

High temperature amperometric total NO_x sensors with platinum-loaded zeolite Y electrodes

Jiun-Chan Yang, Prabir K. Dutta*

Department of Chemistry, The Ohio State University, Columbus, OH 43210-1185, USA

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Abstract

An amperometric total-NO_x sensor that integrates a Pt-loaded zeolite Y (PtY) catalyst for NO_x equilibration with electrochemical oxidation of NO on an yttria-stabilized zirconia (YSZ) electrolyte is described in this paper. PtY is found to be an effective catalyst for equilibrating mixtures of NO, O₂ and NO₂ at temperatures in excess of 400 °C. By applying a low anodic potential of 80 mV, the NO in the NO_x equilibrated mixture can be oxidized at a Pt working electrode on the YSZ electrolyte at 500 °C. The current thus generated provides a measure of the total NO_x in the gas stream and is the basis of the sensing measurements in this study. The PtY can be held separate from the YSZ or coated onto the YSZ as a film, the latter being more appropriate for the practical embodiment of this design. We demonstrate that this sensor exhibits total-NO_x detection capability, a low NO_x detection limit (<1 ppm), high NO_x selectivity relative to CO and oxygen, and linear dependence on NO_x concentration. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Nitrogen oxides are emitted from high temperature combustion processes, including transportation vehicles and power plants. Since NO_x species are considered to be precursors to urban smog and acid rain, there is considerable regulatory pressure to reduce NO_x emissions. With the availability of fast response NO_x sensors, emissions can be monitored, but more importantly, optimizing the combustion process via feedback control can also reduce emissions. For example, new automotive engine designs, such as lean-burn gasoline and direct-injection diesel engines, provide significant improvement on fuel efficiency, but commercialization depends on minimizing the relatively high NO_x emissions [1]. NO_x adsorber–catalyst systems have been developed for such engines with periodic regeneration [2]. A sensitive, rapid response NO_x sensor is essential for monitoring the concentration of residual NO_x and triggering regeneration processes.

Several types of solid-state NO_x sensors have been discussed in the literature for operation in high temperature combus-

tion environments. Among those, electrochemical devices using oxygen-ion-conducting yttria-stabilized zirconia (YSZ) for high temperature operation (>500 °C) show significant promise [3]. Potentiometric measurements exploiting the difference of the extent of NO_x equilibration between two electrodes provide a measure of NO_x concentration [4–6]. Other studies have shown that NO_x detection can be done in the amperometric mode by polarizing the working electrode to a constant potential and recording the steady-state current [1, 7–10]. Regular amperometric devices usually contain diffusion barriers and are operated in the diffusion-limit mode. The corresponding limiting current, which bears a linear relation with NO_x concentration, is a unique feature of the diffusion barrier and not significantly influenced by the aging of the microstructure of the electrode/YSZ interface [4]. Such sensors though lead to poor signal/noise ratios at low NO_x concentrations.

Although electrochemical NO_x sensors show promise, selectivity is a major limitation. First, the two main components of nitrogen oxides in combustion environments are NO and NO₂, and sensors need to distinguish between them or provide a total NO_x measurement. Second, CO, hydrocarbons, O₂ and ammonia interferences are of concern. Many papers focus on detecting NO [1, 3, 7, 9, 10] yet NO₂ can also be an important constituent. Since NO₂ tends to get reduced and NO tends to get oxidized,

* Corresponding author. Tel.: +1 614 292 4532; fax: +1 614 292 0462.
E-mail address: dutta.1@osu.edu (P.K. Dutta).

the presence of both gases can lead to opposing signals. Oxygen interference is probably the most difficult to be overcome because it is involved in the NO_x equilibrium, as well as the concentration of O_2 is significantly higher than NO_x in combustion environments.

Multi-chamber design is the most common approach to detect total NO_x in fluctuating oxygen [9]. In this design, the gas mixture diffuses through a narrow channel into one or two chambers constructed of laminated YSZ sheets. The first chamber is equipped with oxygen pumping electrodes, which can selectively remove oxygen from the gas mixture to minimize the oxygen interference. A pair of noble metal electrodes then electrochemically converts the NO_x mixture into NO or NO_2 exclusively, which is detected by either potentiometric or amperometric methods at the last stage.

Other strategies for minimizing the interferences include use of adsorption and catalytic filters [11–16]. We have reported that platinum-loaded zeolite Y (PtY) was effective in equilibrating NO_x and oxidizing CO in the presence of oxygen at temperatures higher than 400°C , as shown in the following reactions [17]:



The equilibrated NO_x was measured by a YSZ-potentiometric sensor with a metal/metal oxide electrode. As long as the zeolite filter is kept at a temperature different from the sensor, a total NO_x signal is obtained.

In this paper, an amperometric sensor based on measuring currents upon application of a low anodic potential ($\sim 80\text{mV}$) to Pt electrodes on a YSZ electrolyte for detecting NO_x is proposed. The invention here utilizes PtY as a separate filter or as a coating on the YSZ to equilibrate the NO_x at the corresponding temperature of the sensor, followed by the amperometric detection at the applied potential. PtY also serves to eliminate the inference from CO by oxidizing it to CO_2 . This sensor design also minimizes the interference from O_2 and provides total NO_x detection extending to $<1\text{ ppm}$, linear calibration and operational temperature of 500°C .

