

Strategies for total NO_x measurement with minimal CO interference utilizing a microporous zeolitic catalytic filter

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Abstract

A strategy is presented for determining total NO_x ($\text{NO} + \text{NO}_2$) in gas streams at temperatures greater than 400 °C. By using a Pt-loaded zeolite Y as a catalyst filter bed placed before a sensor, NO_x species in the gas stream are brought to an equilibrium concentration of NO and NO_2 that is determined by the background oxygen concentration and the filter temperature. The equilibrated NO_x is then measured with a yttria stabilized zirconia (YSZ) sensor using a chromium oxide sensing electrode. In the absence of the filter NO and NO_2 produced responses in opposite directions, while in the presence of the filter, NO and NO_2 gave signals of the same magnitude and direction. By varying the temperature of the filter relative to the sensor, the signal magnitude could be increased. Another advantage of the filter is that CO is oxidized to CO_2 and thus little interference of CO upon NO_x was observed. By introducing a layer of the Pt-zeolite catalyst filter material directly onto a Pt electrode, a pseudo-reference to NO_x was formed. This design provides the opportunity for miniaturization as well as removes the need for an air reference.

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1. Introduction

There is a continuing need for measurements of NO_x species in combustion environments due to the negative effects of these gases on ecosystems and health [1]. Among the many types of NO_x sensors, solid-state electrochemical sensors are an attractive alternative because of their small size, portability, lower costs and operation at high temperatures and harsh environments. Two of the most common solid-state sensors for NO_x detection are the solid electrolyte (potentiometric and amperometric) and semiconducting types [2,3]. One of the drawbacks of these sensors is the lack of selectivity between the two main NO_x components, NO and NO_2 . This is an important consideration since in a combustion environment, though NO is often the dominant NO_x species, NO_2 is also present. The signal from both NO and NO_2 is typically in opposite directions, because NO gets oxidized and NO_2 reduced on the sensors [4]. There are a few examples where the sensor response to NO and NO_2 are in the same direction. An electrochemical sensor using the reaction of Ba^{2+} with NO or NO_2 to form $\text{Ba}(\text{NO}_3)_2$

provided emf signals that were in the same direction for NO and NO_2 [5]. A resistance-based sensor using Si_3N_4 also gave sensor output responses to NO and NO_2 in the same direction, though the mechanism of sensing action was not explained [6]. In addition, tests were not done with mixtures of $\text{NO} + \text{NO}_2$, so it is not clear if the signal would have been additive. Nevertheless, since these sensors respond to both gases, it would be difficult to determine the level of NO and NO_2 in a mixture.

Several strategies have been reported for improving selectivity toward NO or NO_2 . By polarizing the sensing metal oxide electrode relative to a Pt reference electrode for a yttria stabilized zirconia (YSZ) sensor at different voltages, the current produced by the device upon exposure to NO or NO_2 could be modulated to produce a selective NO_x sensor [7]. Besides selectivity to specific NO_x components gases such as CO, which are also present in combustion environments, can interfere with the signal for NO_x [8]. Thus to measure an accurate level of NO_x , the CO cross-sensitivity must be minimized.

Since regulatory agencies, such as the EPA, have strict limits on emissions defined as total NO_x , sensors that provide a measure of the sum of NO and NO_2 as total NO_x are also desirable. One of the methods proposed to do

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this has been to build a two chamber device using YSZ. In the first chamber, electrochemical oxidation of the incoming NO_x gas to NO_2 takes place via noble metal electrodes and then the NO_2 is detected as “total NO_x ” in the second chamber. This method and its variations have been extensively reported in the patent literature [3,9].

In this paper, we report a strategy for measuring total NO_x by combining a catalytic filter with an electrochemical sensor. There are several reports in the literature of using filters prior to a sensor for improving selectivity towards different gases. These filters can be classified into two groups: adsorption or chemical filters. The adsorption filters remove interference by adsorption, as in the use of a zeolite filter for removing isoprene from breath for breath analyzers [10]. Chemical filters can be 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_2 to NO [11] or KMnO_4 for converting NO to NO_2 [10], and are consumed over time. Catalytic filters have been used to oxidize or equilibrate gases before sensors and the advantage is that they are not consumed in the overall reaction. A Pt-SiO₂/WO₃ catalyst layer was used in a solid electrolyte amperometric design to equilibrate NO_x to NO_2 at 150 °C, but the effect of higher temperatures was not investigated [12]. Pt on cordierite, Mn_3O_4 , and Co_3O_4 have been used as catalytic filters ahead of a resistive SnO_2 sensor for total NO_x sensing in the patent literature [13].

In addition to the above mentioned zeolite adsorption filter for isoprene, there are also several other reported examples of use of zeolites as filters. For a NASICON-based CO_2 sensor, the zeolite acted as a filter to remove CO and ethanol, presumably by physical adsorption, though this was unclear from the paper [14]. Another study reported the use of a zeolite filter ahead of a resistive SnO_2 sensor for removing interference from ethanol by physical adsorption, and therefore needed regeneration to remove the adsorbed ethanol [15]. A chemically active zeolite filter that converted

ethanol to C_2H_4 decreased the interference from ethanol in CO detection by a resistive SnO_2 sensor [16]. 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 [17].

