubscript{2} reduction reaction and the NO oxidation reaction. The low overpotential (linear) region of the O\textsubscript{2} polarization curve is shown and the linear + Tafel region is shown for NO. E\textsuperscript{rev}_O_2 is the sensing electrode potential in the absence of NO, which is the O\textsubscript{2} sensor case. When NO is added to the system the potential shifts to the mixed potential E\textsubscript{mix}, which is in between E\textsuperscript{rev}_O_2 and E\textsuperscript{rev}_NO. E'_O_2 is the potential of the air reference electrode. We obtained polarization curves in air for the two electrodes and the sensors were tested in air and 3\%O\textsubscript{2} but there should not be a significant difference in the shape of the polarization curve in 3\%O\textsubscript{2}. As shown in Figures 4.3 to 4.8 the sensor voltage response to NO and NO\textsubscript{2} for the two oxide electrodes had a logarithmic change to increasing NO\textsubscript{x} levels. We discussed the nature of the sensor voltage change in Chapter 3 (section 3.4.2) and used equations from the Butler-Volmer expression to explain the dependence assuming both the O\textsubscript{2} and NO\textsubscript{x} reactions had a Tafel type dependence. The resulting equations that were derived show a logarithmic dependence on the NO\textsubscript{x} concentration for the mixed potential. As we observed in Chapter 4 it is quite possible that the O\textsubscript{2} reduction reaction kinetics
may not be Tafel type and can be represented by a linear form of the Butler-Volmer equation as shown above since we observed linear polarization curves in the range of our sensor voltage. The NO\(_x\) kinetics must still follow Tafel type behavior to maintain a logarithmic voltage dependence as shown in equation 4.17. This is represented in Figure 4.39 where the observed mixed potential is in the linear region of the O\(_2\) reduction polarization curve and the logarithmic region for the NO oxidation polarization curve.

For sensors 4.2 to 4.4 we had an average response of 10mV for Cr\(_2\)O\(_3\) and 1.5mV for the LSCFO electrode to 600ppm NO in 3%O\(_2\)/N\(_2\) and the values for this specific case are shown in Figure 4.39. If we assume that both of the electrodes have the same NO\(_x\) polarization curve but significantly different O\(_2\) polarization curves (as shown in Figures 4.30-4.34) it is clear that when introducing the NO to the system the mixed potential will shift more in the Cr\(_2\)O\(_3\) case because of the higher O\(_2\) overpotential (x-axis), which is why we observe a higher signal for Cr\(_2\)O\(_3\).

Mukundan used a three-electrode system for CO sensing on Au and Pt and found that 600ppm CO hardly affected the polarization curve of O\(_2\) [79]. In reality for NO or NO\(_2\) the polarization curves at a given concentration for Cr\(_2\)O\(_3\) and LSCFO may be different and not identical as shown in Figure 4.39. This is because the two oxides have different catalytic and electrocatalytic abilities that will alter how much NO or NO\(_2\) actually can react at the triple point boundary. This will affect \(E^{\text{rev}}\) and \(i^o\) based on their concentration dependence. In addition the oxides can have different \(k^o\) based on their materials properties. The plot in Figure 4.39 is simplified in that both oxides are shown having equal \(E^{\text{rev}}\) and \(i^o\), which is probably not likely. However, in our measurements in
this chapter the ability for O₂ reduction proved to be most important and this assumption may not be far off.

If the catalytic ability was a dominating factor then the high catalytic activity of Cr₂O₃ would cause the NOₓ reversible potential (E_{rev}^{NO}) to shift closer to the O₂ equilibrium potential as less un-equilibrated NOₓ gets to the triple points [83]. The mixed potential would shift closer to the O₂ equilibrium potential resulting in a lower signal. In addition, a poor adsorption of NOₓ may indicate a poor adsorption at the triple points also causing a shift in E_{rev}^{NO} and i_{O}^{NO}. However, in the case of our porous Cr₂O₃ electrode material, the NOₓ catalytic activity may shift the NOₓ polarization curve but it is probably not the main factor affecting the mixed potential. The larger signal for the Cr₂O₃ is due to the electrical properties of poor O₂ reduction. For the LSCFO, the poor catalytic activity suggests the NO polarization curve would shift away from E_{rev}^{O₂} giving a larger mixed potential signal. Also the higher adsorption property could enhance adsorption at the triple points further increasing the signal. This may be the reason we still see a 1.5mV signal for LSCFO but it is still far lower than the Cr₂O₃ due to its faster O₂ kinetics.

