Integrating NO_x Gas Sensor: Concept, Sensitivity to NO/NO_2 and Benefits of the Integrating Sensing Principle

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Abstract

The novel integrating NO_x gas sensor concept provides the opportunity to detect very low NO_x levels, as they appear for instance downstream of automotive catalytic converters, with a high sensitivity and accuracy. Unlike common gas sensors, the integrating NO_x sensor detects the amount of NO_x during the measurement period instead of the actual NO_x concentration. The integrating sensing concept is realized by using a lean NO_x trap material as sensitive layer, accumulating a constant fraction of the upcoming exhaust NO_x molecules in the sensitive layer. The chemical storage of NO_x in the form of nitrates goes along with a change in the electrical properties of the lean NO_x trap material serving as sensor signal. In this contribution, the details of the integrating sensing concept are explained and the benefits of this novel gas sensing method are pointed out. The measurement data demonstrate the integrating properties of the NO_x sensor. In addition, the issues of varying NO_x concentrations and sensitivities to both NO and NO_2 are addressed.

Introduction

Reliable NO_x sensors with a high sensitivity and a sufficient accuracy especially in the low-ppm detection range are required to meet the stringent automotive emission regulations and particularly the On-Board-Diagnostics (OBD) of exhaust after-treatment systems in modern diesel and lean-burn gasoline vehicles,. For this purpose, the idea of an integrating NO_x-sensor was developed. By using a lean NO_x trap (LNT) material, known from automotive NO_x storage catalysts, as the gas sensitive layer, the presence of very low NO_x-amounts can be detected by accumulating a constant fraction of the upcoming NO_x molecules in the sensitive layer. The integrating sensor concept is especially suited for the challenging demands posed by the OBD requirements because it is measuring the total amount of NO_x in the exhaust during a measurement period instead of detecting instantaneously the low NO_x concentration. Therefore, the output signal of the integrating NO_x sensor correlates linearly with the total accumulated amount of NO_x exposed to it during the measurement interval. In the following, the integrating measurement principle will be described in detail. In addition, the setup of the integrating NO_x sensor will be described and measurement results shown which demonstrate the integrating properties.

Integrating Sensor Concept

LNTs, also known as NO_x storage and reduction catalysts (NSR, NSC), were developed for automotive exhaust aftertreatment systems of leanly operated vehicles to reduce NO_x emissions [1]. In lean atmospheres at about 350-400°C (dependent on the ma terial) they are able to adsorb and store NO_x from the exhaust gas stream. LNTs contain finely dispersed precious metal particles like Pt to oxidize NO molecules to NO_2 (1).

$$NO + \tfrac{1}{2}O_2 \leftrightarrow NO_2 \qquad (1)$$

The NO_x-storage component itself is typically an (earth-) alkaline metal oxide or carbonate, abbreviated M. In excess oxygen, NO_2 can be stored chemically on the storage sites, MCO_3 e.g. $BaCO_3$, by forming nitrates, $M(NO_3)_2$ (2).

$$MCO_3 + 2NO_2 + \tfrac{1}{2}O_2 \leftrightarrow M(NO_3)_2 + CO_2 \qquad (2)$$

Since the storage capacity of the LNT is limited, the storage efficiency decreases with time and the storage sites need to be regenerated to recover the full storage performance. To regenerate automotive LNTs the motor management switches to a rich atmosphere for a short period. In the presence of the reducing gases, the nitrate decomposes and the released NO is reduced to N_2 (3).

$$M(NO_3)_2 + 5H_2 + CO_2 \leftrightarrow MCO_3 + N_2 + 5H_2O \qquad (3)$$

The concept of the integrating NO_x sensor bases on the successive accumulation of NO_x molecules in the form of nitrates in the sensitive LNT layer in between the electrodes. Due to the oxidizing properties of the LNT-material both, NO and NO_2, can be stored as nitrates. This material transformation is accompanied by changes in the electrical properties of the material. Thus, ideally the recording of the electrical properties of the sensitive layer (e.g. the complex impedance $\underline{Z}$) enables the detection of the time-integrated amount of NO_x, A_{NOx}, instead of the actual NO_x-concentration, c_{NOx}.

In Fig. 1, the estimated response of an ideally integrating NO_x sensor (black line) on several NO_x steps (grey bars) is illustrated. The sensor signal is expected to increase in the presence of NO_x due to the formation of nitrates. In intervals with a constant NO_x concentration (grey regions), the sensor signal will increase linearly as the added amount of NO_x stored on the sensor per second is constant. This correlates with the total amount of NO_x offered to the sensitive layer, A_{NOx}, which also increases linearly over the constant NO_x interval. In the absence of NO_x (white regions), A_{NOx} remains constant and the sensor signal is also expected to remain unchanged, with a slope on the time scale equal to zero. The linearity during storage (in constant NO_x) and the sufficient holding capabilities (in the absence of NO_x) are essential for realization of the truly integrating NO_x sensing principle. Since the number of storage sites is finite, the storage capacity is limited and saturation effects lower the sensitivity at the higher loaded state requiring regeneration of the storage sites (e.g. in the rich atmosphere).