2. Experimental

2.1. Pt-loaded zeolite Y (PtY) preparation and characterization

Zeolite Y was selected as the support for platinum because the nanoporous zeolite cavities can stabilize Pt clusters and enhance

the durability of catalysts [18]. The Pt-loaded zeolite Y powder was synthesized starting from Na^+ zeolite Y (NaY, Union Carbide, LZ-Y-52). 1.0 g of NaY powder was added to a 2.5 mM $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution, and stirred for 24 h at room temperature. After centrifuging and washing with distilled water, the Pt-exchanged powder was dried at 70°C for 3 h, heated at 300°C for 2 h, and exposed to 5% H_2 at 300°C to reduce the platinum.

TEM and SEM micrographs were taken by FEI Tecnai TF-20 TEM with a HAADF detector and FEI XL30 FEG ESEM. NO_x was measured by a chemiluminescence NO_x analyzer (Eco-Physics CLD 70S) with either NO or total NO_x mode (converting NO_2 to NO by a molybdenum converter prior to chemiluminescence detection). For NO_x equilibration tests, 40 mg PtY was placed on a porous quartz frit in a quartz tube. The quartz tube was placed vertically and heated by a heating tape. Air, N_2 , NO and NO_2 flowed through the quartz tube at a $200\text{ cm}^3/\text{min}$ flow rate and then sampled by the chemiluminescence analyzer. The analyzer was calibrated with 600 ppm or 30 ppm NO primary standards (Praxair) depending on the concentration range. The BET surface area was measured by a Micrometrics ASAP 2020 analyzer. Atomic spectroscopy (ICP-OES) was used to analyze the Pt content of PtY.

2.2. Sensor fabrication

Fig. 1 shows the two sensor designs used in this study. Both designs are three electrode systems, with Pt working, reference and counter electrodes. For design A, one of the Pt electrodes is covered with PtY. In sensor B, a layer of PtY was deposited on the entire YSZ surface, covering the three Pt electrodes. For the sensor fabrication, YSZ discs (sliced from an 8 mol% yttrium YSZ rod, Custom Technical Ceramics) of 10 mm diameter and 2 mm thickness were used as the solid electrolyte. Working, counter, and reference electrodes were made by attaching a clean Pt wire to the YSZ (99.95%, 0.13 mm in diameter, Fischer Scientific) with a small amount of Pt ink (Engelhard, A4731). One end of the Pt wire was bent and shaped to a disc of 2 mm in diameter in order to increase the electrode–electrolyte contact area. The Pt ink was cured at 1200°C for 2 h to secure the bonding between Pt electrodes and YSZ. The reference electrode was kept well separated from the working and counter electrode to reduce the electrical interference [19]. PtY was mixed with α -terpineol to form a paste and then painted on top of the reference electrode or all three electrodes depending on the particular sensor design. The PtY layer was around $50\text{ }\mu\text{m}$ thick. All sensors were heated at 600°C in air for 2 h and stabilized at 500°C for 5 h prior to electrical measurements.

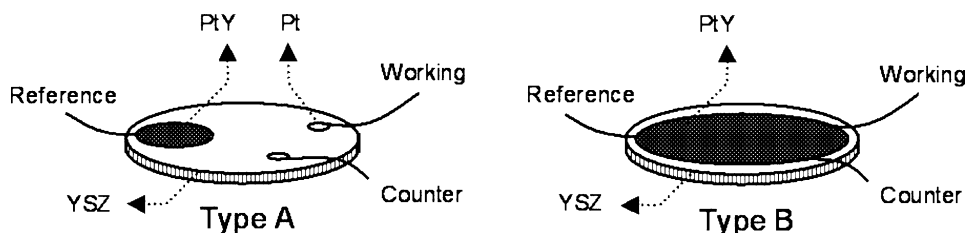


Fig. 1. Schematic representation of sensors composed of YSZ, PtY, and three Pt electrodes: type A, PtY only covers the reference electrode; type B, PtY covers all three Pt electrodes.

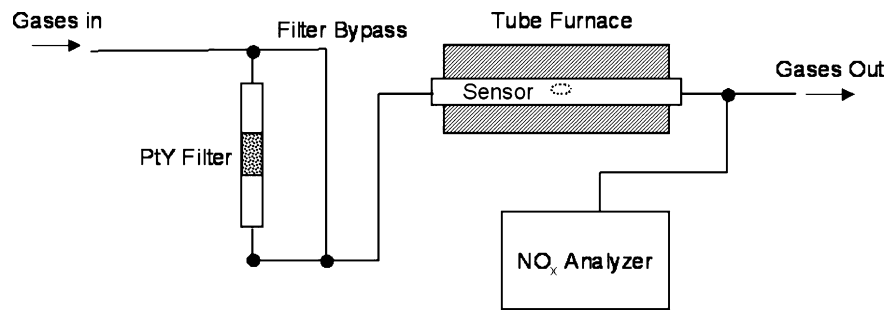


Fig. 2. Sensor test set-up. Gases can be passed through the PtY filter prior to contacting the sensor. The chemiluminescent NO_x analyzer was connected to the outlet of the sensor furnace to monitor the total NO_x concentration.

