

Correlation of sensing behavior of mixed potential sensors with chemical and electrochemical properties of electrodes

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Abstract

The mixed potential response for NO and NO₂ from two different oxide electrodes on yttria-stabilized zirconia (YSZ) was examined at 500 °C. The two electrodes were La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ (LSFCO) and Cr₂O₃. Sensors made with LSFCO electrodes had consistently lower sensitivity towards NO_x as compared to those with Cr₂O₃ and the focus of this paper is to understand the fundamental reasons for the differences in electrode sensitivity. Catalytic activity of the electrodes towards equilibration of NO/NO₂ and electrical properties of the electrodes for O₂/O²⁻ chemistry were examined. Based on these studies, it is being concluded that the larger signals for NO_x on sensors with Cr₂O₃ electrodes arise primarily due to the poorer oxygen electroreduction ability of Cr₂O₃ as compared to LSFCO.

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1. Introduction

NO and NO₂ gases have a deleterious impact on the environment as well as human and animal health [1]. Most industrialized nations have imposed regulations for NO_x emissions. The two sources that have received the most attention are vehicles and coal-fired boilers. Considerable effort is being made towards the development of effective high temperature solid-state NO_x sensors for monitoring processes involved in NO_x abatement technologies [2]. Limitations of current solid-state NO_x sensors are in selectivity and sensitivity at high temperatures. Designs that can detect NO or NO₂ exclusively and sensor systems that can detect total NO_x (NO + NO₂) are few [3–5]. Mixed potential type sensors are commonly examined for gas sensing and form the subject of this paper. The mixed potential developed is a function of various electrode parameters including morphology, adsorption, catalytic and electrocatalytic properties. To get a measurable potential difference between two electrodes,

there must be asymmetry between them. The asymmetry can exist when the two electrodes are exposed to different environments either by physical separation in the case of a fixed air reference or when both are exposed to the same gas, but one electrode is covered with a catalytic filter [6,7]. In addition, if the two electrodes have dissimilar electrode parameters, they will have different “reactivity” towards the sensing gas, thus generating a potential difference.

Various electrode materials have been utilized in the literature, with the earliest example being Pt [7]. Metal-oxide electrodes that are either electronic conducting, mixed conducting, or in the form of ceramic/metal composites (cermet electrodes) are also being studied, especially in fuel cell research [8]. In the case of metal oxides, studies typically screen numerous materials and report their sensing performance [9–14]. Some electrode materials give a large signal for the gas of interest and others give relatively weak signals. There is limited understanding of why different electrode materials have different mixed potential signals. Given the fact that there are few commercial high temperature NO_x sensors, better electrode screening and characterization is necessary.

In this paper, the focus is to understand the mixed potential response to NO and NO₂ for two metal oxide electrodes. In a previous paper, we reported that sensors

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with Cr_2O_3 gave a large response at 500 °C to NO_x gas [3], and have continued its study here. Cr_2O_3 has also been utilized previously as an electrode or sensing material for gas sensors [9–13,15,16]. The second electrode examined is a perovskite type oxide, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSFCO). Lanthanum oxide perovskites have been touted as replacements for catalysts in three-way catalytic converters since the 1970s [17]. They have been used as electrodes on yttria-stabilized zirconia (YSZ) or doped CeO_2 electrolytes for electrochemical NO_x reduction [18], and as fuel cell electrodes for oxygen reduction or hydrocarbon activation [8,19]. Lanthanum oxide perovskites have also been used as sensing electrodes for NO_x , CO and hydrocarbons [20–30]. In the present study, we have found a significant difference in the signal between the Cr_2O_3 and LSFCO electrodes for NO and NO_2 sensing and based on catalytic and electrical studies have developed a model to explain electrode behavior.

2. Experimental

2.1. Sensor design and preparation

Cr_2O_3 powder (99% metals basis) was obtained from Alfa Aesar. The certificate of analysis listed the major impurities to be Fe (0.10%), Ca (0.05%), and Si (.03%). The LSFCO powder was obtained from Superconductive Components with a stoichiometry of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$, which was verified by ICP optical emission spectroscopy. In addition, no significant impurities were observed using ICP and powder diffraction. Both oxide powders were used as received.

