

ELECTRODE MATERIALS FOR MIXED-POTENTIAL NO_x SENSORS

D. L. West, F. C. Montgomery, and T. R. Armstrong
Oak Ridge National Laboratory
PO Box 2008, MS 6083
Oak Ridge, TN
37831-6083

ABSTRACT

The focus of this work is electrode materials for "mixed-potential" NO_x sensing elements operating at temperatures near 650 °C. Several different metal oxides, including Cr-containing spinels and La-containing perovskites, were evaluated as sensing electrode materials and La-containing perovskites were used as conducting materials in the place of Pt. Evaluations included sensing response as a function of temperature, the differing response to NO and NO₂, and the effect of varying O₂ concentration. Strong responses to NO₂ were observed in several instances, and the NO responses were typically weaker and opposite in sign.

INTRODUCTION

The main pollutants from the combustion of low-sulfur fuels are carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x, a mixture of NO and NO₂). Combustion exhausts from spark-ignited, fuel-injected engines are currently passed over a three-way catalyst (TWC) that greatly reduces the levels of all three pollutants. This TWC loses its effectiveness for NO_x removal at high O₂ concentrations,¹ so it cannot be employed for NO_x remediation of the relatively O₂-rich exhausts from diesel and lean-burn gasoline engines.

NO_x remediation of these exhausts may require techniques such as selective catalytic reduction (SCR) with reagent (HC and/or urea) injection. The amount of reagent injection during SCR is critical, as the reagents are themselves pollutants. Therefore it is essential to develop sensors that can rapidly and accurately assess the NO_x levels in these exhausts. A suitable sensor for reagent injection would be operative at T ~ 700 °C and able to measure NO_x concentrations in the range 100 ppm ≤ [NO_x] ≤ 1000 ppm.² At these temperatures the "NO_x" is predicted to be primarily nitrogen monoxide (NO), the dominant species above 500 °C.³

Two approaches to NO_x sensing at "high temperature" (T ~ 700 °C) have appeared in the literature: "Amperometric"^{4,5} and "mixed-potential"^{6,7} methods. Amperometric techniques rely on measuring the oxygen-ion current generated by the electrochemical decomposition of NO_x. In mixed potential sensing, cathodic (reduction) and anodic (oxidation) reactions involving NO_x and O₂ occur simultaneously on a sensing electrode, across which the *net* current (cathodic + anodic) is held at zero.^{8,9} Since each of the reactions (cathodic and anodic) occurring on the sensing electrode should have a single-valued I-V characteristic, a unique voltage should be developed for a given [NO_x] and [O₂].

In this work we are investigating materials for use in high-T, mixed-potential NO_x sensing elements. In particular, different transition metal oxides are investigated as sensing electrode materials and electronically conducting oxides are investigated as replacements for Pt.

EXPERIMENTAL METHODOLOGY

Figure 1a) shows the geometry of the sensing elements prepared for the present investigation.

The YSZ (8 mol% Y_2O_3 -substituted ZrO_2 , TZ-8Y, Tosoh, NJ) substrate was tape cast, laminated, and sintered at 1350 °C for 2 hr in air to produce disks about 16 mm in diameter and 1 mm in thickness. An electronically conducting layer, comprising the reference electrode (RE) and current collector (CC) was screen-printed onto one broad face of the YSZ disks, air-dried, and fired at 1100 °C for 0.3 hr in air. A second screen-printed layer, the sensing electrode (SE), was then patterned over a portion of the CC, air-dried, and fired at 1100 °C for 1 hr in air.