2.3. Sensor testing set-up

The gas sensing experiments were performed with the sensor placed in a quartz tube located inside a tube furnace (Lindberg Blue, TF55035A). The quartz tube was wrapped with a grounded aluminum foil to screen the electric field of the furnace. Four certified NO_x cylinders (30 ppm NO, 30 ppm NO_2 , 2000 ppm NO, 2000 ppm NO_2 , Praxair) were used as NO_x sources. As shown in Fig. 2, the gas mixture from the computer-controlled mass flow controllers (MFC) can be introduced through a plug of PtY. This set-up allows us to compare the effectiveness of an external PtY filter coupled with sensor A and sensor B with PtY coated on the YSZ pellet. The PtY plug (filter) is a vertically placed quartz tube with 40 mg PtY on a supporting frit. A chemiluminescence NO_x analyzer (Eco-Physics CLD 70S) was connected to the outlet of the tube furnace for NO_x monitoring. The current–voltage polarization curve (I – V curve) and amperometric measurements were acquired with a potentiostat (Gamry DC105). The potential difference between electrodes was monitored by a Hewlett-Packard data acquisition system (HP, 34970 A) with $10\text{ G}\Omega$ internal impedance.

3. Result

3.1. Sensor design

In sensor design A (Fig. 1), the PtY covered Pt is used as the reference electrode. The role of the PtY is to ensure that the NO_x passing through it gets equilibrated before it reaches the underlying Pt electrode. Sensor A design was used for demonstrating the current–potential curves with NO and NO_2 and also the effectiveness of an external PtY filter for equilibrating NO_x . Sensor B design (Fig. 1) with PtY covering all three electrodes will be the practical embodiment of the sensor system described in this study. The use of the chemiluminescence analyzer after the gases contact the sensor provides an effective measure of the performance of the sensors.

3.2. Characteristics of Pt-loaded zeolite Y

The electron micrographs in Fig. 3 provide information on the morphological characteristics of PtY. Fig. 3a shows a low-resolution SEM of the PtY thick film on the YSZ electrolyte.

Thickness of the film in both sensors A and B is of the order of 100–200 μm . Fig. 3b with a higher resolution shows the porosity of the zeolite film. The zeolite crystallite size is around 1 μm and the film consists of loosely packed particles allowing for gases to penetrate through the film. The TEM image of the PtY shown in Fig. 3c indicates that the Pt particles were highly dispersed. Most of the Pt particles were less than 5 nm in diameter and no particles larger than 15 nm were found. The Pt loading was determined by elemental analysis to be 4.4% and the surface area of the PtY was determined by the BET method to be $443\text{ m}^2/\text{g}$. The NO_x conversion performance on the PtY is shown in Fig. 4. At a flow rate of $200\text{ cm}^3/\text{min}$, 40 mg PtY is capable of bringing 600 ppm NO or NO_2 to equilibrium mixtures at temperatures higher than $\sim 400^\circ\text{C}$.

3.3. Current–voltage curves

The current–voltage (I – V) curves for the type A and B sensors are shown in Fig. 5. Between each potential scan, the sensor was maintained at 500°C in air for $\sim 5\text{ h}$ to remove any polarization effects. Potential scans from -25 to 100 mV were acquired for a type A sensor with a scan rate of 0.2 mV/s in an environment of 3% oxygen with 600 ppm NO or NO_2 (plots a and b in Fig. 5), with the gases bypassing the PtY filter. The experiment was repeated with 600 ppm NO passing through the PtY filter at 500°C and the I – V curves were reacquired (plot c, Fig. 5). After the experiment, the sensor was cooled and brought out of the furnace. A layer of PtY was then coated on the working and counter electrodes of this sensor, followed by heat treatment in air at 600°C for 2 h. This procedure converted the type A into a type B sensor. I – V measurements were performed on this sensor at 500°C with the gases bypassing the PtY filter with both 600 ppm NO and NO_2 (plots d and e, Fig. 5). Fig. 5f shows the I – V curve obtained in the presence of 3% O_2 with sensor A.

The almost-parallel relation of plots (a) and (b) is reported in previous studies on non-Nernstian NO_x sensors [20,21], indicating the opposite redox tendency of NO and NO_2 . With 600 ppm NO passing through a PtY filter prior to interaction with sensor A (plot c), there is a significant change in the I – V curve, with zero current at zero applied voltage as expected for an equilibrated mixture of NO_x . On the type B sensor, the currents observed for 600 ppm NO and NO_2 (plots d and e) are almost identical.