Sensor fabrication was done as described earlier [3]. The sensor body was a single bore, single closed-end YSZ tube (Vesuvius McDanel, 10.5 mol% YSZ). A Pt paste (Engelhard) reference electrode was utilized on the inside of the closed-end of the tube. The LSFCO or Cr_2O_3 electrode powders were mixed with terpineol to make a 50:50 wt.% paste and painted on top of a Pt wire wrapped around the outside of the YSZ tube and heated to 750 °C with a 6 °C/min heating and cooling rate. The sensor design and an optical image of the oxide electrodes are shown in Fig. 1.

2.2. Surface area measurements

Single point surface area measurements of the LSFCO and Cr_2O_3 powders were done on a Micromeritics Pulse Chemisorb 2700 instrument. Desorption values were used throughout for more accurate readings. Three readings were taken for each sample and averaged. For verification of instrument performance, an alumina standard with a specific surface area of 10 m^2/g was periodically tested.

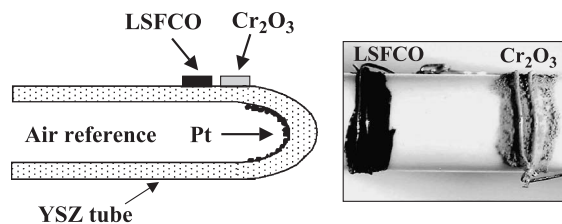


Fig. 1. (Left) Schematic of YSZ sensor with LSFCO and Cr_2O_3 sensing electrodes and Pt reference electrode. (Right) Optical picture of typical LSFCO and Cr_2O_3 electrodes on YSZ with underlying Pt lead wires visible.

2.3. NO_x catalytic activity measurements

Heterogeneous catalysis measurements for NO_x conversion over the powders were done as described earlier [3] using a heated fixed bed quartz reactor and a NO_x chemiluminescence analyzer. A typical weight of electrode material on sensors was 2–3 mg on average as determined by scraping off and weighing with an analytical balance. However, we used 5 mg of powder in the catalytic activity measurements to ensure enough material was present for sufficient reaction and due to size constraints of the quartz tube.

2.4. SEM, XRD, and ICP 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. X-ray powder diffraction was also done at CEOF using a Scintag XDS 2000 instrument. ICP analysis of the powders was done at the Microscopic and Chemical Analysis Research Center (MARC) at The Ohio State University using a Perkin Elmer Optima DV300 instrument.

2.5. Electrical measurements

Sensor tests were done using the set-up described earlier [3,6]. The sensor was placed in a quartz tube that was connected to mass flowmeters and heated to temperatures of 500–700 °C in a tube furnace with a 100 cm^3/min flow rate. The sensor lead wires were connected to an HP multimeter and the signal versus time was measured with a computer.

Current–voltage polarization plots were obtained using a Gamry Instruments potentiostat with software control in Tafel mode with a 1 mV/s scan rate from ± 250 mV relative to the open circuit voltage and a 2-s sample period for all tests. The tests were done in 21% O_2/N_2 at 500 °C. A three-electrode measurement was made between the working electrode (Cr_2O_3 or LSFCO) and two Pt electrodes. The Pt electrodes were a reference (Pt#1) along with a counter electrode (Pt#2) painted on the outside of the tube next to the oxide electrodes. All electrodes were exposed to 21% O_2/N_2 .

3. Results

3.1. Electrode morphology

Fresh LSFCE powder out of the bottle had a particle size between 100 and 200 nm as determined by SEM (Fig. 2) and a surface area of 4.2 m²/g. If a density of 6.50 g/cm³ is assumed for LSFCE, similar to other perovskites of this composition [31], then the calculated specific surface areas for 100 nm and 200 nm diameter spheres are 9.7 and 4.6 m²/g, respectively. Heat-treating the LSFCE powder on an YSZ substrate at 750 °C for 2 h resulted in formation of aggregates greater than 1 μm, as shown in Fig. 2.

Fresh Cr₂O₃ powder did not have a uniform size distribution. Small particles of <200 nm, as well as larger structures were observed, as shown in Fig. 3. The surface area of the fresh powder was 45.9 m²/g. Upon heating the powder at 750 °C for 2 h, the particle size distribution became more uniform with a reduced surface area of 21.5 m²/g. Cr₂O₃ has a density of 5.22 g/cm³ and the calculated surface areas for 100 nm and 200 nm diameter spheres are 11.5 and 5.75 m²/g, respectively, which suggests that some mesoporosity may still be present in the Cr₂O₃ heated sample. Heat-treating the Cr₂O₃ powder on an YSZ substrate at 750 °C for 2 h (Fig. 3) had similar results as heating the powder. These studies suggest that the Cr₂O₃ electrode has a higher surface area than the LSFCE electrode.

