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“NO-selective” NO_x sensing elements for combustion exhausts

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Abstract

Fabrication and characterization of NO_x sensing elements using co-planar oxide and Pt electrodes is described. The sensing elements, based on yttria-stabilized zirconia substrates, could be current-biased to a “NO-selective” sensing condition (for NO_x in the concentration range 50–1500 ppm_V) if the oxide was an alkaline earth-modified lanthanum chromite. Simple variations in electrode geometry (interdigitation of the electrodes or increase of the oxide electrode surface area relative to the Pt electrode) did not affect the magnitude of the NO response or the recovery from exposure to NO. The main effects of temperature appeared to be a decrease in the response magnitude with increasing T and an increase of the recovery time (from NO exposure) with decreasing T.

Keywords: NO_x sensor; Nitric oxide; Gas sensor

1. Introduction

The three main pollutants (excluding CO_2) in combustion exhausts from low-sulfur fuels are carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x, a mixture of NO and NO_2). Currently, for the exhausts from fuel-injected, spark-ignited engines, a three-way catalyst (TWC) is employed that greatly reduces the levels of all three pollutants (CO, HC, and NO_x). The TWC is only effective within a narrow range of O_2 concentrations in the exhaust [1], losing its effectiveness for NO_x removal at higher $[O_2]$. Therefore, the presently used TWC cannot be employed for NO_x remediation of exhausts from diesel and lean-burn gasoline engines, as these tend to be O_2-rich.

If a suitable “lean NO_x” catalyst is not developed, diesel and lean-burn gasoline exhausts will require on-board NO_x remediation with techniques such as selective catalytic reduction (SCR) or lean NO_x traps (LNT). Both of these techniques will require on-board NO_x sensors, to control either reagent injection (SCR) or trap regeneration (LNT). Broadly speaking, a suitable NO_x sensor for these applications would be operative at temperatures near 600 °C and able to measure $[NO_x]$ in the concentration range 10–1000 ppm_V [2,3].

It is important to realize that at these elevated temperatures (∼600 °C) the dominant equilibrium NO_x species is the monoxide (NO) [4], and thus the focus of this work is to develop sensing elements that can respond to NO at temperatures near 600 °C. The technique employed is “biasing”, in which a dc electrical signal is applied to the sensing element. This technique has previously been employed for NO_x sensing by Ho et al. [5], who applied DC voltages to a sensing element consisting of Nd_2CuO_4 and Pt electrodes on opposite sides of a yttria-stabilized zirconia (YSZ) disk. The presence of NO_x produced an increase in DC current (I) at 400 °C. DC voltage biasing of elements similar to those described by Ho et al. was also reported by Grilli et al. [6], except the oxide electrode was $LaFeO_3$ and testing was carried out at 450 °C.

Miura et al. [7] applied DC voltages (in the range 0.1–0.5 V) to YSZ-based sensing elements consisting of one Pt electrode and one $CdCr_2O_4$-coated Pt electrode. Two designs were presented, the first was a tubular design in which only the $CdCr_2O_4$-coated electrode was exposed to the NO_x-containing gas. In the second design, the electrodes were co-planar and both were exposed to the NO_x. The DC current between the electrodes was shown to be proportional to $[NO_x]$ for both designs, and the tubular design could be biased to a “NO-selective” condition at 500 °C.

In this study we are attempting to extend and build upon this prior work by increasing the operating temperature above

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500 °C, and systematically examining the effects of varying both electrode materials and electrode geometry. We also explore the use of constant current (as opposed to constant voltage) biasing, and focus on sensing elements with co-planar electrodes.

2. Experimental procedure

The geometries of the sensing elements prepared for the present investigation are shown in Fig. 1a. All geometries consisted of co-planar oxide and Pt electrodes on a YSZ substrate. Most of the sensing elements prepared had the “semi-circular” (SC) geometry, the other two geometries (“inter-digitated” (ID) and “asymmetric” (AS)) were considered variations on the SC geometry with approximately the same total area. The YSZ (8 mol% Y_2O_3, Tosoh) substrate was produced by tape casting, laminating, and sintering (1400 °C, 2 h, air) to produce disks about 16 mm in diameter and 1 mm in thickness. The electrodes were applied by first screen printing and firing (1100 °C, 0.3 h, air) the Pt (Electroscience) electrode and then screen printing and firing the oxide electrode for one hr. in air. The Pt was obtained as a dispersion ready for screen printing and the screen-printing dispersions for the oxides were produced in-house.