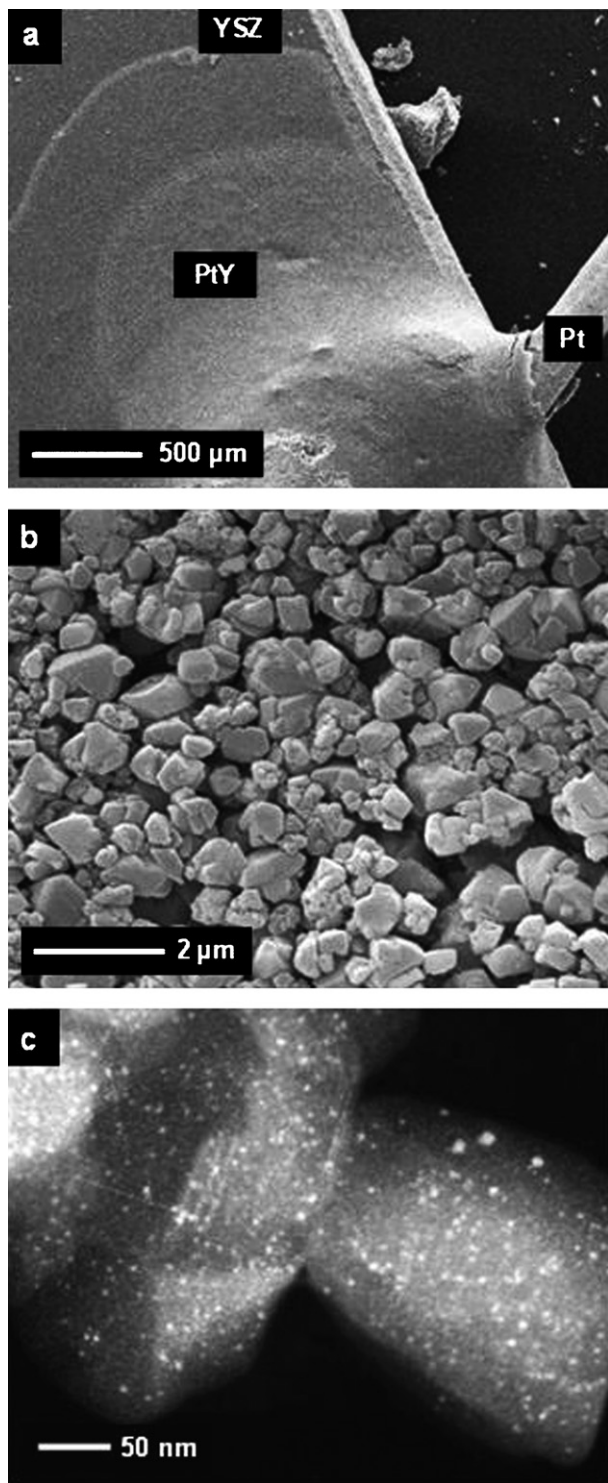


Fig. 3. Electron micrographs of PtY: (a) low-resolution SEM of PtY film on YSZ; (b) SEM of PtY film showing particle packing and porosity; (c) TEM of PtY showing the dispersion of Pt clusters on the zeolite.

3.4. Sensing response to NO_x

A type A sensor at 500 °C was anodically polarized to 80 mV (versus the PtY reference electrode) and the current in the presence of 100–800 ppm NO_x in 3% O_2 was recorded with/without gases passing through the 500 °C PtY filter. The bias potential

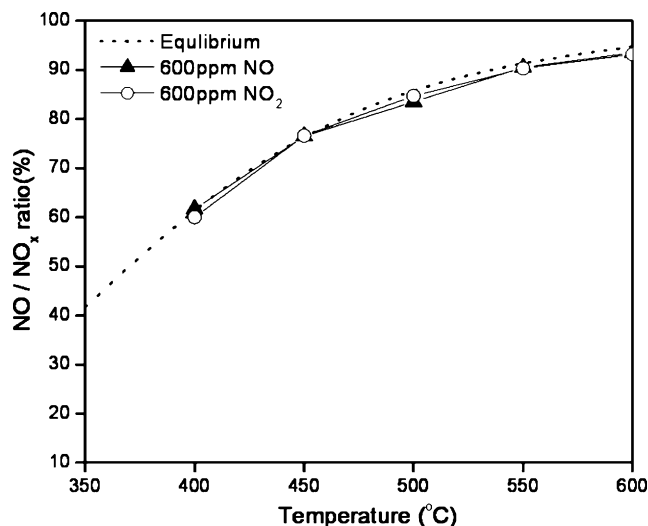


Fig. 4. NO/NO_x ratios at different temperatures obtained by passing 600 ppm NO or NO_2 in 3% O_2 through a 40 mg PtY plug: (\blacktriangle), NO to NO_2 conversion; (\circ), NO_2 to NO conversion; (.), from equilibrium constant calculations.

of 80 mV was chosen based on Fig. 5 since a measurable current in the presence of NO_x was expected. The data shown in Fig. 6 demonstrates that for the gases bypassing the PtY filter, the electro-oxidation of NO produces a very different signal than that from NO_2 (plot a and b). With NO (100–800 ppm) passing through a PtY filter (plot c), the type A sensor produces a signal with lower magnitude, since the equilibrated NO_x mixture contains less NO . With the type B sensor, the calibration curves for 100–800 ppm NO and NO_2 (plots d and e) are almost identical and overlap with plot c obtained with NO for type A sensor. The response curves also exhibit linear relationship between current and concentration of NO_x . The similarity of plots (c)–(e) demonstrates that a separate PtY filter and the PtY thick film coated on the sensor surface can both equilibrate any NO_x mixture and the sensor produces a total NO_x response.