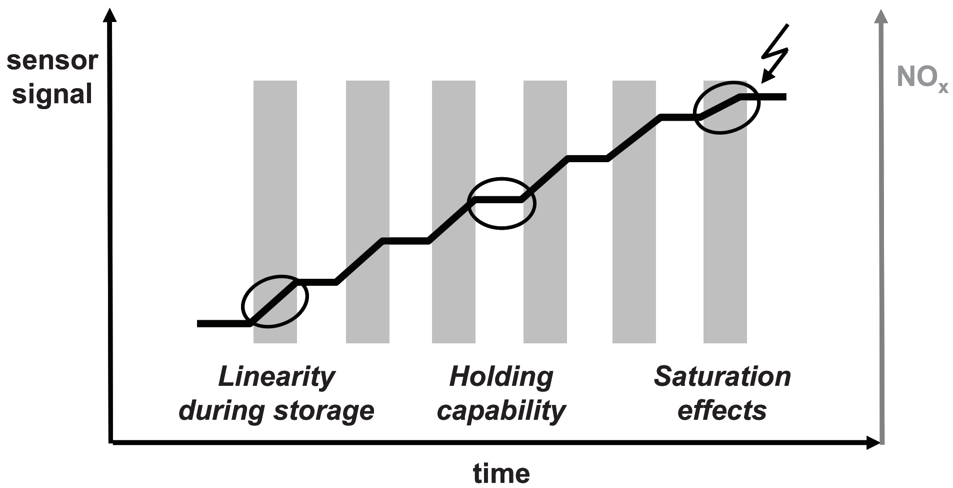

Fig. 1: Expected sensor response of an ideal integrating NO_x-sensor on several NO_x-steps due to successive loading with NO_x. The essential properties are “linearity during storage” and “holding capability” at 0 ppm NO_x.

As can be seen in Fig. 2, the obtained characteristic line gives a linear correlation between the sensor signal and A_{NOx}, being the total amount of NO_x offered to the sensor since its last regeneration period. The sensor requires regeneration as the storage sites fill to the point that characteristic line becomes nonlinear in the presence of constant NO_x. The beginning of the nonlinearity depends on the material and the layer morphology. It may occur above several ten percent of resistance change.

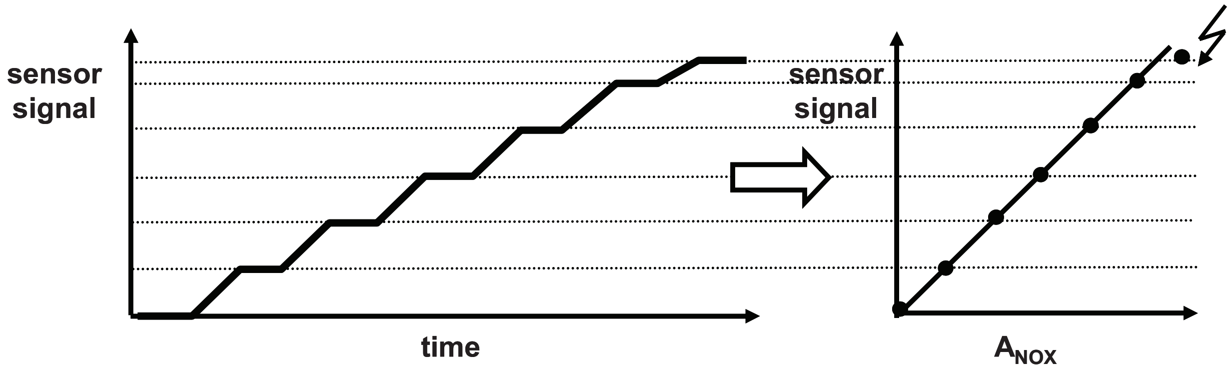

Fig. 2: Characteristic line of the integrating NO_x sensor obtained from measured sensor response on several NO_x-steps: Linear correlation of the sensor signal and the total NO_x-amount A_{NOx} till saturation lowers the sensitivity

This novel, integrating sensing principle promises a higher sensitivity and an increased accuracy especially in the case of very low NO_x concentrations compared to conventional NO_x sensors measuring c_{NOx}. Therefore, the integrating sensing principle seems very well suited for monitoring purposes as for instance required for the OBD in lean burn engines.

Experimental

The proposed integrating NO_x-sensor consists of platinum or gold interdigital electrodes (IDEs) on an alumina substrate coated with a carbonate-based LNT material as NO_x-sensitive layer, as illustrated in Fig. 3.