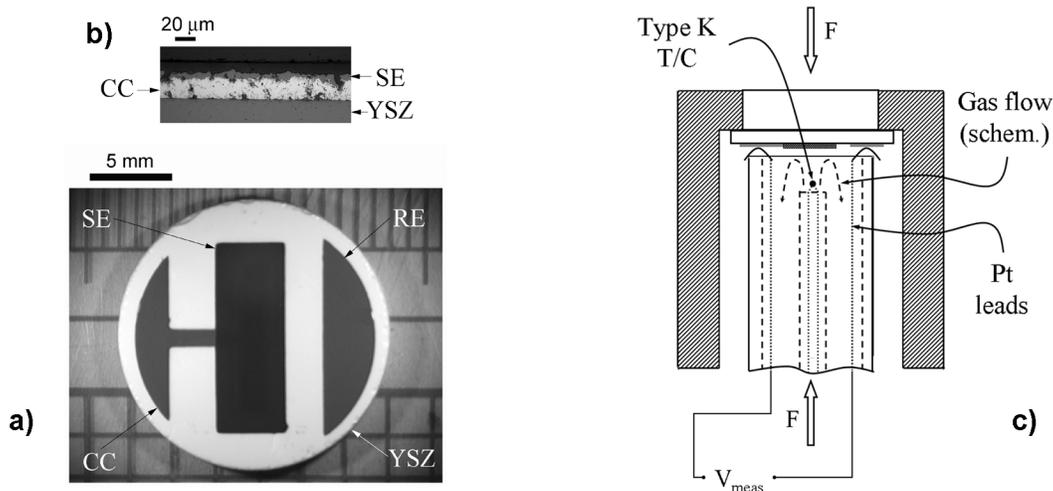


Figure 1: Specimen geometry and test fixture. a) shows the electroded surface of a prototype sensing element. The current collector (CC) extends underneath the sensing electrode (SE) as shown in b). A schematic of the fixture used for electrical connections and provision of the test atmosphere is shown in c).

The sensing elements were mounted in the fixture shown in Fig. 1c). A gas mixing unit (EnviroNics (Tolland, CT) 4000) was used to mix N_2 , O_2 , and NO_x (NO or NO_2 , 5000 ppm_v in N_2) at room temperature. Mixture compositions were in the range $7 \text{ vol } \% \leq [\text{O}_2] \leq 20 \text{ vol } \%$, $300 \text{ ppm}_v \leq [\text{NO}_x] \leq 1500 \text{ ppm}_v$, with the balance being N_2 . These gas mixtures were presented to the electroded side of the sensing elements as shown schematically in Fig. 1c), and the voltage developed between the SE/CC and RE (V_{meas} in Fig. 1c)) was measured with a Keithley (Cleveland, OH) 617 electrometer. To simulate elevated temperature service, the fixture shown in Fig 1c) was placed (centrally located) in a horizontal tube furnace.

The sensing performance of the elements was evaluated with two different techniques. Isothermal testing was conducted (at 600 and 700 °C) to characterize the sensing performance as a function of $[\text{NO}_x]$ (at fixed $[\text{O}_2]$) and $[\text{O}_2]$ (at fixed $[\text{NO}_x]$). For these isothermal measurements the “sensing response” (ΔV) was taken as the change in voltage with a given $[\text{NO}_x]$ and $[\text{O}_2]$ relative to that measured with 0 ppm_v input NO_x and 7 vol % O_2 . This “baseline” voltage was small, typically less than 2 mV in magnitude. To characterize the sensing performance as a function of T the sensing elements were subjected to 5 minute “pulses” of 450 ppm_v NO_x (in 7 vol % O_2 , balance N_2) while the temperature was ramped at 120 °C/hr.

Table I lists some representative compounds that have been investigated for use as sensing electrode materials. Inks for screen-printing were produced from the powders in Table I using proprietary methods and materials. All the materials in Table I were used as sensing electrodes with Pt (ElectroScience (King of Prussia, PA)) as the RE/CC (recall Fig. 1) material. Significantly more compounds than those listed in Table I have been investigated as SE materials, but

the observations presented here about the materials in Table I hold generally for most of the SE compounds (and mixtures) evaluated with the sensing element geometry shown in Fig. 1a).

Table I: Compounds investigated for use as sensing electrode materials

Material	Supplier
NiO	J. T. Baker (Philipsburg, NJ)
Cr ₂ O ₃	EM Science (Gibbstown, NJ)
NiCr ₂ O ₄ (NC2)	Cerac (Milwaukee, WI)
CoCr ₂ O ₄ (CC2)	“ “
La _{0.80} Ca _{0.21} Cr _{1.01} O ₃ (LCC)	Praxair (Woodinville, WA)
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃ (LSCF)	“ “

In addition to investigating materials for use as sensing electrodes, we have also explored the use of the electronically conducting oxides La_{0.85}Sr_{0.15}CrO₃ (LSC) and La_{0.80}Sr_{0.20}FeO₃ (LSF) as substitutes for Pt. The SE oxides chosen for this were LSCF and NC2. As was the case with the different SE materials, inks for screen printing the LSC and LSF were produced from commercially available (Praxair) powders. Table II lists the components of sensing elements that were fabricated to investigate the substitution of electronically conducting oxides for Pt.