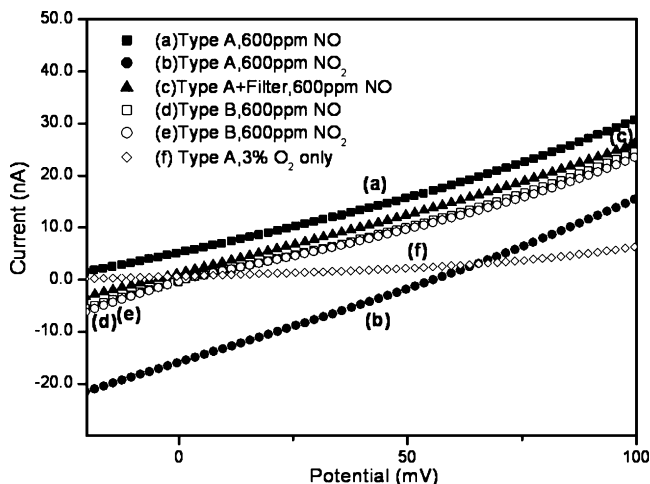


Fig. 5. I - V curves acquired in 600 ppm NO or NO_2 with 3% O_2 : (a) type A sensor with 600 ppm NO ; (b) type A sensor with 600 ppm NO_2 ; (c) type A sensor with 600 ppm NO after passing through the PtY filter; (d) type B sensor with 600 ppm NO ; (e) type B sensor with 600 ppm NO_2 ; (f) type A sensor in 3% O_2 .

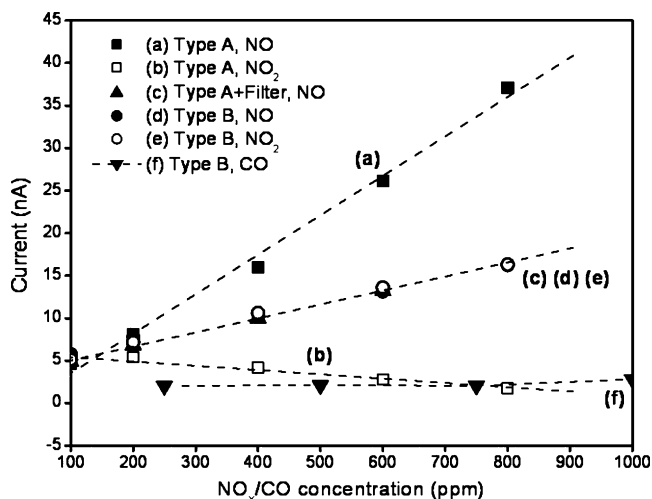


Fig. 6. Calibration curves for 100–800 ppm NO_x and 250–1000 ppm CO in 3% O_2 : (a) type A sensor with NO; (b) type A sensor with NO_2 ; (c) type A sensor with NO passing through the PtY filter; (d) type B sensor with NO; (e) type B sensor with NO_2 ; (f) type B sensor with CO.

For concentrations of NO_x between 1 and 120 ppm, the signal from a type B sensor was compared with the data from a chemiluminescence NO_x analyzer, which was connected to the outlet of the furnace (Fig. 2) so that both measuring devices sample the same gas. Fig. 7 shows identical response transients of the NO_x sensor and chemiluminescence analyzer. The calibration curves in the concentration region of 1–120 ppm NO_x are shown in Fig. 8, the slope for 1–10 ppm (0.4 nA/ppm) is steeper than 20–120 ppm (0.2 nA/ppm), which implies that the sensor has higher sensitivity under 10 ppm. This phenomenon was also observed on a type A sensor using a PtY filter.

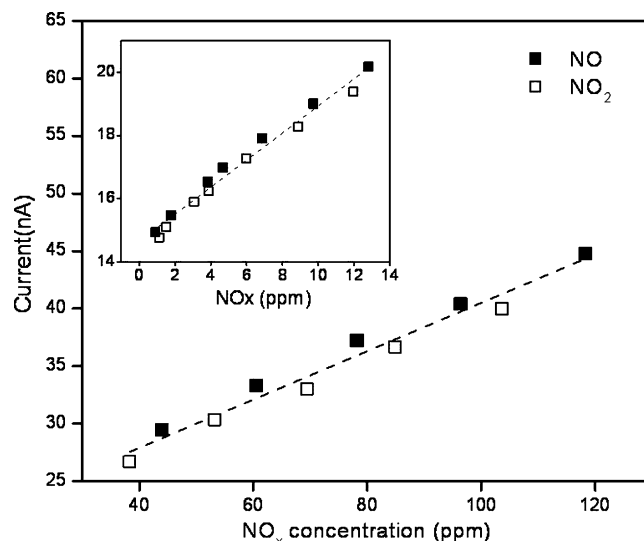


Fig. 8. Calibration curves for a type B sensor with 1–120 ppm NO_x in 3% O_2 . The NO_x concentration was determined by a chemiluminescent NO_x analyzer.