We report in this study a system that can measure total NO_x in a background of O_2 and N_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 sensor with a Cr_2O_3 sensing electrode. The zeolite filter acted as both a NO_x equilibration and CO oxidation catalyst. The sensor signal was magnified by keeping the filter bed and sensor at different temperatures.

2. Experimental

2.1. Sensor design and preparation

Two different sensor electrode arrangements (sensor 1 and sensor 2) for detecting total NO_x were tested. Sensor 1 consisted of a single closed-end YSZ tube (Vesuvius McDanel, 8 mol% YSZ) that was 30 cm long and had an i.d. of 8 mm and a wall thickness of 2 mm (Fig. 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 Corp., lot A4731), which was painted onto the inside of the YSZ tube. The Pt ink was then cured at 1250 °C for 2 h 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. For the sensing electrode (S), a paste was made from Cr_2O_3 powder (Alfa Aesar) consisting of a 50:50 (w/w) mixture of the oxide and terpineol organic solvent. A Pt wire was wrapped around the outside of the YSZ tube and the Cr_2O_3 paste was painted on top of the wire in a band around the tube circumference. The Cr_2O_3 paste

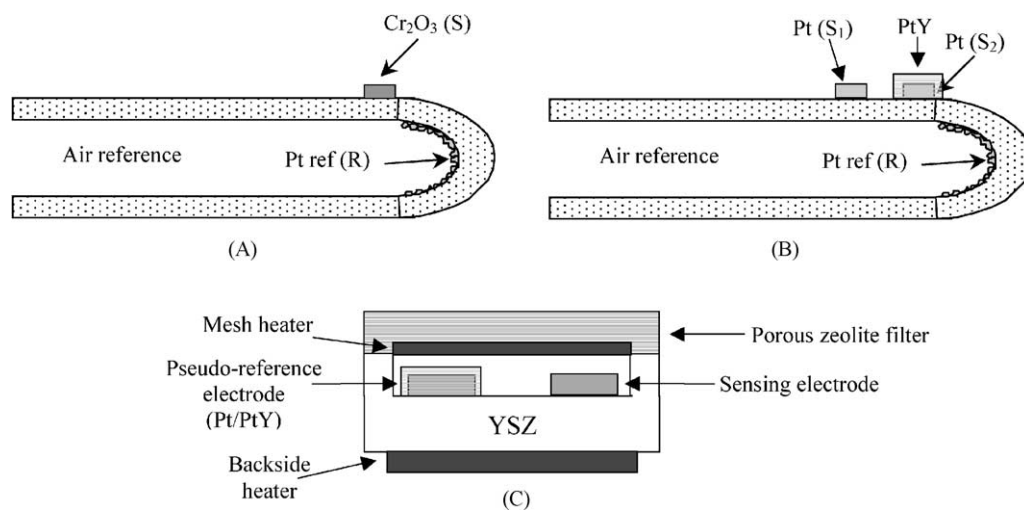


Fig. 1. (A) Sensor 1: closed-end sensor with an air reference; (B) sensor 2: closed-end sensor with two sensing electrodes, that can also function as a planar sensor; (C) diagram of a prototype design incorporating a catalyst filter and electrode assembly.

was then cured in air at 750 °C for 2 h with a 6 °C/min heating and cooling rate.

Fig. 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 2 h to form two Pt electrodes in the planar configuration (S_1 , S_2). A Pt-loaded zeolite Y (PtY) powder was mixed with terpeneol solvent in a 50:50 (w/w) mixture to form a paste and painted directly onto S_2 . The sensor was then heated to 500 °C for 1 h 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.

2.2. 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 [18]. First 1.0 g of commercial NaY powder was dried at 100 °C for 4 h. A 5 mM solution of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ 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 h and then centrifuged and washed with distilled water. The resulting powder was dried at 70 °C overnight and then calcined at 300 °C for 2 h. Finally the zeolite powder was exposed to a flowing gas mixture of 5% H_2 balance N_2 to form Pt metal. The resulting zeolite PtY powder had a dark brown appearance. Previous studies have reported a loading level of 1.05% Pt on NaY using a 2.5 mM $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution for ion-exchange (80 °C for 4 h) [18,19].

2.3. Sensing apparatus

2.3.1. Sensor chamber

The gas sensing experiments were performed within a quartz tube located inside a high temperature tube furnace

(Lindberg Blue model). The sensor was placed into the quartz tube while the electrode wires were connected to additional Pt wires that led outside the furnace. The tube furnace was used to heat and cool the sensor at a programmed rate as well as maintaining a fixed temperature. Air, N_2 and test gases, NO (2000 ppm source tank), NO_2 (2000 ppm source tank), and CO (2000 ppm source tank) were metered through Sierra brand mass flow controllers to form gas mixtures of various compositions. The Pt air reference electrode was exposed to static atmospheric air outside of the tube furnace. The voltage output of the sensor electrode response to changes in the gas concentrations versus time was monitored by a Hewlett-Packard data acquisition unit (model 34970A) and recorded by Hewlett-Packard Benchlink software on a Windows-based PC.