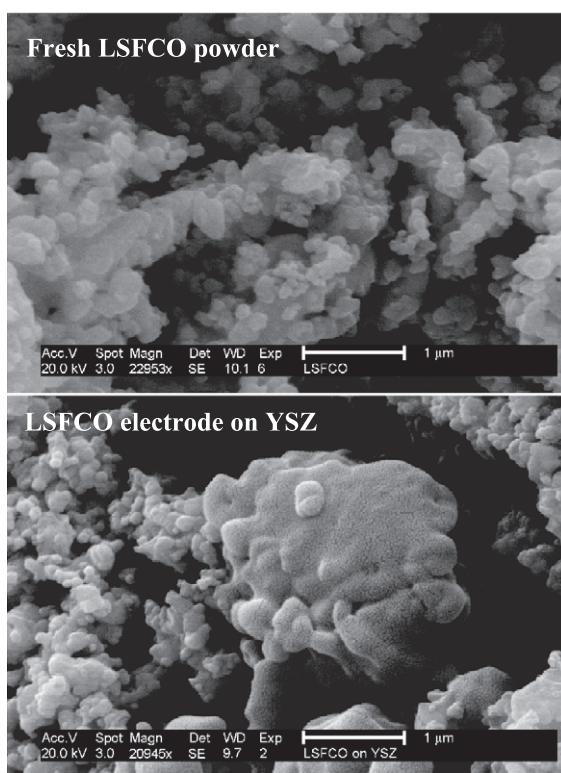


Fig. 2. SEM images of fresh LSFCE powder (top) and as an electrode on YSZ (bottom, after heat treatment).

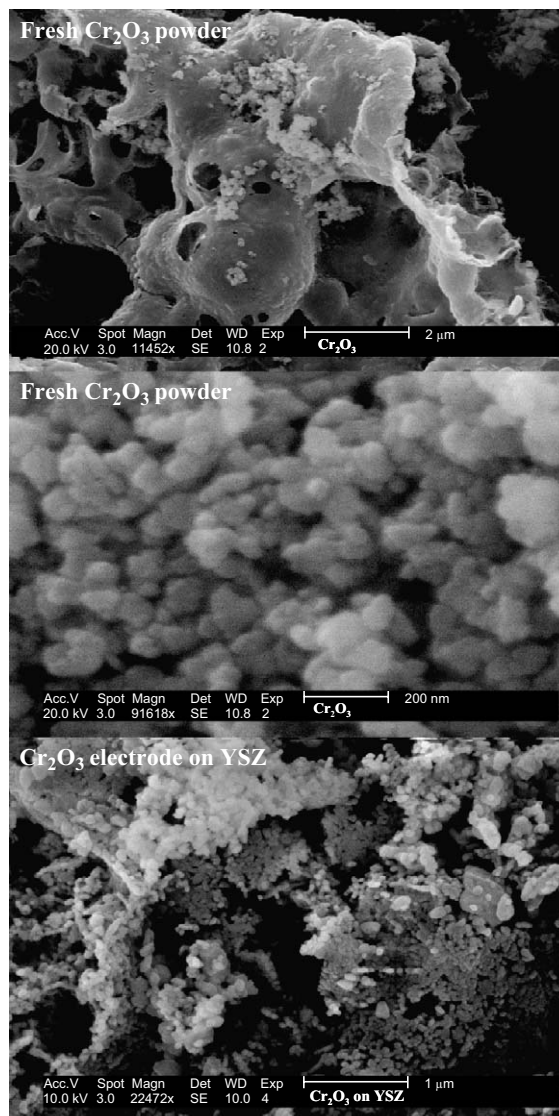


Fig. 3. SEM images of fresh Cr₂O₃ powder (top two pictures of different regions) and as an electrode on YSZ (bottom, after heat treatment).