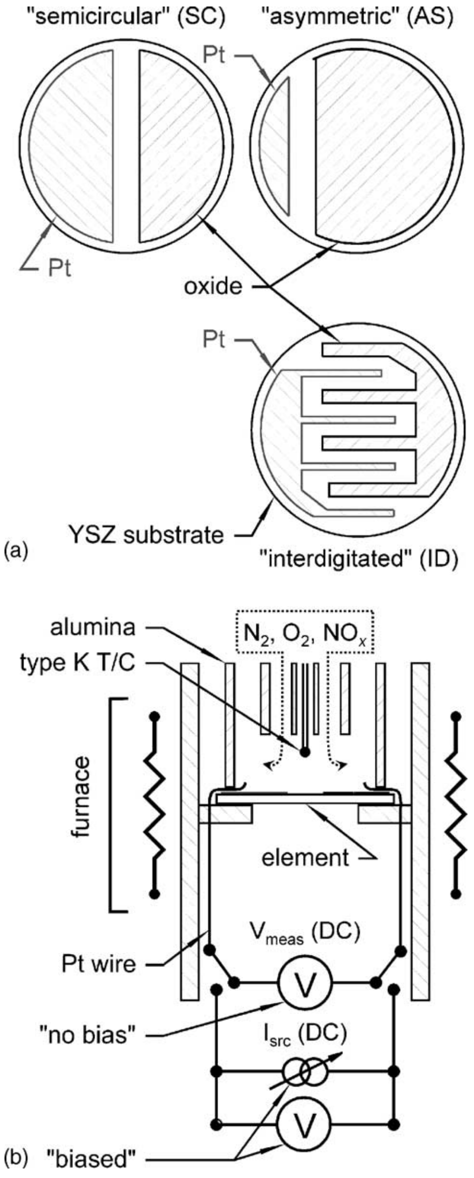

Fig. 1. Schematic view of sensing element geometries (a) and the test apparatus for evaluating NO_x sensing performance (b).

Table 1
Electrode materials and firing conditions

Material	Vendor	Firing T, t (°C, h)
Pt	Electroscience	1100, 0.3
NiO	J.T. Baker	1100, 1.0
ZnO	Alfa Aesar	1100, 1.0
$La_{0.80}Sr_{0.20}FeO_{3-\delta}$ (LSF)	Praxair	900, 1.0
$La_{0.85}Sr_{0.15}CrO_3$ (LSC)	Praxair	900, 1.0
$La_{0.85}Ba_{0.15}CrO_3$ (LBC)	Praxair	900, 1.0

Several different oxides were employed as electrode materials, and these are listed in Table 1. These were selected either for their reported usefulness as semiconducting gas sensor materials (ZnO and NiO [8]), or materials with high electrical conductivity (LSF, LSC and LBC [9]). The firing temperatures of the oxide electrodes are listed in Table 1, it can be seen there that the perovskite (LSC, LBC, and LSF) electrodes were fired at lower temperature than the binary oxide (NiO and ZnO) electrodes. This was done in order to avoid reaction between the La-containing perovskites and the YSZ, as described by Yamamoto et al. [10].

Fig. 1b shows schematically the apparatus used to characterize NO_x sensing performance. The elements were placed, centrally located, in a resistively heated furnace and pressure contacts to the elements were made with Pt wire. An Environics 4000 gas mixing unit (not shown in Fig. 1b) was used to mix N_2, O_2, and NO_x (5000 ppm NO or NO_2 in N_2) and these mixtures were presented to the electroded side of the sensing elements at a flow rate of 0.75 l/min. A type K thermocouple was placed approximately 1 cm from the electroded element surface and was used to monitor the sensing element temperature. The temperature indicated by this thermocouple typically was about 3–5° lower than that indicated by the furnace control thermocouple, which was located just outside the resistive heating elements of the furnace. As indicated in Fig. 1b, voltage measurements were made both with and without bias. For measurements without bias, a Keithley 617 electrometer was used to measure the DC voltage developed across the element electrodes, and for measurements with bias, a Keithley 2400 source meter was placed in parallel with the electrometer.

Primarily, two types of NO_x sensing performance evaluations were carried out, both at constant temperature and a constant $[O_2]$ of 7 vol.%. In the first type, intended to gauge the effect of different current biases on the NO_x response of the elements, the bias was stepped at discrete levels (e.g.,