2.3.2. Catalytic filter bed chamber

A second quartz tube was placed outside of the tube furnace and connected to the first quartz tube holding the sensor by metal to glass fittings to stainless steel tubing and a valve flow system. 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 and 700 °C by wrapping with a heater tape and a type K thermocouple that were connected to an Omega controller in a feedback loop. Fig. 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.

2.4. Catalytic activity measurements of the filter via chemiluminescence and gas chromatography

The activity of the filter materials towards NO_x equilibration ability was investigated by chemiluminescence and CO oxidation was determined by gas chromatography.

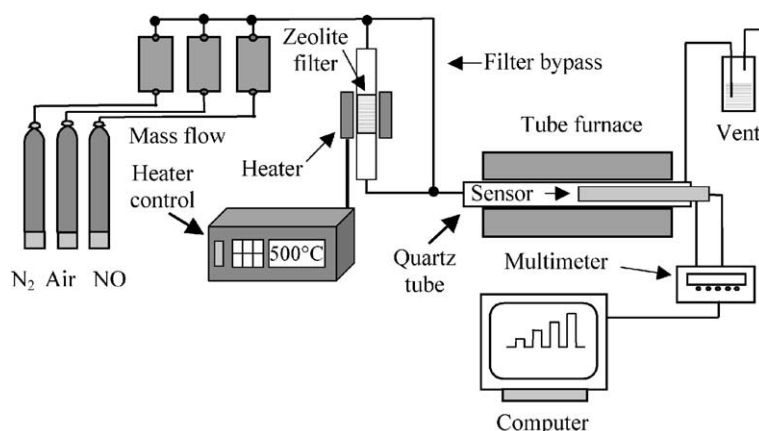


Fig. 2. Diagram of sensor testing set-up and catalytic filter bed chamber system.

NO_x equilibration measurements were done on an EcoPhysics CLD 70S NO/NO_x analyzer system with the ability to measure in either NO or total NO_x mode. An 80 mg sample of PtY or NaY catalyst was tested under a flow rate of $200 \text{ cm}^3/\text{min}$, as per the instrument requirement, while the catalyst was heated to 500°C . The analyzer was calibrated with gas standard of 600 ppm $\text{NO}/\text{balance N}_2$ (Praxair). EcoPhysics NO_x View software output the NO or NO_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_2 concentrations in the range of 0–7000 ppm. An 80 mg sample of PtY or NaY was placed into the quartz tube heated to 500°C . A typical experiment involved flowing 0–1000 ppm CO in a background of 3% O_2/He at $100 \text{ cm}^3/\text{min}$ over the catalyst bed and CO_2 production was monitored by injecting a portion of the outgoing gas onto the GC column.

3. Results

3.1. Sensor 1 response to NO_x mixtures

Sensor 1a was heated to 500°C under a $100 \text{ cm}^3/\text{min}$ flow of a background gas of 3% $\text{O}_2/\text{balance N}_2$ and the sensing behavior towards 0–1000 ppm NO and NO_2 was investigated.

Fig. 3 shows the emf as a function of NO_x gas concentration. The inset in Fig. 3 is a plot of the emf versus logarithm of the concentration for both NO and NO_2 . As expected, the responses to NO and NO_2 are in opposite directions, and the emf has a linear relationship with $\ln[\text{NO}_x]$, typical of mixed potential type sensors [20].

A range of mixtures of NO and NO_2 at a total NO_x concentration of 600 and 1000 ppm was also tested. Fig. 3 shows the results of the 600 ppm tests. With both NO_x species present, the absolute magnitude of the emf decreases from that of NO or NO_2 alone (a similar result was obtained for the 1000 ppm NO_x test). At a level of 500 ppm NO and 100 ppm NO_2 , the signal is almost close to the baseline of -33 mV (due to 3% O_2/N_2).

3.2. Evaluation of NO conversion over zeolite catalytic filter beds by chemiluminescence

The conversion of NO to NO_2 was examined after passage through the filter at a temperature of 500°C . Two zeolite filters, 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. The average conversion (with the variation for one standard deviation) of 600 ppm $\text{NO}/3\% \text{ O}_2/\text{N}_2$ flowing over the PtY filter bed at 500°C for five trials was $13.61 \pm 0.80\%$ and comparable with the calculated value of 13.66% using thermodynamic parameters [21]. Therefore with PtY as the filter material, the oxidation of NO reached close to its calculated equilibrium

