Sensors and Actuators B 187 (2013) 153–161

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

The effect of SO_2 on the sensitive layer of a NO_x dosimeter

A. Groß[a], D. Hanft[a], G. Beulertz[a], I. Marr[a], D.J. Kubinski[b], J.H. Visser[b], R. Moos[a,*]

[a] University of Bayreuth, Functional Materials, Universitätsstr. 30, 95440 Bayreuth, Germany
[b] Ford Research and Advanced Engineering, 2400 Village Road, Dearborn, MI 48124, USA

ARTICLE INFO

Article history:
Available online 24 October 2012

Keywords:
Low level NO_x detection
SO_2 poisoning
Dosimeter
SO_2 sensor
Lean NO_x trap
NO_x storage and reduction catalyst

ABSTRACT

The accumulating-type or integrating-type NO_x sensor works like a dosimeter being well suited for long-term total amount detection of low levels of NO and NO_2 while information about the instantaneous NO_x concentration is obtained from the signal derivative. A potassium-based lean NO_x trap material, known from automotive catalysts, is applied as sensitive material. It accumulates NO_x in the form of nitrates and thereby changes its conductivity with the NO_x loading state. Since SO_2 is known to poison the catalytic properties of LNTs, the effect of SO_2 on the sensing characteristics is addressed now. The competition between SO_2 and NO_2 for the accessible storage sites was found to affect the sensor signal in two ways: due to sulfate formation, the resistance of the LNT material decreases in the presence of SO_2 and the accumulating NO_x sensing properties are strongly reduced. However, a high reversibility of sulfur poisoning was obtained by desulfurization of the sensitive device at 650 °C in H_2 containing gas. The results reveal that with the presented setup, SO_2 detection is possible with a linear correlation between the conductivity and the exposed SO_2 amount. Since at 380 °C, the sensitivity to SO_2 is about half compared to NO_x, cross sensitivities need to be concerned. At higher temperatures nitrates are decomposed and the sensor is selective to SO_2.

1. Introduction

The integrating NO_x sensor is specially suited to detect low levels of NO and NO_2 (e.g. less than 5 ppm) for applications in harsh environments like the automotive exhaust or for air quality monitoring purposes [1]. By accumulating the analyte molecules in the sensitive layer, the total amount of the analyte species in a defined period is measured, enhancing the accuracy especially in the low ppm area [2]. The integrating NO_x sensor uses a lean NO_x trap (LNT) material as the sensitive coating. This material is known from NO_x storage catalysts (NSC), recently also called NO_x storage and reduction catalysts (NSR). NSRs reduce NO_x emissions in the automotive exhaust in two steps: Under excess oxygen conditions (lean exhaust gas) NO_x molecules are oxidized and stored in the carbonate-based materials as nitrates for some minutes, as described by Eq. (1) for a potassium-based catalyst, whereas they are later released and reduced to harmless N_2 during short (few seconds) rich-burn intervals [3–7].

$$K_2CO_3 + 2NO_2 + \tfrac{1}{2}O_2 \leftrightarrow 2KNO_3 + CO_2 \quad (1)$$

In addition to the alkaline (-earth) metal oxides and carbonates which are the NO_x storage components, LNT materials usually contain finely dispersed precious metal particles (like platinum) used as redox catalyst (e.g. to oxidized NO to NO_2 prior to the storage reaction), and oxygen storage materials (like ceria) to provide a buffer of oxygen. All the components are deposited together on nano-sized Al_2O_3 as support oxide [4–8].

The NO_x conversion of LNTs is hindered by SO_2 poisoning, particularly as SO_2 competes with NO_x for the accessible storage sites forming highly stable alkaline (-earth) sulfates, e.g. K_2SO_4 according to Eq. (2).

$$K_2CO_3 + SO_2 + \tfrac{1}{2}O_2 \leftrightarrow K_2SO_4 + CO_2 \quad (2)$$

Since it is known that SO_2 deteriorates the catalytic properties of LNTs [3–6,9,10], it is the aim of this study to investigate how SO_2 in the analyte gas affects the properties of the integrating NO_x sensor, as it has an LNT-based sensitive layer. The effect of SO_2 poisoning of the NO_x storage sites on the NO_x sensing characteristics and the possibility of regeneration will be discussed in detail.