There have been reports of lanthanum oxide perovskites reacting with YSZ to form non-conducting phases at temperatures above 1100 °C [32,33]. Mixtures of LSFCE and YSZ powders and Cr₂O₃ and YSZ powders (1:1 by weight) were heat-treated at 750 °C for 72 h in air. Using XRD analysis, no new phases were observed. Thus, no significant chemical reactivity between YSZ and the electrode material is expected to occur under the present sample preparation and sensing conditions.

3.2. NO_x equilibration chemistry on the Cr₂O₃ and LSFCE powders

The ability for LSFCE and Cr₂O₃ to equilibrate NO/NO₂/O₂ was investigated. The experiment was done with 600 ppm NO or 600 ppm NO₂ in 3%O₂ at temperatures between 200 and 700 °C and gas flow rates of 200 cm³/min.

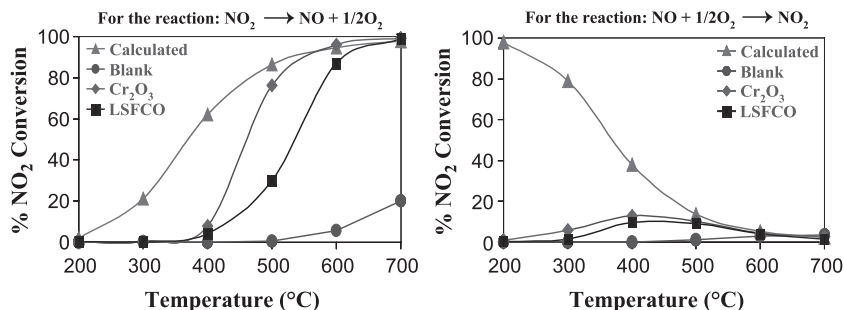


Fig. 4. Conversion of 600 ppm NO or NO₂ in 3%O₂ on the LSFCO and Cr₂O₃ powders over a range of temperatures.

Powders were added to the flow reactor and heated to 700 °C to simulate sensor preparation and then testing started at 200 °C (the Cr₂O₃ powder had a larger volume than the LSFCO for the same weight due to its lower density/higher surface area). Fig. 4 compares the NO_x conversion, 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 Cr₂O₃ showed a higher conversion for NO₂ than the LSFCO (76% to 30%) and comparable conversion for NO (10% to 9%). Both oxides brought the system close to equilibrium at temperatures exceeding 600 °C.

3.3. Electrical measurements

3.3.1. NO_x sensor response

The transient response at 500 °C for 200–800 ppm NO and NO₂ in 21%O₂ is shown in Fig. 5. The Cr₂O₃ electrode had a larger sensitivity than the LSFCO electrode for both NO and NO₂ but a slower recovery time (e.g. *t*₉₀ for 800 to 0 ppm for NO₂ for Cr₂O₃ and LSFCO were 74 and 8 min, respectively). Several sensors were fabricated and tested for reproducibility. Fig. 6 shows a histogram plot of three sensors for response to 600 ppm NO and NO₂ in 3%O₂. There was some variation in the absolute signal magnitude for NO or NO₂ of the different sensors (e.g. 22.5% relative standard deviation of the Cr₂O₃ electrode signals to 600 ppm NO₂), presumably due to the fabrication process.

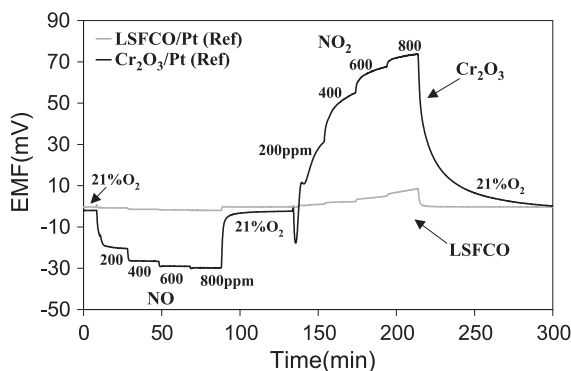


Fig. 5. Transient response for NO and NO₂ in 21%O₂ at 500 °C.

Nevertheless, the trend remained that at a given NO_x concentration, the sensors with Cr₂O₃ always had a higher signal than those with LSFCO. Also, the trend was maintained immaterial of the position of the oxide on the YSZ tube (Fig. 1), indicating that any modification of the gas concentration by reaction on one of the electrodes as it flowed past was minimal.