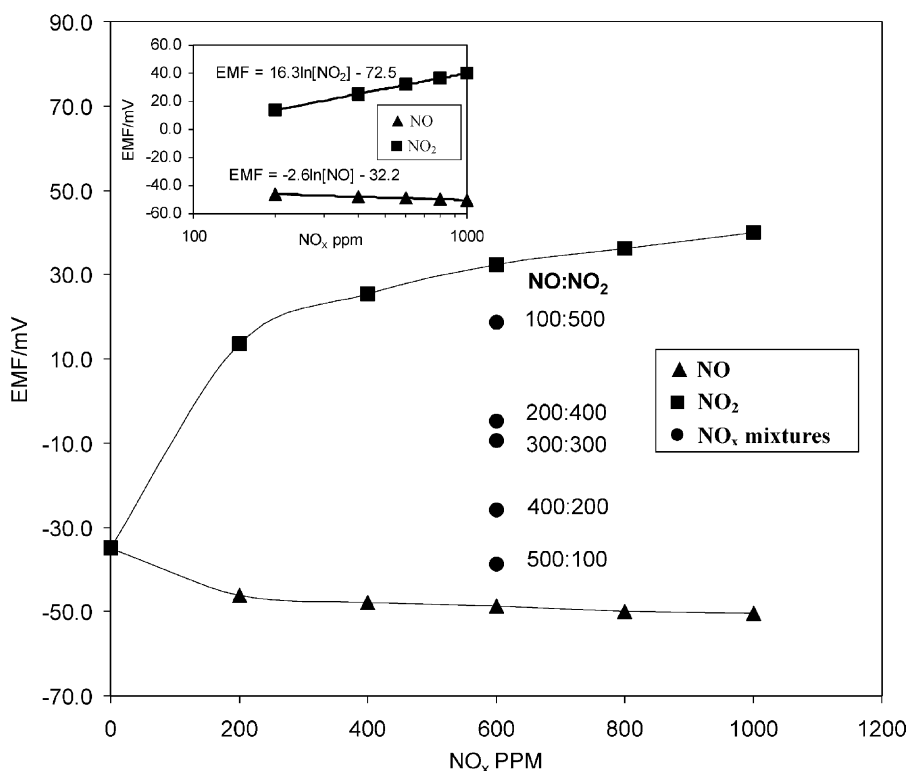


Fig. 3. Sensitivity plots of sensor 1a for individual NO , NO_2 (0–1000 ppm) and NO_x mixtures with a total of 600 ppm. Inset: emf vs. $\ln[\text{NO}_x]$ plot.

value. Using NaY as the filter material at 500 °C, equilibration of 600 ppm NO was not achieved (3.80% conversion to NO₂).

3.3. Total NO_x sensing utilizing zeolite catalytic filter with sensor

3.3.1. Sensor and filter bed at same temperature

With the sensor assembly and the catalyst filter both at 500 °C, the empty quartz catalyst reactor (blank) was tested. A 600 ppm sample of NO or NO₂ in 3% O₂ flowed directly onto the sensor to give an absolute signal of −55 mV for NO and +35 mV for NO₂ with the baseline at −34 mV (3% O₂/N₂). When the gas was directed through the empty heated reactor, there was less than a 1% decrease in the sensor response to NO, whereas NO₂ exhibited a diminished signal of 13%. The conversion for NO₂ 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. There was a decrease in the sensor signal for both 600 ppm NO (about 1.5%) and NO₂ (about 18%), and the NO and NO₂ responses were in opposite directions.

Fig. 4 compares the sensor response as change in emf from the baseline (3% O₂/N₂) for 1000 ppm NO and 1000 ppm NO₂ and the same gases passed through the PtY catalytic filter. It is clear that without the filter NO and NO₂ signals are in the opposite direction, but with the PtY filter the signals for NO and NO₂ 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_x, but different ratios of NO and NO₂. Data for four different ratios at a total NO_x of 1000 ppm are shown in the inset of Fig. 4. The

signals are of comparable magnitude, despite different starting ratios of NO and NO₂.

3.3.2. Sensor and filter bed at different temperatures

NO and NO₂ at concentrations between 0 and 1000 ppm in 3% O₂ were passed over the PtY filter bed at temperatures ranging from 400 to 700 °C, with the sensor at 500 °C. These data are shown in Fig. 5. A set of measurements were made with another sensor 1 at 400 °C, while the PtY filter bed was varied from 400 to 600 °C, and the data is shown in Fig. 6. 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. Second, the signals due to NO and NO₂ 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% O₂, whereas the reverse is true if 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.

