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Sensors and Actuators B 106 (2005) 758–765

SENSORS AND ACTUATORS B CHEMICAL

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Use of $La_{0.85}Sr_{0.15}CrO_3$ in high-temperature NO_x sensing elements

D.L. West*, F.C. Montgomery, T.R. Armstrong

Metals and Ceramics Division, Oak Ridge National Laboratory, Bldg 4508, MS 6083, Oak Ridge, TN 37831, USA

Received 17 March 2004; received in revised form 15 September 2004; accepted 23 September 2004

Abstract

This work focuses on use of the electronically-conducting oxide $La_{0.85}Sr_{0.15}CrO_3$ (LSC) in solid electrolyte-based NO_x sensing elements intended for operation at $T \sim 650\,^{\circ}C$. Two different investigations are described, in the first LSC was used as a direct substitute for Pt. The substitution led to decreased sensitivity to NO_2 and an enhancement of the NO response, although the NO_2 response was still much larger in magnitude and opposite in sign. Fabrication and evaluation of sensing elements with co-planar LSC and Pt electrodes comprised the second investigation. The measured NO_x sensing performance of these elements was commensurate with that of the elements fabricated in the first phase of the investigation (e.g., 450 ppm_v NO_2 in 7 vol% O_2 produced ~50 mV at 600 °C) and the response/recovery times for NO_2 sensing were improved. The results indicate that LSC could be useful in these types of sensing elements, both as a substitute for, and in combination with, Pt.

Keywords: Gas sensors; Lanthanum strontium chromite; Nitrogen dioxide; Nitrogen monoxide

1. Introduction

Oxides of nitrogen ("NO_x", a mixture of primarily NO and NO_2) are formed during combustion processes and are considered pollutants if exhausted to the atmosphere. These pollutants are typically removed from large-scale, fixed installations by selective catalytic reduction (SCR) and other technologies [1]. Currently, NO_x is removed from spark-ignited, passenger-car engine exhausts with a three-way catalyst (TWC), but the TWC is only effective for NO_x removal if the oxygen level in the exhaust is controlled within narrow limits [2]. Therefore, the current TWC cannot be applied to exhaust treatment for diesel engines and "lean-burn" gasoline engines, as the exhaust from these engines is too oxygen-rich for effective operation of the TWC.

If a TWC suitable for use in oxygen-rich exhausts is not developed, then some type of on-board remediation scheme must be employed to reduce the NO_x levels. Many of the on-board remediation techniques under investigation (such as SCR with urea) require the injection of species that themselves would be considered pollutants (or decompose into pollutants) if exhausted or "slipped" into the atmosphere. Thus, it is essential to develop compact and accurate sensors that can measure NO_x levels in oxygen-rich exhausts to aid in the precise dispensation of reducing agents. The ideal sensor would be operative at temperatures around 700 °C, capable of sensing NO_x levels in the range of 100–1000 ppm, and relatively insensitive to $[O_2]$ variations in the exhaust gas [3].

Two approaches to NO_x sensing at "high temperature" ($T \sim 700\,^{\circ}C$) using electroceramics have appeared in the literature: "amperometric" or "limiting-current" methods [4,5] and "mixed-potential" methods [6,7]. Amperometric techniques rely on measuring the oxygen-ion current generated by electrochemical decomposition of NO_x. The major challenge for this technique is separating the current due to the decomposition of NO_x from that due to the decomposition of O_2. One approach [8] which has been commercially applied, employs sequential chambers (reaction zones), the first zone for removal of O_2 and the second for electrochemical decomposition of NO_x (specifically, nitric oxide (NO)).

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* Corresponding author. Tel.: +1 865 576 2264; fax: +1 865 574 4357.
E-mail address: westdl@ornl.gov (D.L. West).

0925-4005/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2004.09.028

“Mixed-potential” sensing typically involves measuring the potential developed between two different electrodes. A mixed potential [9,10] arises when cathodic (reduction) and anodic (oxidation) reactions involving NO_x and O_2 occur simultaneously on an electrode. Each of the reactions has a defined V–I characteristic. If the net current ($I_{cathodic} + I_{anodic}$) across the electrode is held at zero, then there will be a unique voltage at which $|I_{cathodic}| = |I_{anodic}|$ for a given [NO_x] and [O_2]. The mixed potential is an example of a “non-Nernstian” or “non-equilibrium” phenomenon [5], wherein the potential developed between two electrodes on an oxygen-ion conducting electrolyte is not governed strictly by the partial pressure of O_2 over each electrode.