3.3.2. Sensor electrode response times to O₂ transients

The response of the oxide electrodes to O₂ concentrations changing from 21% to 5% at 500 °C was examined. The time traces are shown in Fig. 7. The response time of the sensor with Cr₂O₃ is slower than the LSFCO electrode. The *t*₉₀ response time for a step change from 21%O₂ to 15%O₂ for LSFCO was 1 min, whereas the signal for Cr₂O₃ did not reach a stable value in the 16 min allotted for the 21% to 15% O₂ step (*t*₉₀ response time was 9.5 min). Moreover, in 21%O₂, the LSFCO had a baseline of 0.06 mV and the Cr₂O₃ baseline was −5.07 mV suggesting a slower equilibrium for the electrochemical O₂ reaction, O₂ + 4e[−] → O^{2−} on Cr₂O₃ [28,34]. The *t*₉₀ recovery time from 5%O₂ to 21%O₂ for LSFCO was 40 s, and for Cr₂O₃ 6.4 min. The slope of the LSFCO electrode was Nernstian at 16.85 mV/decade (calculated value 16.65 mV/decade) while the slope of the Cr₂O₃ response was 15.44 mV/decade. Upon heating to 700 °C, both electrodes produced the same response. This data was consistent amongst all sensors tested.

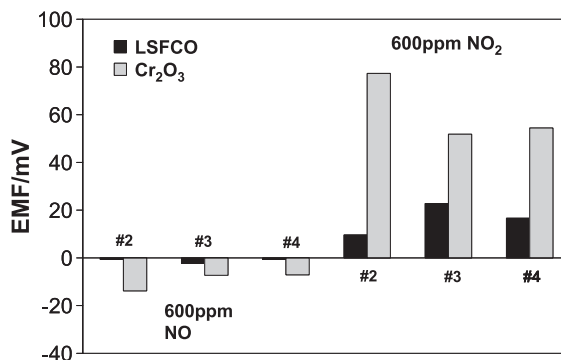


Fig. 6. Comparison of three different sensor responses at 500 °C for 600 ppm NO and NO₂ in 3%O₂.

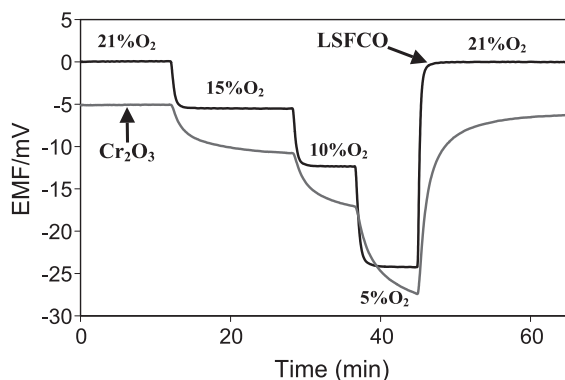


Fig. 7. O_2 transient responses of sensor using Cr_2O_3 and LSFCO electrodes at $500\text{ }^\circ\text{C}$.

3.3.3. Current–voltage polarization curves

Current–voltage polarization curves were done in an attempt to determine if there was a significant difference in the O_2 reduction ability between the two oxide electrodes. Fig. 8 shows the polarization curves from -250 to 250 mV in air for Cr_2O_3 and LSFCO electrodes at $500\text{ }^\circ\text{C}$. The most noticeable result is that the total current for the LSFCO electrode is far greater than that with Cr_2O_3 . For example, at 15 mV the sample with the LSFCO electrode had a current of $0.97\text{ }\mu\text{A}$ compared to 5.1 nA for Cr_2O_3 .

4. Discussion

As shown in Fig. 5, there was significant variation in sensor response to NO or NO_2 , with the Cr_2O_3 electrode giving a larger signal over the LSFCO electrode. The microstructure, interface formation, and thickness of the electrodes can influence the triple point boundary (TPB) interface, catalytic/electrocatalytic activity and adsorption properties, thereby affecting the observed sensor signal. It has been suggested that the difference in chemical and electrochemical properties of electrode materials will result in different gas sensor signals [9,14,25–27]. On the bulk electrode material the following reaction can occur:



Whereas at the interface, the following electrochemical reactions can take place:



The next sections examine possible reasons for the different NO_x signals of the Cr_2O_3 and LSFCO.