3.4. Sensor design using a pseudo-reference electrode

Sensor design 2 which is represented in Fig. 1B was examined. The sensor side (S₁ and S₂) was exposed to NO_x at 100 cm³/min, with a static air reference at the internal Pt electrode (R). Three simultaneous emf values were recorded upon exposure to NO_x, (S₁, R), (S₂, R) and (S₁, S₂), and shown in Fig. 7 with the sensor at 500 °C and the PtY filter at 600 °C. It is seen that for (S₂, R) no response was observed when exposed to NO or NO₂ in 3% O₂. For, (S₁, R) with the bare Pt sensing electrode, the response to NO or NO₂ was

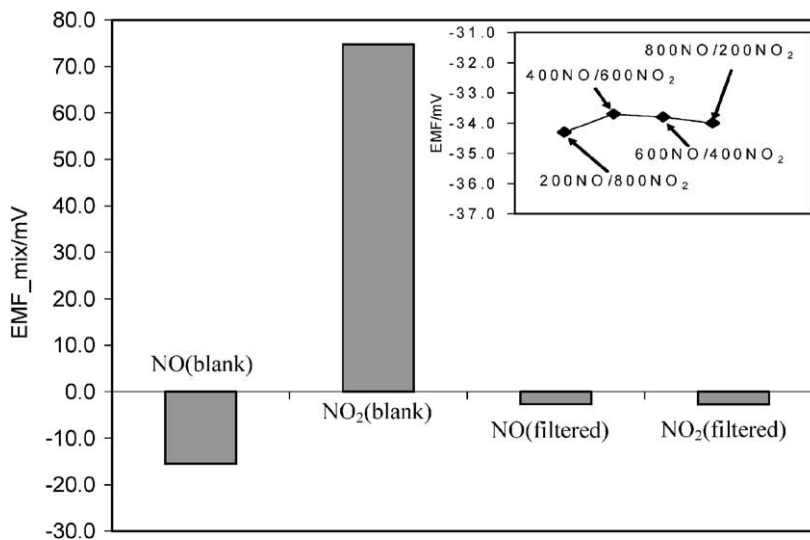


Fig. 4. Histogram for absolute mixed potential response of sensor 1a to 1000 ppm NO_x/3% O₂ with and without the PtY filter bed. Sensor and filter bed both at 500 °C. Inset shows plot of electrode signal for four ratios at a total NO_x of 1000 after passing through the PtY.

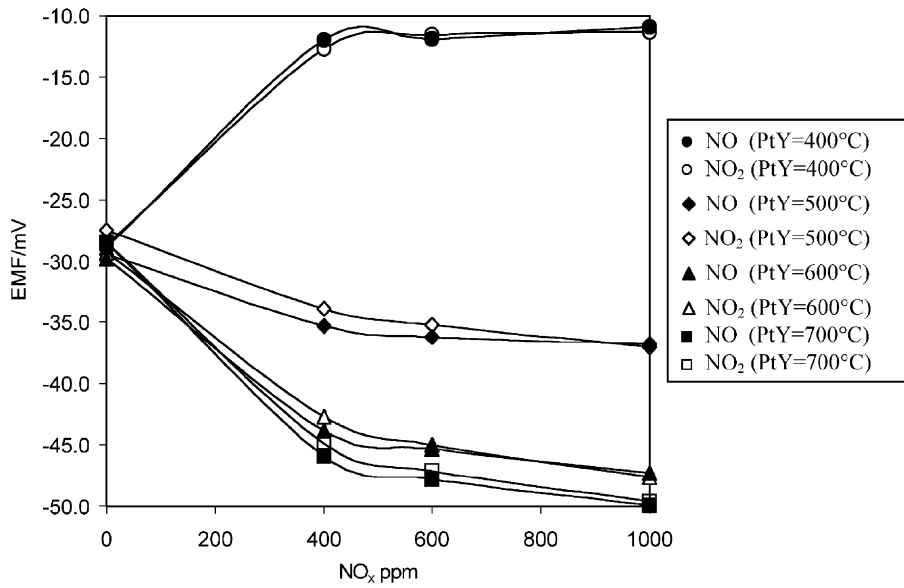


Fig. 5. Sensor 1 response at 500 °C with varying temperatures of PtY filter from 400 to 700 °C.

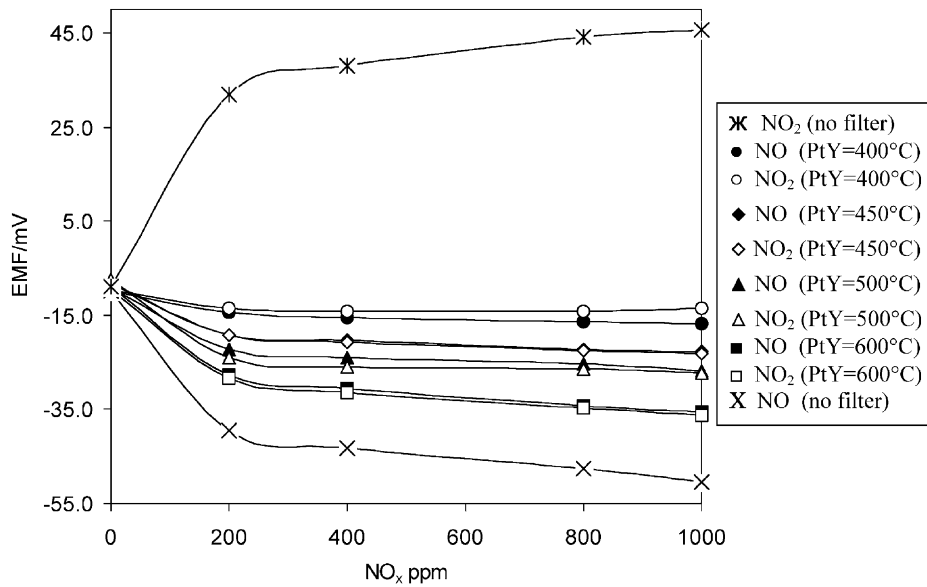


Fig. 6. Sensor 1 response at 400 °C without filter and for varying temperatures of PtY filter from 400 to 600 °C.