2. Technical background and existing knowledge

2.1. The integrating NO_x sensor

The detection of small analyte concentrations with classical gas sensors is error-prone since base-line drifts and noise adulterate

* Corresponding author. Tel.: +49 921 55 7401.
E-mail address: Functional.Materials@Uni-Bayreuth.de (R. Moos).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.10.039

the sensor signal [11]. Additionally, in some applications like emission monitoring of automotive exhausts or air quality monitoring, the interest is instead on the cumulated amount or dose of the analyte in a given period of time or driven distance and the corresponding mean values of the concentration rather than on the instantaneous curve of the actual analyte concentration [12–14]. The integrating NO_x sensor is intended for long-term monitoring of low levels of total NO_x as the sum of NO and NO_2 in lean gas mixtures, e.g. in the ambient air atmosphere or in the exhaust of leanly operated vehicles. During a sorption period, the integrating NO_x sensor works similar to a dosimeter. By chemically accumulating NO_x molecules in the sensitive storage layer, the sensor signal $|\Delta R|/R_0$ correlates with the total amount of NO_x, A_{NO_x}. In general, the actual amount or dose of analyte gas, A_{gas}, in a given time interval can be calculated from the analyte concentration, $c_{gas}(t)$, and the flow rate, $\dot{V}(t)$, according to Eq. (3):

$$A_{gas} = \int c_{gas}(t) \cdot \dot{V}(t)\,dt \quad (3)$$

In the case of a constant gas velocity, A_{gas} is proportional to the timely integral of $c_{gas}(t)$, i.e. $A_{gas} \propto \int c_{gas}(t)\,dt$ with the unit ppm s. After the sorption period, the storing material has to be regenerated either in reducing atmospheres or at high temperatures to release the formerly stored analyte molecules. Then, the next sorption period starts.

The potassium carbonate-based material used as sensitive layer is able to accumulate NO_x molecules chemically by forming nitrates according to Eq. (1). This material conversion (from carbonate to nitrate) results in changing electrical properties. In particular, the conductivity was found to increase with progressive nitrate formation enabling the *in situ* monitoring of the catalyst [15–17]. The integrating NO_x sensor, as a novel approach, utilizes the dependency of the conductivity of LNT materials on the NO_x loading state to sense the level of NO_x in the surrounding atmosphere [2,18].

In Fig. 1, the accumulating gas sensing principle is described schematically for the case of a constant gas velocity. Since with the integrating sensor the amount, A_{gas}, of a gas species (here NO_x, A_{NO_x}) is determined directly, the characteristic line correlates the sensor signal, $|\Delta R|/R_0$, with A_{NO_x}. A_{NO_x} is the accumulated amount of NO_x that was exposed to the sensor during the measurement period, as shown in Fig. 1a. Ideally, this is a linear correlation characterized by the sensitivity, S_{NOx}, which is the slope of the characteristic line as defined by Eq. (4). Linearity occurs if the NO_x uptake does not depend on the loading level, if the sensitive layer provides a sufficient number of storage sites and if saturation effects do not limit the NO_x storage reaction. To achieve integrating sensing properties, nitrate has not only to be formed progressively in the presence of NO_x, but additionally NO_x must not be released from the formed nitrate in the case of a decreasing NO_x concentration in the gas phase, particularly in 0 ppm NO_x. For the gas sequence shown by the dashed line Fig. 1c, the NO_x uptake and storage results in a step-like curve of $|\Delta R|/R_0$ as shown in Fig. 1b: $|\Delta R|/R_0$ increases if NO_x is present and remains constant in the absence of the analyte (holding capability). Since $|\Delta R|/R_0$ correlates linearly with A_{NO_x} in the low loading state, the slope of the curve depends on the actual NO_x concentration, c_{NO_x}. This linearity between the signal derivative, $|d(R/R_0)/dt|$, and c_{NO_x} can be used to obtain information about the instantaneous NO_x level as demonstrated in the solid line of Fig. 1c.