The 90% response and recovery time (t_{90}) of 100 ppm NO is 30 and 45 s, respectively. In fact, the real response/recovery time should be significantly faster because our gas delivery system is not optimized for response/recovery time tests. The dead volume and the time needed for the gas mixtures to reach a steady state in the 200 cm^3 quartz test chamber limits the time resolution. In support of this argument, we found that the chemiluminescence analyzer showed that ~ 3 ppm NO_x still remained in the testing gas line for duration of a minute after turning 600 ppm NO_x off, and will increase the sensor recovery time.

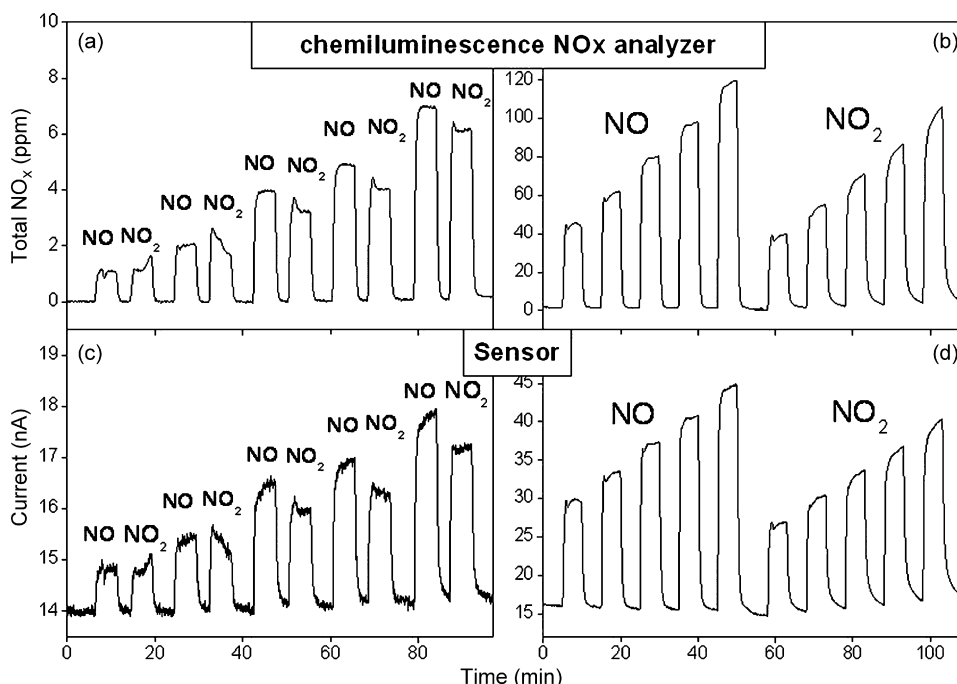


Fig. 7. Comparison of responses to 1–110 ppm total NO_x between a type B sensor and a chemiluminescent NO_x analyzer; (a) and (b) signals from the NO_x analyzer; (c) and (d) signals from sensor B.

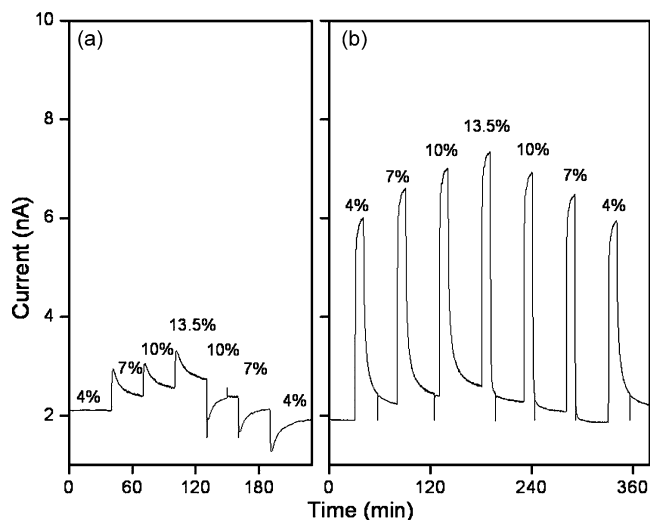


Fig. 9. Oxygen interference test on a type B sensor: (a) oxygen changed between 4% and 13.5%; (b) 100 ppm NO₂ in 4–13.5% O₂.

3.5. Interferences

3.5.1. CO

The interference of CO on a type B sensor was examined by changing CO concentration from 250 to 1000 ppm in 3% O₂. The current remains unchanged as a function of CO (plot f, Fig. 6). PtY has been demonstrated to have high activity for CO oxidation to CO₂, the latter being electrochemically inactive [17].