To demonstrate the integrating properties, the sensor samples were measured at 350℃ in lean gas atmospheres with and without NO_x (10% O_2, 5% CO_2, 2% H_2O in N_2). These sensors were later regenerated in rich atmospheres (1,5% H_2, 5% CO_2, 2% H_2O in N_2) to clean the storage sites.

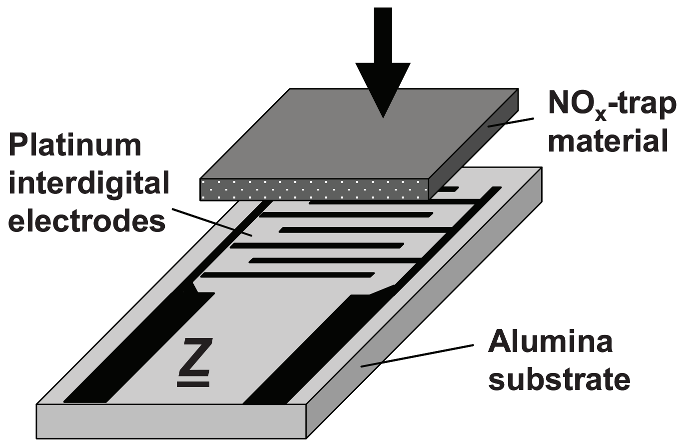

Fig. 3: Sensor setup consisting of an electrical transducer in the form of interdigital electrodes on an alumina substrate covered with a lean NO_x-trap material.

First tests demonstrated, that the complex impedance of the LNT material can be described by the model of a resistance in parallel to a capacitor (R||C equivalent circuit) [2,3]. Therefore, in our tests the resistance value R was calculated from the complex impedance measured continuously at a frequency of 1000 Hz and an applied ac voltage of 1 V. We define the sensor signal as the absolute value of the relative resistance change, $|\Delta R/R_0|$, relative to the resistance in the unloaded state, R_0.

Results and discussion

The measurement data plotted in Fig. 4 verify that the proposed integrating NO_x sensor using a carbonate-based LNT-material as sensitive layer works as expected. The sensor signal, the relative resistance change $|\Delta R/R_0|$, increases in periods with NO in the gas stream but remains almost constant in the absence of the analyte gas (Fig. 4a). The exposure to 10 ppm NO instead of 5 ppm results in a double increase of $|\Delta R/R_0|$ on the time scale demonstrating the required linearity. Using those measurement data, the resulting characteristic line in Fig. 4b gives a linear correlation of $|\Delta R/R_0|$ and A_{NO} independent on the actual c_{NO}, whereas the increase of $|\Delta R/R_0|$ on the time scale depends linear on the actual NO-concentration.

These data demonstrate that the integrating NO_x sensor is able to detect even very low levels of NO like 5 ppm for 25 s with a high sensor signal, that the sensor signal correlates linearly with the NO-amount and that the material is not desorbing the stored NO_x in periods with 0 ppm (holding capability).

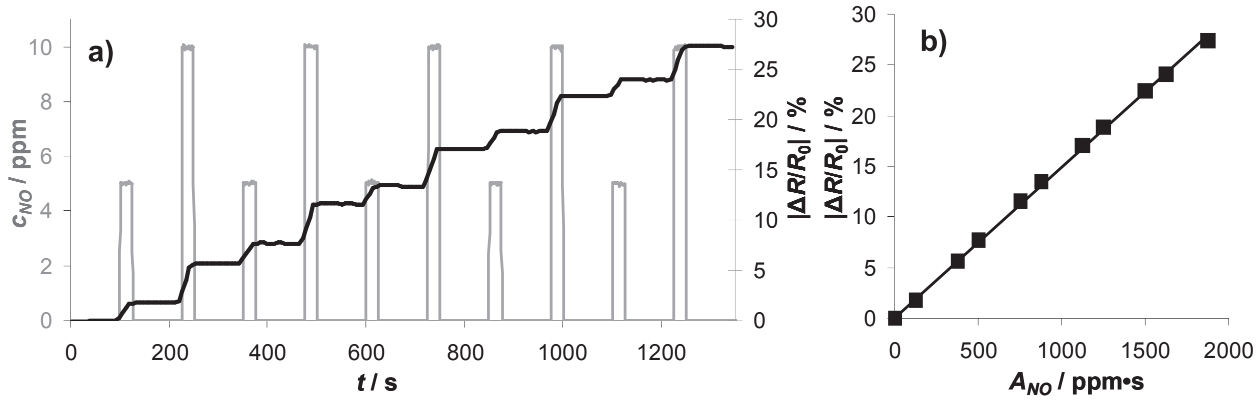

Fig. 4: a) Sensor response $|\Delta R/R_0|$ to 5 x 5 ppm NO for 25 s alternating with 5 x 10 ppm NO;
b) Resulting characteristic line correlating $|\Delta R/R_0|$ with A_{NO}.