Table II: Specimens prepared to investigate the substitution of oxides for Pt.

SE material	RE/CC material	Sample ID
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	Pt	LSCF/Pt
NiCr ₂ O ₄	Pt	NC2/Pt
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	La _{0.85} Sr _{0.15} CrO ₃	LSCF/LSC
NiCr ₂ O ₄	La _{0.85} Sr _{0.15} CrO ₃	NC2/LSC
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	La _{0.80} Sr _{0.20} FeO ₃	LSCF/LSF
NiCr ₂ O ₄	La _{0.80} Sr _{0.20} FeO ₃	NC2/LSF

RESULTS AND DISCUSSION

Evaluation of Sensing Electrode Materials

Figure 2a) shows NO₂ response traces (at 7 vol % O₂) for a sensing element constructed with LSCF as the SE material and Pt as the RE/CC material. A rapid and reproducible response to NO₂ at 600 and 700 °C was possible with the LSCF SE. Fig. 2b) shows that both LSCF and NC2 were capable of a strong response to NO₂ at 600 °C in 7 vol % O₂. The responses of these sensing elements to varying [NO₂] at fixed [O₂], as well as to varying [O₂] at fixed [NO₂], were well-described by logarithmic expressions:

$$\Delta V_{\text{fixed } [O_2]} = V^I + m_1 \log[NO_2], \quad \Delta V_{\text{fixed } [NO_2]} = V^{II} + m_2 \log[O_2], \quad (1)$$

where V^I , V^{II} , m_1 , and m_2 are constants. m_1 and m_2 are taken here to define the *sensitivity* of the sensing element to [NO₂] (at fixed [O₂]) or [O₂] (at fixed [NO₂]), respectively. Smaller absolute value(s) of m_1 and m_2 correspond to smaller changes in ΔV with gas composition over the concentration ranges investigated.

The NO sensing performance for LSCF and NC2 (and the other materials listed in Table I) was poor, with input NO producing only a small (in comparison to NO₂) signal that was opposite in sign to that produced by NO₂. This asymmetry in sensing response held over a wide tem-

perature range for all the materials in Table I. Representative data are shown in Fig. 3, which shows the response of the sensing elements with Cr_2O_3 and NiCr_2O_4 SE's to 450 ppm_v NO_x (in 7 vol % O_2) over the temperature range $450^\circ\text{C} \leq T \leq 700^\circ\text{C}$. Always, the NO_2 response is larger in magnitude and opposite in sign than that for NO . These observations are not unique, and have been reported by other investigators for “mixed-potential” NO_x sensing elements of various geometries.¹⁰