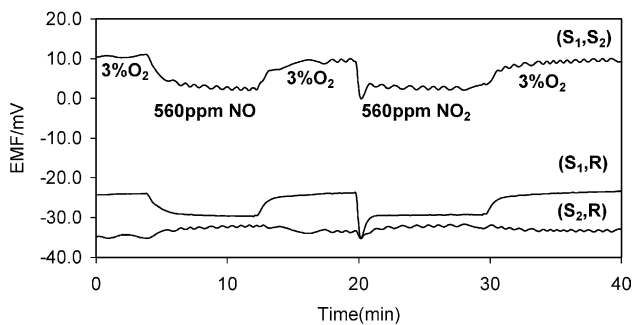


Fig. 7. Transient plot of the three sensor type 2 electrode couples for 560 ppm NO_x/3% O₂ with PtY filter and pseudo-reference electrode (S₁: Pt electrode; S₂: Pt electrode covered with PtY; R: reference electrode).

similar in magnitude and direction. When the signal between the two electrodes (S₁, S₂) is considered, it also shows the same signal for the two NO_x species.

3.5. Evaluation of CO conversion over filters by gas chromatography

The influence of the zeolite filters on CO oxidation chemistry was examined. The filter was heated to 500 °C and the CO₂ formation was monitored by GC. Initially the blank heated quartz reactor at 500 °C was tested with 7000 ppm CO/3% O₂ and its conversion to CO₂ was minimal (4%). PtY had a high conversion for 7000 ppm of CO and a complete conversion for 1000 ppm CO to CO₂ whereas NaY did not.

Table 1 shows the percent conversion for the two zeolites for the two concentrations of CO tested.

3.6. CO sensing studies

Sensor 1a with the Cr₂O₃ sensing electrode was tested at 500 °C, and the data shown in Fig. 8 for 0–1000 ppm CO. The direction of the sensor response to CO is in the same

Table 1
Percent conversion of CO to CO₂ at 500 °C in 3% O₂ over NaY and PtY zeolites

Zeolite type	Percent conversion of 7000 ppm CO	Percent conversion of 1000 ppm CO
Blank	4.4	–
NaY	17.4	32.9
PtY	88.9	100

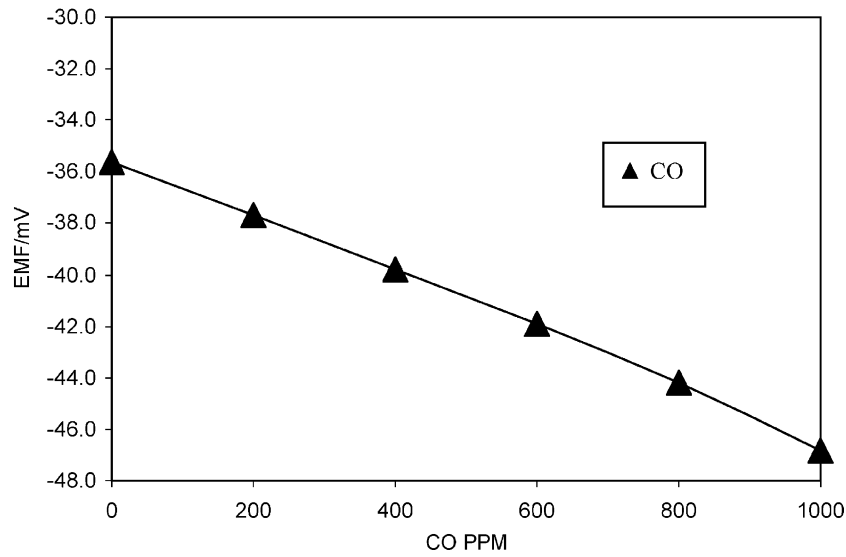


Fig. 8. Sensor response to 0–1000 ppm CO/3% O₂ for sensor 1a at 500 °C.