For the application of a NO_x-sensor in the automotive exhaust of a leanly operated engine, it is essential that the sensitivity to NO and NO_2 are the same to have a total NO_x-sensor, since the NO/NO_2-ratio is influenced by many parameters and thus is fluctuating with time. As can be learned from equation (2) the storage sites of LNTs are not able to store NO but NO_2 molecules. Therefore, a sufficient oxidizing activity of the present Pt particles to convert NO into NO_2 (equation (1)) is critical for the desired sensor response of the integrating NO_x-sensor to NO_x.

To compare the sensor responses to NO and NO_2, both gases were offered to another integrating NO_x sensor sample. In Fig. 5 the sensor signal during exposure to 5 ppm NO alternating with 5 ppm NO_2 for 50 s each is shown. On the time scale (Fig. 5a), the sensor signal raises with about the same rate independent whether NO or NO_2 is present in the gas. Like in the previous diagram, $|\Delta R/R_0|$ isn't changing in the absence of NO_x. The sensitive layer seems not to desorb stored NO_x-molecules; the holding abilities are independent on the offered analyte species. Looking on the resulting characteristic line in Fig. 5b, it becomes clear that the sensitivity to NO and NO_2 is equal, the characteristic line is not influenced by the analyte species. Therefore, the integrating NO_x sensor can be used to detect small amounts of NO_x independent on the NO/NO_2-ratio.

The integrating properties, the sensitivity and the linear measurement range were found to be dependent on the working temperature of the sensor device [3] and especially on the thickness of the sensitive layer. Therefore it seems that the performance of the integrating NO_x sensors can be adapted to a certain extent to the requirements of the application.

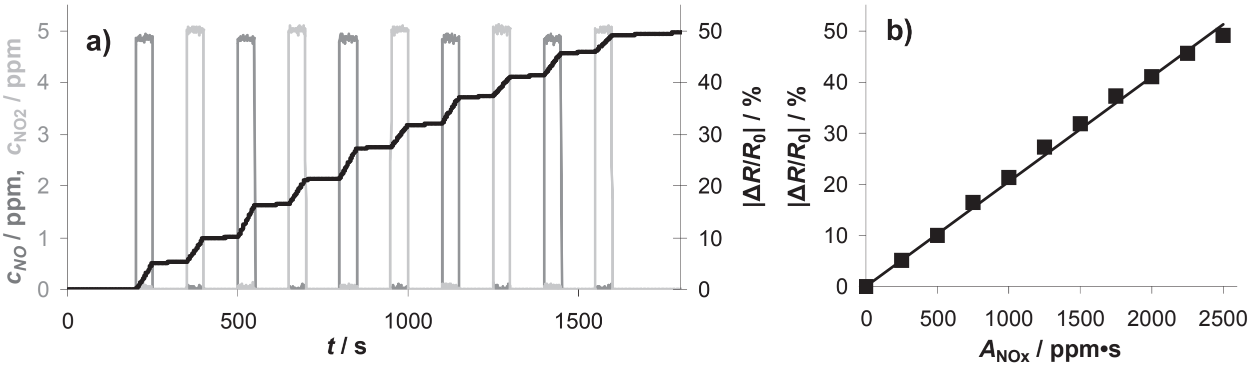

Fig. 5: a) Sensor response $|\Delta R/R_0|$ to 10 x 5 ppm NO_x for 50 s (alternating NO- and NO_2-steps); b) Resulting characteristic line correlating $|\Delta R/R_0|$ with the NO_x-amount A_{NOx}.

Summary

The novel integrating NO_x sensing principle was developed for the detection of very small levels of NO_x and is ideally suited for an OBD-sensor. Using a lean NO_x trap material as the sensitive layer, NO_x can be successively accumulated in the sensitive layer. The material transformation while storing NO_x leads to changing electrical properties which can be used a sensor signal. Contrarily to conventional gas sensors, the integrating NO_x sensor signal correlates linearly with the total accumulated amount of NO_x in the gas stream over a time interval instead of the actual concentration at a particular moment in time. Therefore, this accumulative measurement method offers advantage in applications which require the monitoring of low levels of analyte gas over a long measurement period.

In different measurements it was shown that the properties of the proposed integrating NO_x sensor are in accordance with the theory of the integrating sensing principle. The sensor signal correlates linearly with the amount of NO_x independent of the NO/NO_2 ratio. The presented measurement results show, that even 5 ppm NO or NO_2 in the gas stream over a period of only 25 or 20 s can be detected with a sensor signal change in the range of a few percent.

The integrating NO_x sensor shows great potential for the high sensitive and accurate detection of low levels of NO_x and affords advantages compared to NO_x sensors detecting continuously the actual NO_x-concentration due to the accumulative measurement principle.

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