Miura obtained the polarization curves for an air reference sensor (described above) using a Pt and Pt + spinel system. It was observed that both electrodes had the same O₂ polarization curves but the Pt + spinel showed a higher signal for NOₓ suggesting an enhanced adsorption at the triple points [7].

Also in chapter 3 we observed that when the NO and NO₂ gases are already in equilibrium before reaching the sensor electrode (from the zeolite PtY filter) there was a very low signal because the electrode was towards the equilibrium potential for O₂.
Finally, when we change the NO gas concentration equations 4.14, 4.16 show that $i_o$ and $E_{\text{rev}}$ change logarithmically. This is why $E_{\text{mix}}$ changes logarithmically with NO concentration because it is a function of $i_o^\text{NO}$ and $E_{\text{rev}}^\text{NO}$ as shown in equation 4.17. A way to visualize this in the model polarization plots in Figure 4.39 is that when the NO gas concentration is increased the NO polarization curve will shift up logarithmically on the y-axis because $i_o^\text{NO}$ is increased and logarithmically to the right on the x-axis since $E_{\text{rev}}^\text{NO}$ increases.

4.5 Conclusions

The observed signal for an electrode is due to a complex and convoluted set of parameters. Figure 4.10 depicted the three reaction zones that are believed to influence the signal. It appears that there are several factors of importance that can be considered for a mixed potential NO$_x$ sensor that could function independently:

1) The bulk electrode catalytic activity to equilibrate the reaction of NO + 1/2O$_2 \leftrightarrow$ NO$_2$ (assuming no conversion to N$_2$O or N$_2$)

2) The adsorption of NO$_x$ (on the oxide or at the triple points)

3) The adsorption of O$_2$ (on the oxide or at the triple points)

4) The electrochemical catalytic activity of the electrode for the O$_2$ reaction

5) The electrochemical catalytic activity of the electrode for the NO$_x$ reaction

The complex nature of sensor response makes it difficult and time consuming to evaluate materials carefully and the majority of papers in the field have resorted to mass screening methods of different materials. It is believed that if each parameter is carefully evaluated, then a model for each electrode system could be obtained. We have evaluated
one electrode system using two oxide materials and have developed a model, which can be used as a starting point for a better understanding of future electrode studies and systems for electrochemical sensors.
<table>
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<td>LaMnO₃</td>
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<td>CO/HC sensing at 400°C</td>
<td>1997</td>
<td>[10]</td>
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<tr>
<td>LaCoO₃</td>
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<tr>
<td>La₆CuO₄</td>
<td>NOₓ reduction in electrochemical pumping design NOₓ sensor at</td>
<td>Tried various oxides some selective for NO or O₂ reduction.</td>
<td>1997</td>
<td>[45]</td>
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<tr>
<td>La₆NiO₃</td>
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<tr>
<td>La₆FeO₃</td>
<td>200ppm NO/NO₂ sensor at 600°C</td>
<td>Pt/YSZ/Pt/oxide. Low signal for NOₓ.</td>
<td>1998</td>
<td>[7]</td>
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<td>La₆CrO₃</td>
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</table>

Table 4.1. Listing of various sensors from the literature that have tested lanthanum based perovskites as a sensing material.
Table 4.1 continued. Listing of various sensors from the literature that have tested lanthanum based perovskites as a sensing material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Uses</th>
<th>Sensor design/information</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>La0.6Sr0.4Co0.8Cu0.2O3-δ</td>
<td>O₂ pumping in NO₅ sensing</td>
<td>Pumping type sensor. LSCCO at 550°C</td>
<td>2001</td>
<td>[33]</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>NO₂ at 450°C</td>
<td>Pt/LaFeO₃/YSZ or Nasicon/Pt</td>
<td>2001</td>
<td>[51]</td>
</tr>
<tr>
<td>La₂Sr₂MnO₃</td>
<td>NO reduction in N₂ at 700°C</td>
<td></td>
<td>2002</td>
<td>[52]</td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>HC/CO</td>
<td>LMO sputtered Au/LMO/YSZ/Y₀.1₆Tb₀.₃₀Zr₀.₅₄O₂₋ₓ/Au</td>
<td>2002</td>
<td>[11]</td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>HC/CO at 600°C</td>
<td>LMO sputtered Pt/LMO/Ce₀.₈Gd₀.₂O₁.₉/Pt</td>
<td>2002</td>
<td>[53]</td>
</tr>
</tbody>
</table>