4.1. Chemical reactivity

At the sensing temperature of $500\text{ }^\circ\text{C}$, a higher conversion of NO_2 was observed over Cr_2O_3 as compared to LSFCO (76% to 30%) and both oxides showed similar conversion of NO (10% to 9%). The Cr_2O_3 powder has a higher surface area than the LSFCO powder. Since the chemical conversion on the Cr_2O_3 is more pronounced than LSFCO, less unequilibrated gas would reach the electrode–electrolyte interface and a weaker sensor signal is expected. This is not the case. 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 [28,30,35,36].

Recently, Miura et al. [35] have screened four oxide materials, $ZnFe_2O_4$, $NiCr_2O_4$, $ZnCr_2O_4$, and $CrMn_2O_4$ for their sensitivity to NO or NO_2 at $700\text{ }^\circ\text{C}$. They found the order of sensitivity to 200 ppm NO or NO_2 in 21% O_2 to be $ZnFe_2O_4 > NiCr_2O_4 > ZnCr_2O_4 > CrMn_2O_4$. They did catalytic conversion measurements of NO_2 to NO over a range of temperatures ($200\text{--}700\text{ }^\circ\text{C}$). At $700\text{ }^\circ\text{C}$ all the oxides fully equilibrated the NO_2 but at lower temperatures (below $550\text{ }^\circ\text{C}$) the catalytic activity was reduced in the order $ZnCr_2O_4 > NiCr_2O_4 = CrMn_2O_4 > ZnFe_2O_4$. The conclusion was that since the $ZnFe_2O_4$ had the lowest activity at $550\text{ }^\circ\text{C}$ this was the reason for the higher signal at $700\text{ }^\circ\text{C}$. Interestingly, the $ZnCr_2O_4$ had the highest NO_2 conversion but still gave a larger signal than the $CrMn_2O_4$ electrode and the catalytic activity of $NiCr_2O_4$ and $CrMn_2O_4$ were the same but the $NiCr_2O_4$ gave a larger signal. Thus, features other than chemical reactivity must play a role in determining sensitivity.

4.2. Electrical behavior

The polarization curves in general exhibit two regions. At low applied potential, there is a linear region that has ohmic behavior and at higher overpotentials an exponential characteristic is exhibited, which is indicative of Tafel

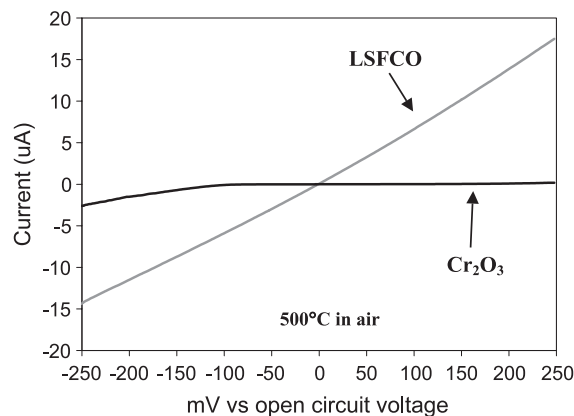


Fig. 8. Polarization curves of the electrode couples for Cr_2O_3 and LSFCO using a three-electrode set-up in air at $500\text{ }^\circ\text{C}$.

behavior. In the range of our sensor voltage (± 50 mV) we observed a linear characteristic for both oxide electrodes. We additionally tested the Cr_2O_3 and LSFÇO electrodes up to potentials of ± 1 V (not shown). We found a limiting current behavior on the Pt/ Cr_2O_3 while the Pt/LSFÇO exhibited Tafel behavior. Tsiakaras et al. [37] observed symmetric polarization curves for the cathodic and anodic reactions of O_2 reduction and O^{2-} anion oxidation of LSFÇO on YSZ at 800°C consistent with our results at lower temperatures.

These results suggest that the higher current observed in the polarization tests for LSFÇO is due to its good O_2 reduction ability [38]. 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 as well at the double phase boundary of the oxide/gas resulting in a high transport of O_2 species. On the contrary, the Cr_2O_3 can only catalyze the electroreduction of O_2 gas at the TPB, similar to that of other electronic conductors, and hence the lower rate of charge transfer than LSFÇO.