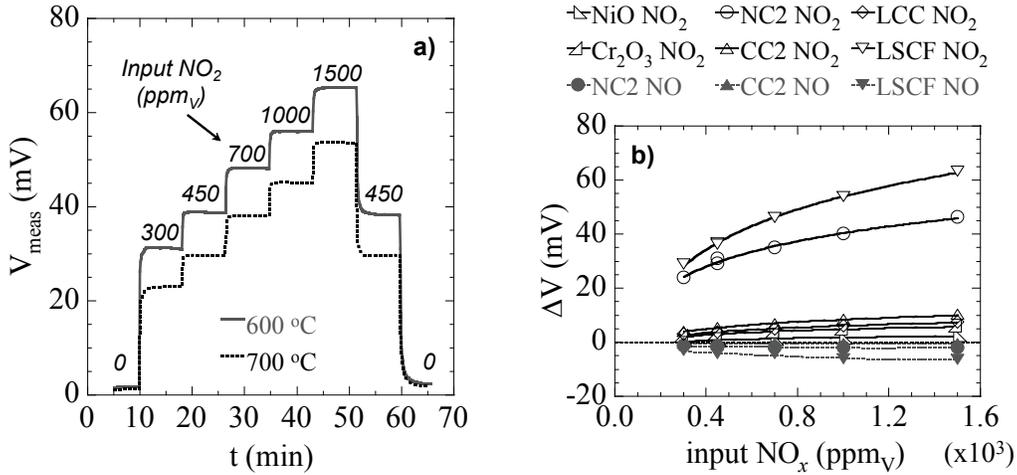


Figure 2: NO_2 response of a sensing element with a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) SE and Pt RE/CC in 7 vol % O_2 (a). b) shows the NO_2 response (at 600°C and 7 vol % O_2) for the samples in Table I. The NO responses for selected materials in Table I are also shown. Lines drawn in b) are logarithmic fits for NO_2 and polynomial fits (2^{nd} order) for NO .

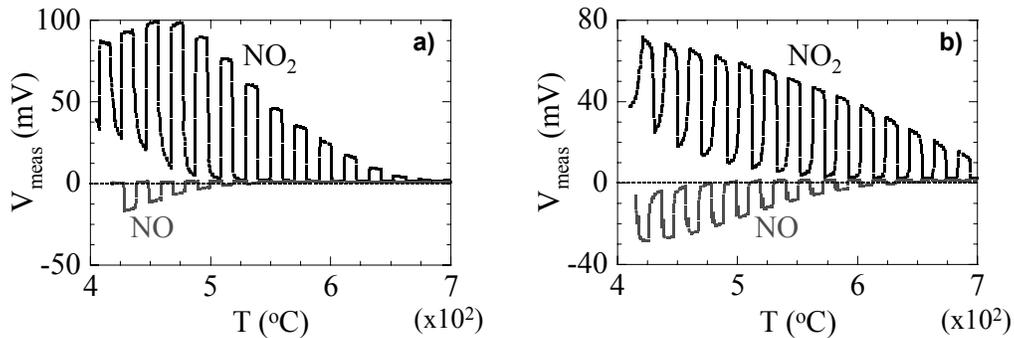


Figure 3: NO_x response of sensing elements with Cr_2O_3 (a) and NiCr_2O_4 (b) sensing electrodes as a function of T . Data collected by pulsing NO_x (5 min. 450 ppm_v NO_x , 5 min. 0 ppm_v NO_x , both in 7 vol % O_2) while ramping T at 120°C/hr .

It is believed that the reduction of NO_2 to NO is responsible for the NO_2 sensing response, while the response to NO involves the oxidation of this species up to NO_2 .⁸ Given that NO is the dominant NO_x species above 500°C , it is not surprising that the response to NO is poor at higher temperatures if the sensing mechanism involves the oxidation of NO to NO_2 . However, the weak NO response even at lower temperatures ($\sim 450^\circ\text{C}$, Fig. 3) suggests that the oxidation of NO up to NO_2 is more difficult than the reduction of NO_2 to NO on these sensing electrode materials.

Substitution of Conducting Oxides for Pt

Figures 4a) and b) show the response (at 600 °C and 7 vol % O₂) of the sensing elements in Table II to input NO₂ and NO, respectively. The substitution of either LSC or LSF for Pt consistently resulted in a decreased sensitivity to NO₂ (i.e., $|m_1|$ in Eqn. (1) decreased), and an enhanced response to NO. Further, substituting LSC or LSF for Pt changed the algebraic sign of the NO_x responses for the sensing elements that had LSCF sensing electrodes.