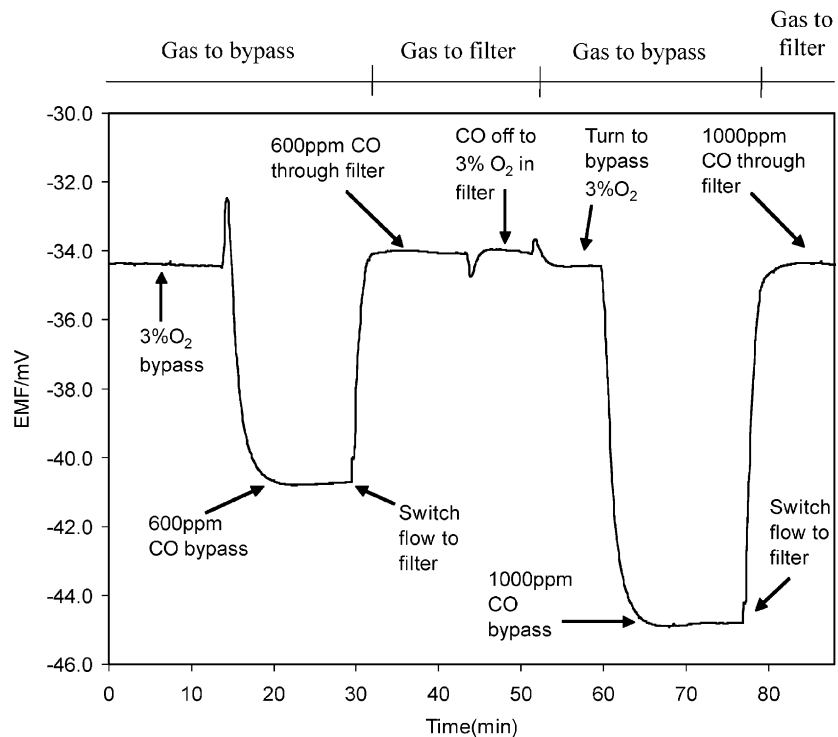


Fig. 9. Sensor 1a response to CO for gases bypassing or passing through the PtY filter bed.

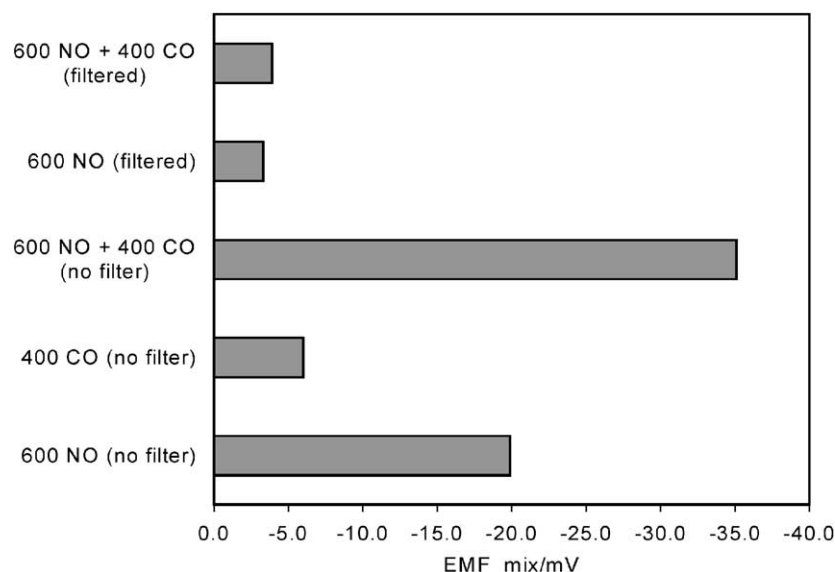


Fig. 10. Bar graph showing absolute mixed potential response to CO with and without PtY filter in the presence of NO.

direction as that of NO. However, unlike the dependence of the signal on the logarithmic value of the concentration of NO or NO₂ shown in Fig. 3, the response had a linear relationship with CO concentration, and is consistent with previous studies [22,23].

Flowing the gas through the empty heated reactor showed no signal change 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 from -35 mV. For 80 mg of PtY zeolite however, there was no net signal for CO, as shown in Fig. 9. 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. Fig. 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 ppm CO + 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.

4. Discussion

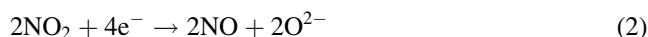
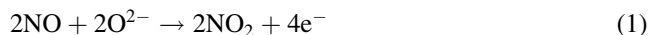
The discussion is divided into four sections: (1) mixed potential nature of the signal; (2) role of the zeolite filter; (3) enhancement of signal by differential temperature measurement; and (4) suggestions for a prototype sensor that incorporates the filter and a pseudo-reference electrode.

4.1. Mixed potential response

A major advancement in improving the sensitivity of YSZ solid electrolyte sensors has been the use of metal oxide

sensing electrodes [4,7,12,23,24]. Many metal oxide sensing electrodes have been investigated for NO/NO₂ detection with a large variation in sensitivity [25,26].

In this study, we used Cr₂O₃ as the sensing electrode system, primarily because previous studies have shown that several compounds of chromium demonstrate high sensitivity [4,25]. For metal oxide electrodes, it is well recognized that the response for NO and NO₂ are usually in opposite directions with the NO₂ response being larger [7] as seen in Fig. 3. The electrochemical reactions are shown below:



For these gases, the mixed potential (E_m) at a fixed O₂ concentration takes the form shown in Eqs. (4) and (5) for NO and NO₂, respectively [4]:

$$E_m = \text{constant} - k_{\text{NO}} \ln[\text{NO}] \quad (4)$$

$$E_m = \text{constant} + k_{\text{NO}_2} \ln[\text{NO}_2] \quad (5)$$

where the constants k_{NO} and k_{NO_2} are determined by adsorption properties of the gases, as well as electrochemical parameters.