4.3. Development of a model

The discussion in Sections 4.1 and 4.2 show that the catalytic activity of Cr_2O_3 is high but the sensor signal is also high as compared to LSFÇO. For three sensors examined, the average response to 600 ppm NO in 3% O_2/N_2 was 10 mV for Cr_2O_3 and 1.5 mV for the LSFÇO electrode. A significant difference in O_2 reduction between the two electrodes was also observed, suggesting that electrochemical factors may play a larger role than chemical reactivity in determining the sensor signal.

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 [35,39–42]. Early models considered the sensing gas reaction to be more important (i.e. Eq. (3) or (4)) in determining the electrode potential. However, as has been recently pointed out, since O_2 is in excess in the sensing environment (1–10%) compared to the sensing gas concentration (100–1000 ppm), the reduction of O_2 (Eq. (2)) becomes important [35,39]. It is quite possible that a linear form of the Butler–Volmer equation can represent the O_2 reduction kinetics since we observed linear polarization curves in the range of our sensor voltage. The NO_x kinetics must then still follow Tafel type behavior to maintain a logarithmic voltage dependence on concentration. This is represented in Fig. 9 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. E_{O_2} is the reference potential, $E_{\text{O}_2}^{\text{rev}}$ is the reversible (or equilibrium) potential of the electrodes in the background gas, and E_{mix} is the electrode mixed potential in the presence of NO. The two electrodes have significantly different O_2 polarization curves (as seen in Fig. 8). According to Fig. 9, the mixed potential shift due to NO will be

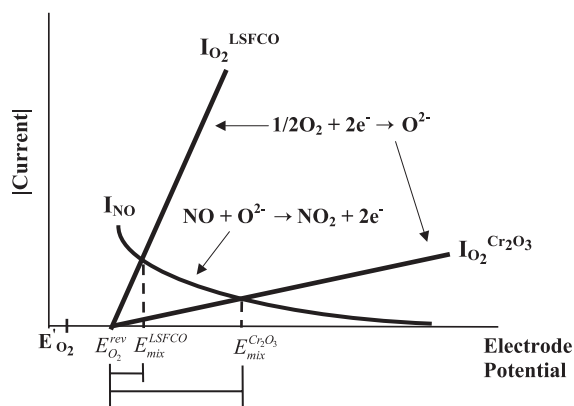


Fig. 9. Model polarization curves depicting the mixed potential reactions.

higher for Cr_2O_3 because of the higher O_2 overpotential (x -axis). The model presented in Fig. 9 is similar to that presented by the Los Alamos group for CO and hydrocarbon sensors using Pt and Au electrodes [39]. The absolute magnitude of the mixed potential signal is determined by the NO/NO_2 couple relative to the O_2/O^{2-} couple and is of the order of millivolts, which is considerably smaller than the mixed potential signals observed with CO, because of its much higher electrode potential as compared to the oxygen couple. We are making the assumption that the NO or NO_2 polarization curves for Cr_2O_3 and LSFÇO are similar and needs to be verified, especially given the fact that for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ electrodes, Reinhardt et al. [43] showed that the NO/NO_2 kinetics was much faster than the oxygen reduction.

In the model shown in Fig. 9, if heterogeneous chemistry was playing an important role, then the higher catalytic activity of Cr_2O_3 would cause the NO_x reversible potential to shift closer to the O_2 equilibrium potential [35] and result in a lower signal. Since this is not the case, the chemical reactivity of NO_x on the electrode is not the controlling feature for the signal. The larger signal for the sensor with the Cr_2O_3 electrode is due to poorer O_2 electroreduction as compared to LSFÇO.

5. Conclusions

The observed signal for an electrode is due to a complex set of parameters. Two electrode systems, lanthanum strontium iron cobalt oxide (LSFÇO), and Cr_2O_3 on YSZ were examined for NO_x sensing. Cr_2O_3 was found to have a higher surface area and chemical reactivity towards NO/NO_2 equilibration, and a higher sensor signal as compared to LSFÇO. Based on our evaluation of these two oxide materials, we conclude that electrochemical activity of the electrode for the O_2 reaction is the primary factor for determining the NO_x signal. The model can be used as a starting point for a better understanding of electrodes and systems for electrochemical sensors.

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