Table 4.2. Listing of various sensors from the literature that have tested Cr₂O₃ as a sensing material.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensor Design/comments</th>
<th>Temp (°C)</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO/NO₂</td>
<td>Au mesh/Cr₂O₃/Nasicon/Ptₐir Best response to NO₅ out of single metal oxides screened</td>
<td>250</td>
<td>1995</td>
<td>[54]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt mesh/Cr₂O₃/YSZ/Ptₐir Gave response of -19mV to 500ppm NO and 18mV to 100ppm NO₂</td>
<td>500</td>
<td>1996</td>
<td>[55]</td>
</tr>
<tr>
<td>CO/H₂</td>
<td>In₂O₃ loaded with Cr₂O₃ on a resistive type sensor gave a poor response compared to other types of loaded oxides</td>
<td>300</td>
<td>1996</td>
<td>[56]</td>
</tr>
<tr>
<td>CO/H₂</td>
<td>Pt mesh/Cr₂O₃/YSZ/Ptₐir No response to 200ppm CO and H₂</td>
<td>600</td>
<td>1996</td>
<td>[57, 58]</td>
</tr>
<tr>
<td>CO/H₂</td>
<td>Pt wire/Cr₂O₃/YSZ/Ptₐir No response to 200ppm CO and H₂</td>
<td>600</td>
<td>1998</td>
<td>[59]</td>
</tr>
<tr>
<td>CH₄/C₃H₆</td>
<td>Pt wire/Cr₂O₃/YSZ/Ptₐir For 100ppm of the gases the sensor gave a very low response.</td>
<td>600</td>
<td>2000</td>
<td>[60]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Pt wire/Cr₂O₃/YSZ/Ptₐir Very low response to 200ppm NO or NO₂</td>
<td>600</td>
<td>2000</td>
<td>[61]</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Tested Cr₂O₃ or SnO₂+Cr₂O₃ on varistor type gas sensor</td>
<td>200-600°C</td>
<td>2001</td>
<td>[62]</td>
</tr>
</tbody>
</table>
Figure 4.1. A. Sensor#4.1 schematic having Pt, LSCFO, Cr$_2$O$_3$ sensing electrodes labeled E1, E2, and E3, respectively. In sensor#4.1 the Cr$_2$O$_3$ is placed on top of a Pt paste electrode. B. Schematic of sensors#4.2-4.4 having LSCFO and Cr$_2$O$_3$ sensing electrodes labeled E1, E2, respectively. In sensors#4.2-4.4 the oxides were placed directly onto the YSZ without a Pt paste underneath.

Figure 4.2. Optical images of a typical sensor of the design in Figure 4.1. The left image shows Cr$_2$O$_3$ and Pt electrodes on YSZ. Both Cr$_2$O$_3$ and Pt pastes were pasted on top of Pt lead wires, which are visible in the image. The left photo shows a LSCFO (black) and Cr$_2$O$_3$ (green) electrode. Again the Pt lead wires are visible. The color difference in the Cr$_2$O$_3$ electrode resulted from the lighting and the layer in the left image is thicker.
Figure 4.3: Plot of the sensor#4.1 signal at 500°C to 200-800ppm NO or NO₂ in 21% O₂ for the electrode couples E1/Pt_ref, E3/Pt_ref and E1/E3.
Figure 4.4. Sensitivity plots of the various electrode combination of the "blank" sensor#4.1 at 500°C for NO$_x$ (A) and CO (B) in 21% O$_2$. The lines connecting the points are simply for the eye to follow.
Figure 4.5. Sensitivity plot of sensor#4.1 at 500°C in 21% O₂ to compare E3 before and after the Cr₂O₃ was added.
Figure 4.6. Comparison of electrode response of sensor#4.1 to NO₃ and CO at 500°C. E1 = Pt, E2 = LSCFO and E3 = Cr₂O₃ on Pt.
Figure 4.7. Transient response to compare the response times from the data in Figures 4.6 of the Pt paste (E1), LSCFO (E2), and Cr$_2$O$_3$ (E3) electrodes to NO, NO$_2$, and CO at 500°C in 21% O$_2$. 