The present investigation explores the application of the electronically-conducting oxide $La_{0.85}Sr_{0.15}CrO_3$ (LSC) [11,12] in non-Nernstian NO_x sensing elements. First, LSC was employed as a direct substitute for Pt. Pt is costly and can be catalytic for oxidation and other electrochemical phenomena. Therefore, such a substitution could lower the materials cost of the elements, afford more opportunity to engineer the element microstructure, and allow (through composition modification of the electronically-conducting oxide) one to tailor the electrochemical and catalytic behavior of the elements. The general approach for this phase of the investigation was to fabricate sensing elements differing only in the material used as the electronic conductor (LSC or Pt).

For the second phase of the investigation, sensing elements with co-planar LSC and Pt electrodes were fabricated. This material combination has been used previously for potentiometric NO_x sensing devices [13], but the present investigation differs in that a co-planar design without an air reference was employed.

2. Experimental procedure

Fig. 1 shows the multi-layered sensing element geometry for the first phase of the investigation (substitution of LSC for Pt). The substrate for the sensing elements was yttria-stabilized zirconia (YSZ) (8 mol% Y_2O_3–substituted ZrO_2, TZ–8Y, Tosoh, NJ). The YSZ was tape cast, laminated, and sintered at 1350 °C for 2 h in air to produce disk-shaped forms about 1.6 cm in diameter and 0.1 cm in thickness.

Table 1
Specimens prepared to investigate the substitution of $La_{0.85}Sr_{0.15}CrO_3$ (LSC) for Pt

Sample ID	SE material	RE/CC material
NC2/Pt	$NiCr_2O_4$[a]	Pt[b]
NC2/LSC	$NiCr_2O_4$	$La_{0.85}Sr_{0.15}CrO_3$[c]
LSCF/Pt	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$[d]	Pt
LSCF/LSC	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	$La_{0.85}Sr_{0.15}CrO_3$

The RE/CC and SE are defined in Fig. 1. For all electrode materials other than Pt, screen-printing inks were fabricated in-house from the listed oxides.

[a] Cerac (Milwaukee, WI) #N-1086.

[b] Electroscience (King of Prussia, PA) #5547-1F-P.

[c] Praxair Specialty Ceramics (Woodinville, WA) #03-P3286.

[d] Praxair #03-P4065.

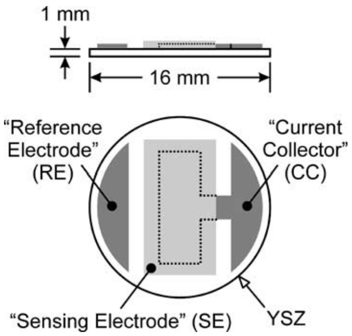

Fig. 1. Sensing element geometry for investigating the substitution of LSC for Pt. The element consists of two screen-printed layers on a yttria-stabilized zirconia (YSZ) substrate.

A patterned layer of either LSC or Pt, comprising the reference electrode (RE) and current collector (CC) (Fig. 1), was screen-printed onto one broad face of the YSZ disks, air-dried, and fired at 1100 °C for 0.3 h in air. A second screen-printed layer, the sensing electrode (SE), was then patterned over a portion of the CC as shown in Fig. 1, air-dried, and fired at 1100 °C for 1 h in air.

The effect of substituting an electronically-conducting oxide (LSC) for Pt was studied by fabricating two pairs of sensing elements with nominally identical SE materials. The elements prepared are listed in Table 1 and consisted of $NiCr_2O_4$ (NC2) SE layers and $La_{0.8}Sr_{0.2}Co_{0.4}Fe_{0.6}O_3$ (LSCF) SE layers on both Pt and LSC RE/CC’s.

Element geometries for the second phase of the investigation are shown in Fig. 2. These LSC|YSZ|Pt elements also were based on a YSZ substrate and consisted of co-planar LSC and Pt electrodes prepared by screen printing and thermal treatment as described above. One element geometry consisted of semicircular electrodes on opposite halves of one face of the YSZ substrate while the other consisted of interdigitated LSC and Pt electrodes.

The response of the prototype devices was measured with the apparatus shown in Fig. 3. A four-inlet gas-mixing unit (Environics (Tolland, CT) 4000) was used to mix N_2, O_2, and NO_x (either NO (7000 ppm$_v$ in N_2) or NO_2 (5000 ppm$_v$ in N_2)) at room temperature. The composition of the test gas mixtures was typically in the range 7 vol% $\leq [O_2] \leq$ 20 vol%, 300 ppm$_v$ $\leq [NO_x] \leq$ 1500 ppm$_v$, with the balance being N_2.

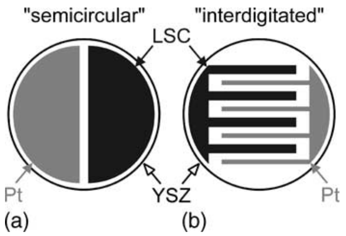

Fig. 2. Sensing elements with co-planar LSC and Pt electrodes. The diameter and thickness of the YSZ substrate are identical to the element shown in Fig. 1.