The inset in Fig. 3 shows that the Cr₂O₃ indeed shows a linear response with $\ln[\text{NO}_x]$, with the slopes of NO and NO₂ having opposite sign, suggesting mixed potential behavior.

Fig. 3 also shows that for mixtures of NO and NO₂, signals intermediate between that of NO and NO₂ alone are observed. For a mixture of gases, both NO and NO₂ 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 [27,28]. For a gas mixture with NO₂ in excess of the equilibrium con-

centration (NO, NO₂, O₂) at a fixed temperature T and potential E , the anodic (i_a) and cathodic (i_c) currents are:

$$i_a = k_{\text{O}_2}[\text{O}_2]\exp\left[\frac{\alpha_{\text{O}_2}FE}{RT}\right] \quad (6)$$

$$i_c = k_{\text{NO}}[\text{NO}]\exp\left[\frac{\alpha_{\text{NO}}FE}{RT}\right] - k_{\text{NO}_2}[\text{NO}_2]\exp\left[\frac{-(1-\alpha_{\text{NO}})FE}{RT}\right] \quad (7)$$

where α 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 $\alpha = 0.5$:

$$k_{\text{O}_2}[\text{O}_2]\exp\left[\frac{FE_m}{2RT}\right] = -k_{\text{NO}}[\text{NO}]\exp\left[\frac{FE_m}{2RT}\right] + k_{\text{NO}_2}[\text{NO}_2]\exp\left[\frac{-FE_m}{2RT}\right] \quad (8)$$

$$E_m = \frac{RT}{F} \ln\left(\frac{k_{\text{NO}_2}[\text{NO}_2]}{k_{\text{O}_2}[\text{O}_2] + k_{\text{NO}}[\text{NO}]}\right) \quad (9)$$

Eq. (9) predicts that for the limiting condition $k_{\text{O}_2}[\text{O}_2] \gg k_{\text{NO}}[\text{NO}]$, E_m should become independent of the concentration of NO. For NO concentrations in excess of equilibrium values, similar to Eqs. (6)–(9) can also be set up.

4.2. Role of the filter

If the NO and NO₂ mixture is in the equilibrated state, the sensor signal should 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_x mixtures occurs when the NO:NO₂ ratio is close to 500:100. The equilibrium ratio of NO:NO₂ for 600 ppm NO in 3% O₂ at 500 °C is calculated to be 518:82 [21].

NO_x reactions on the zeolite filter bed can be represented as:



Analysis showed that in 3% O₂ 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 NO₂ were similar and small in magnitude.

4.3. 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_x to re-equilibrate at the electrodes. By controlling the temperature of the filter relative to that of the sensor, an ‘NO₂’ or an ‘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 NO₂, and the sensor output for all NO_x compositions resembles a NO₂-like signal. Whereas,

for the filter temperature at 700 °C, the sensor provides a NO-like signal.

The sensor signals for pure NO or NO₂ shown in Figs. 3 and 6 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 NO₂. Thermodynamically this can only happen at filter temperature extremes of 150 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 NO_x below 400 °C. Thus the filter needs to be maintained between 400 and 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 NO_x signal. Even with these restrictions, a wide range of operating conditions are possible for the filter and sensor temperature combinations to measure total NO_x. Over time, long-term drifts have been observed in the sensor signal and are the subject of future studies.

4.4. Insensitivity to CO

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



With both NO and CO present, there was an enhanced signal (Fig. 10) 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.

4.5. Prototype sensor design

Sensor 2 (Fig. 1B) demonstrated that it is possible to get rid of the air reference (Fig. 7). The layer of PtY placed directly onto one of the Pt electrodes (S₂) leads to an equilibrium NO_x mixture, with little driving force for the NO_x to react electrochemically at the sensor. It acts as a pseudo-reference towards NO_x and CO. This idea has its origin in the work of Okamoto et al., who demonstrated about 20 years ago that by using Pt/Al₂O₃ as a CO oxidation catalyst, a pseudo-reference electrode could be created for CO gas sensing on YSZ [29]. The second bare Pt electrode (S₁) acted as the sensing electrode.

Fig. 1C shows a possible prototype design that incorporates the filter and the sensing electrodes into one unit and is an extension of a planar design sensor that we have recently reported [8]. This design could be used for a total NO_x sensor with a planar format, that allows the elimination of the air reference, and discriminates against CO.

5. Conclusions

A total NO_x 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 NO_x 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 NO_x 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 the electrode lead to the formation of a pseudo-reference electrode, thus eliminating the need for an air reference. A design for fabricating a miniaturized version of the PtY filter/sensor assembly is proposed.

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