3.5.2. Oxygen

The influence of different oxygen concentrations on the B-type sensor is shown in Fig. 9. In the presence of varying concentrations of O₂, an increase in current is noted with increasing O₂ concentration, as shown in Fig. 9a. With a background of 100 ppm NO₂, increasing oxygen also leads to an increase

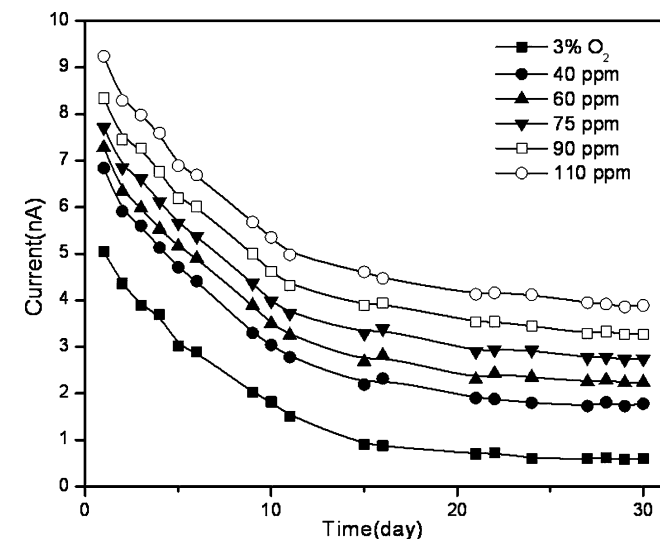


Fig. 10. Long term stability test for a type B sensor at 500 °C over a 30-day testing period. With a background of 3% oxygen, the NO₂ was changed from 0 to 110 ppm everyday and the experiment repeated.

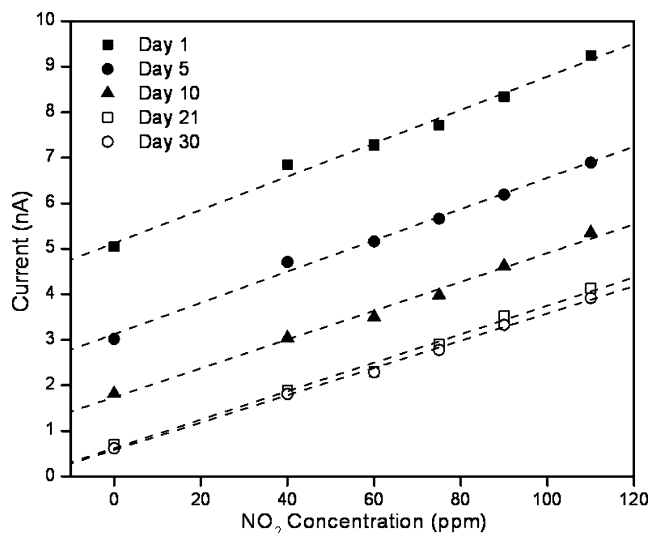


Fig. 11. Calibration curves during the 30-day test period obtained from the data in Fig. 10.

in signal, as shown in Fig. 9b. This behavior can be understood from the *I*–*V* curves, as increasing the concentration of O₂ should give rise to an increased current at a fixed potential. The total increase in current from the change in O₂ between 4% to 13.5% is ~1 nA, and the change in baseline with O₂ accounts for the increase in signal with both NO₂ and O₂ present.

3.6. Stability

To test the long-term stability of the sensor, a type B sensor was tested at 500 °C for 30 days with O₂ (3%) and NO_x (40–110 ppm), and the data is presented in Fig. 10. There is a drift in the background signal with time, which approaches steady state after 15 days. The calibration curves obtained at various times are shown in Fig. 11. The slopes of the calibration curves are similar, which implies that the signal drift could be corrected periodically from the baseline signal.

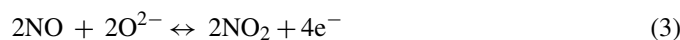
4. Discussion

Detection of NO or NO₂ by application of a bias potential, followed by measurement of current due to the electrochemical oxidation or reduction, has been reported in the literature [8,22]. The novelty of this study is the use of PtY to equilibrate the NO_x prior to electrochemistry, thus providing a total NO_x sensor at high temperatures. In order for the efficient equilibration of the NO_x species, an active catalyst is necessary. Previous studies have shown that Pt/Al₂O₃ is effective for NO_x equilibration [15]. In our earlier study, the Pt dispersed within and outside zeolite Y was found to equilibrate NO_x at temperatures over 400 °C [17]. In this study, the Pt loading has been decreased to 4 wt% and as shown in Fig. 4 is an effective catalyst for NO_x equilibration at 500 °C. The advantage of using zeolite as a support is its porosity and high surface area and its ability to stabilize nanometer-sized Pt clusters.