In the operation of dosimeter-like sensors sensing periods alternate with regeneration steps. The latter are necessary to recover the storage capacity as saturation effects occur and the linearity diminishes. In the case of the LNT-based cumulative NO_x sensor presented here, the correlation was found to be linear up to a resistance change of about 40 % at an operation temperature of 380 °C [1]. The formed nitrates can be decomposed in rich gas atmospheres at 380 °C or at elevated temperatures, e.g. at 650 °C [4,19].

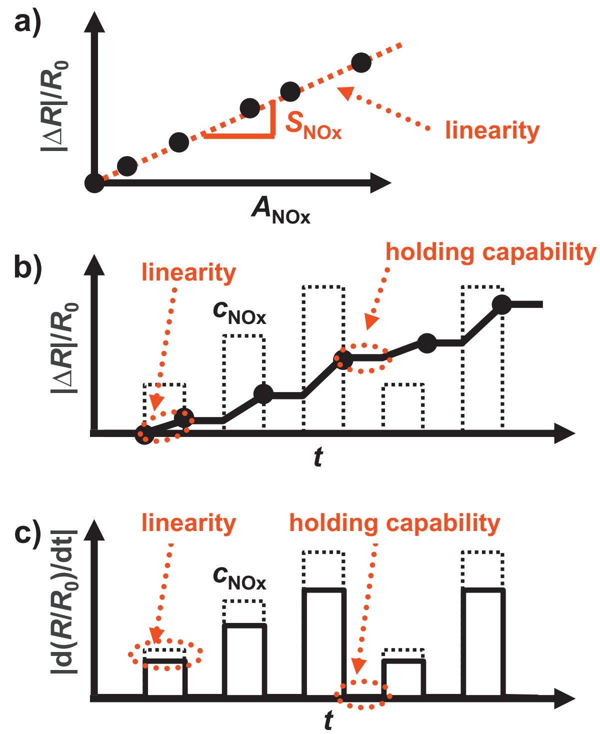

Fig. 1. Schematic description of the accumulating sensing principle: (a) the characteristic line gives a linear correlation between the sensor signal, $|\Delta R|/R_0$, and the total analyte amount A_{NO_x}, (b) $|\Delta R|/R_0$ increases in the presence of NO_x with a slope correlating with the NO_x concentration, c_{NO_x}, (c) determination of the curve of $c_{NO_x}(t)$ using the signal derivative $|d(R/R_0)/dt|$. The actual concentration is shown by the dashed lines in (b) and (c).

Applying accumulating sensing layers is not only suited for measuring directly the cumulated amounts and mean values during long-term applications. In particular, it is also advantageous for low level detection applications as it helps to overcome uncertainties in the 0 ppm sensor response which plague the accuracy of most sensors in this regime. By accumulating analyte molecules in the sensitive layer, even small levels contribute to the sensor signal. The approach outlined in Fig. 1c reduces deterioration of the sensor accuracy in low levels of NO_x due to long-term baseline drifts (i.e. drifts in the 0 ppm response) caused by a slowly varying resistance of the base material as it ages. The sensitivity to NO and NO_2 was found to be almost equal which is the result of the oxidizing properties of the sensitive coating [1]. Measuring changes in the NO_x loading state instead of steady state values results in very fast sensing characteristics. The response and recovery times of $|d(R/R_0)/dt|$ are found to be faster than 8 s (the gas exchange time of the system in [1]). A_{gas} can be determined properly even if the flow rate varies by using a special channel-type setup that stores all incoming analyte molecules [20]. Cross sensitivities of the integrating NO_x sensor to CO_2 and O_2 in the ambience are addressed in [2] and are found to be negligible between 1.5% and 10% CO_2 and between 2.5% and 7.5% O_2. Additionally, it was demonstrated that the sensing characteristics depend on the temperature with a trade-off between an increasing sensitivity and a decreasing linear measurement range as the operation temperature increases [18]. A more detailed description of the sensing principle and its benefits for long-term monitoring applications with low levels of analytes can be found in [1].