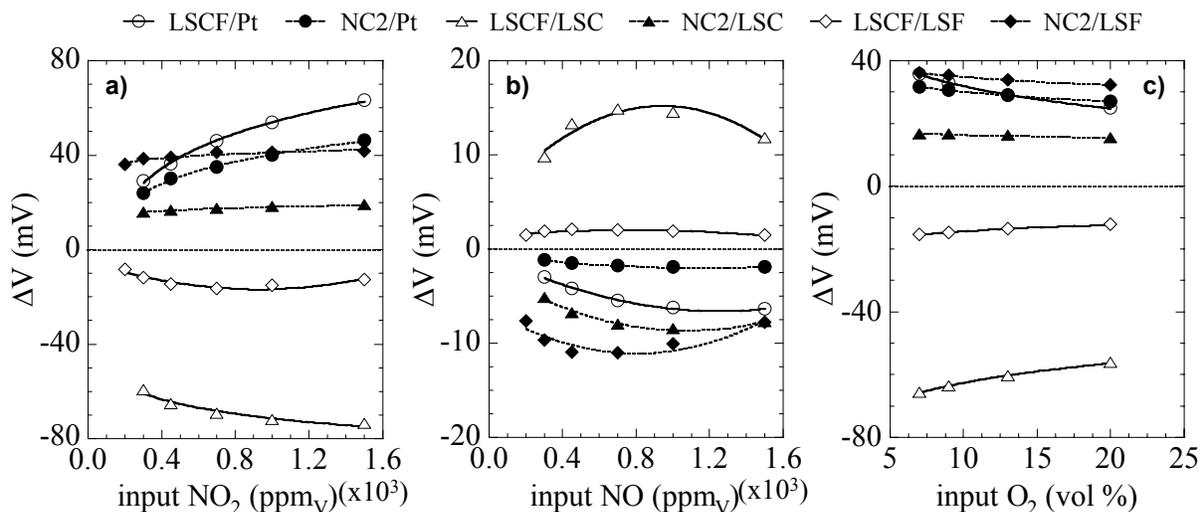


Figure 4: NO_x sensing performance (at 600 °C) of the sensing elements in Table II. The NO_x responses (7 vol % O₂) are shown in a) and b) while c) shows the [O₂] dependence of the response to 450 ppm_v NO₂. The lines drawn in a) (except for LSCF/LSF and NC2/LSF) and c) correspond to logarithmic fits, all other lines drawn are 2nd order polynomial fits.

Although use of LSC and LSF has enhanced the NO response at fixed [O₂], Fig. 4b) indicates that the response is no longer a single valued function of [NO]. For example, for the LSCF/LSC sensing element, $(\partial V_{\text{meas}}/\partial[\text{NO}])$ is >0 for [NO] < 700 ppm_v but <0 for [NO] > 1000 ppm_v. Presently we believe that this reflects the sensing element responding to NO₂, as the two species can inter-convert *via* (where p stands for partial pressure)



The equilibrium (2) favors NO₂ at room temperature, and shifts to the left with increasing T .³ It is difficult to state the exact position of the equilibrium (2) at the sensor surface, but formation of some NO₂ is predicted irrespective of the value of K_p . Further, the sensing elements with oxides as the conducting material had the smallest sensitivity for NO₂ (i.e., the voltage change induced by 300 ppm_v NO₂ is nearly equal to that induced by 1500 ppm_v NO₂ (Fig. 4a)) and thus these sensing elements might be predicted to respond strongly to small amounts of NO₂. Therefore, we tentatively attribute the observed “reversal” in the NO response (Fig. 4b)) to the formation of NO₂ in the mixture of NO, O₂, and N₂. The small “reversal” in the NO₂ sensitivity of the LSCF/LSF sample (Fig. 4a)), and the change in sign of the NO_x responses with the LSCF SE are more difficult to explain and remain under investigation.

Figure 4c) shows the [O₂] dependence of the NO₂ response (450 ppm_v NO₂, 600 °C) for the

samples in Table II. The data are well fit by logarithmic expressions, but there is no systematic trend in the $[O_2]$ sensitivity at fixed NO_2 (m_2 in Eqn. 1) as was found for the NO_2 sensitivity.

CONCLUSIONS

Investigation of compounds for sensing electrode materials has revealed two promising candidates for NO_2 sensing at 600 °C: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and $NiCr_2O_4$. The weak response of these and other materials to NO indicates that utilization of these “mixed-potential” sensing elements for NO_x sensing at $T \sim 650$ °C will be difficult, as NO is the dominant equilibrium NO_x species at these temperatures. It may be possible to substitute electronically conducting oxides for Pt in these types of sensing elements, and the substitution can affect the magnitude and sign of the NO_x and O_2 sensitivities.

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