200
Figure 4.8. Comparison of LSCFO (top) and Cr$_2$O$_3$ (bottom) electrode signal responses to 200-800 ppm NO and NO$_2$ in 21% O$_2$ from the first day of testing and the third day.
Figure 4.9. Change in response at 500°C from the baseline to 600 ppm NO or NO₂ in 3% O₂ for the LSCFO and Cr₂O₃ electrodes on sensors#4.2-#4.4. Sensor#4.1 response in 21% O₂ is shown for comparison.

**Electrochemical Reactions at TPBs**

- **Chemical reactions on bulk electrode**
  
  \[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

- **Adsorption/Desorption**
  
  \[ \text{NO}_x(\text{g}) \rightarrow \text{NO}_x(\text{ad}) \]
  
  \[ \text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{ad}) \]

- **Electrochemical Reactions at TPBs**
  
  \[ \text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-} \]
  
  \[ 2\text{NO} + 2\text{O}^{2-} \rightarrow 2\text{NO}_2 + 4\text{e}^- \]

Figure 4.10. Diagram of three reaction zones on a sensor electrode.
Figure 4.11. EDX spectrum of a carbon coated sample of LSCFO.

Figure 4.12. XRD pattern of fresh LSCFO used for sensor electrodes. Inset is XRD of rhombohedral La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$ for comparison [71].
Figure 4.13. EDX spectrum of carbon coated Cr$_2$O$_3$.

Figure 4.14. Secondary electron SEM image of fresh LSCFO at 22953x magnification.
Figure 4.15. Secondary electron SEM images of fresh LSCFO at different magnifications.
Figure 4.16. Secondary electron SEM images of heat treated LSCFO + terpineol on the YSZ sensor. Top image: a thin region of the LSCFO electrode where the YSZ is visible. Middle and bottom images: selected electrode regions showing agglomerated LSCFO after the heat treatment.
Figure 4.17. SEM images of fresh Cr$_2$O$_3$ powder showing distinct particles.
Figure 4.18. SEM images of porous agglomerated region of fresh $\text{Cr}_2\text{O}_3$ powder.
Figure 4.19. SEM images of different regions of heated Cr$_2$O$_3$ + terpineol on YSZ.
Figure 4.20. NO\textsubscript{2} conversion in 3\% O\textsubscript{2} as a function of temperature for 5 mg Cr\textsubscript{2}O\textsubscript{3} and LSCFO at a flow rate of 200 cm\textsuperscript{3}/min. The points are connected for the eye to follow.

Figure 4.21. NO conversion in 3\% O\textsubscript{2} as a function of temperature for 5 mg Cr\textsubscript{2}O\textsubscript{3} and LSCFO at a flow rate of 200 cm\textsuperscript{3}/min. The points are connected for the eye to follow.
Table 4.3. Percent conversion of 600 ppm NO or NO₂ in 3% O₂ at 200 cm³/min for Cr₂O₃ and LSCFO versus weight of material. Total surface area also given for reference. The calculated conversion under these conditions for NO is 13.7% and for NO₂ is 86.3%.

<table>
<thead>
<tr>
<th>Weight (mg)</th>
<th>%NO conversion (Cr₂O₃)</th>
<th>%NO₂ conversion (Cr₂O₃)</th>
<th>Total surface area (Cr₂O₃)</th>
<th>%NO conversion (LSCFO)</th>
<th>%NO₂ conversion (LSCFO)</th>
<th>Total surface area (LSCFO)</th>
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<tbody>
<tr>
<td>5</td>
<td>10.2</td>
<td>76.3</td>
<td>0.108 m²</td>
<td>9.2</td>
<td>30</td>
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<td>9.5</td>
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<td>83.8</td>
<td>2.16</td>
<td>13.3</td>
<td>86</td>
<td>0.42</td>
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Figure 4.22. Schematic of the adsorption and desorption experiment with an empty reactor and with an adsorbing electrode material.
Figure 4.23. NO adsorption and desorption transients of Cr$_2$O$_3$ and LSCFO compared with the empty reactor.