When NO_x was passed through a 500 °C PtY filter, a thermodynamic equilibrium with 3% O₂ was reached, as evident from

the drop in current to ~ 0 nA at 0 mV in the I - V curve since there is no thermodynamic driving force for the electrochemical NO_x reaction with equilibrated NO_x (plot c, Fig. 5). Plots d and e in Fig. 5 from the type B sensor have almost identical shapes and similar to sensor A with NO passing through the 500 °C PtY filter (plot c). This indicates that the coated PtY layer in type B sensor works well to equilibrate NO_x , and the performance is similar to the PtY filter. These data also suggest that if the working electrode is polarized to certain potential between 100 and -25 mV, the same current will be observed regardless of the NO/ NO_2 ratio, and is the basis for the sensing strategy in this paper.

In optimizing the sensor response, choices needed to be made involving the type of polarization (cathodic versus anodic) and the magnitude of polarization. We chose to apply an anodic potential based on the I - V data shown in Fig. 5. Anodic polarization promotes reaction (3).



and at 80 mV, the currents from NO or NO_2 in the anodic polarization range overlap with each other, as shown in Fig. 5, leading to a total NO_x sensor.

Also, choice of 80 mV for the anodic polarization should minimize the electrode degradation. Even at this low voltage, the long-term tests show a drift in background signal with 3% O_2 , as shown in Fig. 10. Several studies have reported the formation of surface Pt-O species [23]. The aging effect can arise from coarsening of electrode microstructure, an effect especially marked at large polarizations [24–26]. AFM studies have shown that polarization can also create morphological change on the surface of the YSZ underneath the Pt electrode [27].

Comparison with amperometric sensor designs employing cathodic polarization is helpful. In particular, the reduction of NO to N_2 has also been used for NO detection:



Even though reaction (4) is thermodynamically favorable, breaking the strong N-O bond leads to high activation energy [7,28]. Thus, high cathodic polarization (more negative than -400 mV) is required to promote the reaction [9,29]. In the presence of oxygen, competitive oxygen reduction will also create a current, which could be significant [30,31], thereby necessitating that such devices remove oxygen thoroughly before the gas mixture reaches the NO reduction electrode.

Sensor B shows higher sensitivity by a factor of two at 1–10 ppm NO_x as compared to 20–120 ppm NO_x concentrations. The interpretation of this observation is not clear. One possibility is that NO_x equilibration at higher concentrations is incomplete, but that is unlikely since the type A sensor with a PtY filter also shows this effect. Another possibility is that the electrochemical conversion of NO to NO_2 under anodic polarization is incomplete at high concentrations, thereby leading to smaller signals.

The sensing strategy proposed in this paper is similar to a previous report using NASICON (Na^+ -superionic conductor) as an electrolyte and Pt/ WO_3 as a double catalyst layer [22]. This

amperometric device worked up to temperatures of ~ 150 °C and measured total NO_x down to ~ 1 ppm. A higher temperature system based on CdCr_2O_4 electrode and YSZ electrolyte, operating at a bias potential of +100 mV detected NO at 500 °C with discrimination against NO_2 , H_2 , CO, CH_4 , CO_2 and water vapor. Long-term operation of these sensors was not examined [8].

The device presented in this paper allows for total NO_x measurements due to the use of Pt-loaded zeolite Y at a temperature of 500 °C. In addition, as shown in Fig. 7, the response and recovery times of sensor B track the extensively used chemiluminescence analyzer, the most common technique for NO_x detection. A drift in the background is observed which takes 2 weeks to stabilize, though the slopes of the calibration curves over month-long operation remained unchanged. The use of PtY in this study leads to the removal of CO interference due to the oxidation of CO to CO_2 , which is electrochemically inactive under the operational conditions of the sensor. The present device does exhibit minor oxygen interference, which can be further minimized by operating at a lower anodic polarization, but will also lead to a reduced NO_x signal.

5. Conclusion

This study reports on the design and performance of an amperometric device to detect total NO_x at temperature of 500 °C. By use of a Pt-loaded zeolite, the NO/ NO_2 is brought to equilibrium in the presence of O_2 . The current measured arises due to imposition of an anodic polarization (80 mV) that oxidizes the equilibrated NO further. The Pt-zeolite can be integrated with the sensor as a coating to simplify the sensor design. This total- NO_x sensor has a low NO_x detection limit, high NO_x selectivity as compared to oxygen, no CO response and a linear response with NO_x concentration. However, aging effects were observed and good stability was observed only after several days of operation, though the calibration curves maintained the same slope over a month-long testing period.

Acknowledgement

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Biographies

Jiun-Chan Yang received his BS degree in 1995 from National Chiao-Tung University, Hsin Chu, Taiwan, and a MS degree in Chemistry from National Taiwan University in 1997. He is currently working for his PhD degree in Chemistry at the Ohio State University, where his research is focused on solid-state electrochemical devices for gas sensing.

Prabir K. Dutta received his PhD degree in Chemistry in 1978 from Princeton University. After 4 years of industrial research at Exxon Research and Engineering Company, he joined The Ohio State University, where currently he is the Robert K. Fox Professor and Chairman of the Department of Chemistry. His research interests are in the area of solid state chemistry and materials science.