Figure 4.24. A. "Zoom in" of adsorption curve region from Figure 4.23. B. "Zoom in" of desorption curve region from Figure 4.23.
Figure 4.25. Comparison of NO\textsubscript{x} and NO PSA transients from 600ppm NO over LSCFO at 500°C.

Figure 4.26. 600ppm NO\textsubscript{2} over 100mg of Cr\textsubscript{2}O\textsubscript{3} and LSCFO measured in NO\textsubscript{x} mode. A. Adsorption curve region for NO\textsubscript{2}  B. Desorption curve region for NO\textsubscript{2}.
Figure 4.27. Comparison of NO\textsubscript{x} and NO PSA transients from 600ppm NO\textsubscript{2} over LSCFO at 500°C.

Figure 4.28. Response of sensor#4.1 to varying O\textsubscript{2} levels at 500°C for the LSCFO and Cr\textsubscript{2}O\textsubscript{3} electrodes.
Figure 4.29. Transients for changing O\textsubscript{2} levels from 3-21\% O\textsubscript{2} at varying temperatures on sensor\#4.4
Figure 4.30. Polarization curves of the symmetrical Cr$_2$O$_3$ and LSCFO cells in air at 600°C (bottom) and 700°C (top).
Figure 4.31. Polarization curves of the electrode couples on sensor#4.4 for Cr$_2$O$_3$ and LSCFO verses the Pt reference in air at 500°C.

Figure 4.32. Polarization curves of the electrode couples on sensor#4.4 for Cr$_2$O$_3$ and LSCFO verses the Pt reference in air at 600°C.
Figure 4.33. Polarization curves of the electrode couples on sensor#4.4 for Cr$_2$O$_3$ and LSCFO verses the Pt reference in air at 700°C.

Figure 4.34. Polarization curves of the electrode couples on sensor#4.4 for Cr$_2$O$_3$ verses LSCFO (planar configuration) in air at 500°C, 600°C, and 700°C.
Figure 4.35. Impedance spectra for the LSCFO and Cr$_2$O$_3$ electrodes verses the Pt reference electrode at 500°C in air represented as Nyquist plots with a 10mV AC signal varied from $10^6$ Hz to 0.1 Hz. Bottom graph is enlargement at higher frequencies.
Figure 4.36. Impedance spectra for the LSCFO and Cr$_2$O$_3$ electrodes versus the Pt reference electrode at 500°C in air represented as Nyquist plots with a 10mV AC signal varied from $10^6$ Hz to 0.1 Hz. Bottom graph is enlargement at higher frequencies.
Figure 4.37. Impedance spectra for the LSCFO and Cr$_2$O$_3$ electrodes verses the Pt reference electrode at 500°C in air represented as Nyquist plots with a 10mV AC signal varied from $10^6$ Hz to 0.1 Hz. Bottom graph is enlargement at higher frequencies.
Table 4.3. Comparison of the total resistance at 0.1 Hz for the two electrode couples at various temperature. Data from Figures 4.35-4.37.

<table>
<thead>
<tr>
<th>Couple</th>
<th>500°C</th>
<th>600°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pt}_{\text{ref}}/\text{Cr}_2\text{O}_3$</td>
<td>255,000 Ω</td>
<td>96,911 Ω</td>
<td>30,366 Ω</td>
</tr>
<tr>
<td>$\text{Pt}_{\text{ref}}/\text{LSCFO}$</td>
<td>23,784 Ω</td>
<td>3318 Ω</td>
<td>753 Ω</td>
</tr>
</tbody>
</table>

Figure 4.38. Impedance spectra for LSCFO verses $\text{Cr}_2\text{O}_3$ from 500-700°C in air represented as Nyquist plots with a 10 mV AC signal varied from $10^6$ Hz to 0.1 Hz.
Figure 4.39. Model polarization curves depicting the mixed potential reactions on Pt_{ref}/LSCFO and Pt_{ref}/Cr₂O₃ for NO/3%O₂ at 500°C.
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