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The influence of SO_2 and the thickness of the sensitive layer on the performance of the Integrating NO_x Sensor

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Abstract:
Due to its chemical accumulation abilities, the integrating NO_x sensor is potentially well suited for low ppm-level sensing of NO and NO_2. The sensitive layer consists of a potassium-based automotive lean NO_x trap (LNT) catalyst storing NO_x chemically by forming nitrates. The accumulative sensing principle and the NO_x concentration detection properties have been published recently. Now, two factors influencing the sensing performance are addressed: Sulfur poisoning and the thickness of the sensitive layer. The measurement results reveal that the competition between SO_2 and NO_2 for the available storage sites, known from LNT catalysts, affects the sensor signal in two ways: First, the resistance of the sensitive layer (even without NO_x) decreases in the presence of SO_2 (sulfate formation), allowing for integrative SO_2 detection. Secondly, the linear NO_x measurement range decreases due to a diminished NO_x storage capacity upon SO_2 blocking the storage sites. A high reversibility of sulfur poisoning was obtained by desulfation at 650 °C in H_2 containing gas. The resistance in the unloaded state was found to correlate with the inverse thickness of the LNT layer. More relevant, the thickness was found to highly influence the sensitivity and the linear measurement range of the integrating NO_x sensor. Therefore, variations in the thickness are an effective tool to adapt the sensor performance (sensitivity and linear measurement range) to the application requirements without loosing the benefits of the integrating sensing principle.

Key words: Accumulating sensing principle, low ppm-level NO_x sensing, sulfur poisoning, sensitive layer thickness, SO_2 / NO_2 competition, sensitivity / measurement range adaption

Introduction

The integrating-type NO_x sensor has been developed to detect low levels of NO / NO_2 (e.g., < 5 ppm) in harsh environments like the diesel exhaust. The general sensing characteristics as well as the effect of O_2, CO_2 and the temperature have been reported [1-4]. In this contribution, the effect of sulfur poisoning of the catalytically active layer and the thickness of the sensitive layer on the sensing performance will be addressed.

Accumulating sensing principle

In contrast to classical gas sensors measuring continuously the actual analyte gas concentration c_{gas} in a given instant, the sensor response of integrating-type sensors correlates directly with the total amount of analyte gas A_{gas} occurring during the entire measurement period [1-4]. We have shown that such a sensor can still provide instantaneous concentration information in the low ppm range without a baseline drift [1]. This originates from the chemical accumulation of the analyte molecules in the sensitive layer (chemisorption, chemical reaction) to obtain the total amount without applying mathematical integration.

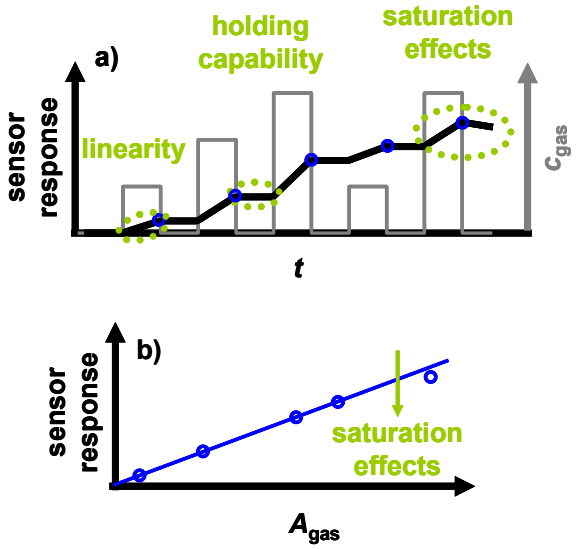

Fig. 1. Fundamentals integrating sensing principle: a) sensor response to various c_{gas} on the time scale, b) resulting characteristic line: correlation with A_{gas}.

As illustrated in Fig. 1a, the sensor response of an ideal integrating sensor increases in the presence of analyte gas and the slope correlates with c_{gas} (linearity), resulting in a constant response at 0 ppm (holding capability). In the high loaded state, saturation effects occur and a controlled regeneration of the sensitive layer is required. The resulting characteristic line (Fig. 1b) gives a linear correlation between the sensor response and A_{gas} until saturation limits the sensing performance.

In the case of the presented integrating NO_x sensor, a potassium-based lean NO_x trap (LNT) material [5], known from automotive NO_x storage and reduction catalysts (NSC), serves as the sensor material. Thereby, NO_2 is stored chemically in the LNT layer by forming nitrates (for a K_2CO_3 based catalyst: eq. 1) which is accompanied by a change in the conductivity [1-5]. Since the catalyst provides oxidizing properties, NO is oxidized to NO_2 followed by nitrate formation and the presented integrating sensor works as a total NO_x sensor providing about the same sensitivity to NO and NO_2 [1].

$$K_2CO_3 + 2\ NO_2 + ½\ O_2 \rightleftharpoons 2\ KNO_3 + CO_2 \qquad (1)$$

As published recently [1], the presented integrating NO_x sensor offers two operation modes: The relative resistance change $|\Delta R|/R_0$, with R_0 being the resistance in the unloaded state, serves as sensor response to determine directly A_{NOx}, while the signal derivative dR/dt correlates with the curve of c_{NOx}. Nitrate decomposition in rich gas atmospheres or at higher temperatures recovers the storage sites and allows for controlled regeneration.

Experimental

The resistive-type integrating NO_x sensor consists of a LNT layer screen-printed on a 96 % pure alumina substrate equipped with gold (DuPont) or platinum (Heraeus) interdigital electrodes (area: 5 x 6 mm; electrode width and spacing: 100 µm). The potassium-based LNT raw material was provided by Johnson Matthey and the composition is described in [5]. The screen-printable paste was made by mixing the catalyst powder with organic additives (Zschimmer & Schwarz). The resistance values were calculated from the complex impedance at 1 kHz with 1 V (rms) applying an R||C (a resistance in parallel to a capacitance) equivalent circuit model. Since the gas compositions were varied, they are described separately for each test setup below.

The effect of SO_2 poisoning

Despite the fuel sulfur content was reduced and is limited by law, sulfur is still an ingredient in diesel and gasoline fuels, forming SO_2 during fuel combustion [6]. Therefore, sulfur tolerant exhaust gas aftertreatment systems, including catalysts and sensors, are required and subject of research activities [6-9]. The catalytic properties of LNTs are known to be constricted by SO_2, since it competes with NO_2 for the carbonate storage sites [6], poisons catalytically active precious metals [8], and reacts with support oxides [6-9]. Sulfates formed in the LNT have a higher thermodynamic stability compared to the corresponding nitrates resulting in a blocking of the storage sites [7]. This diminishes the storage capacity for NO_x and requires a high temperature desulfation in rich gas atmospheres [6-9].

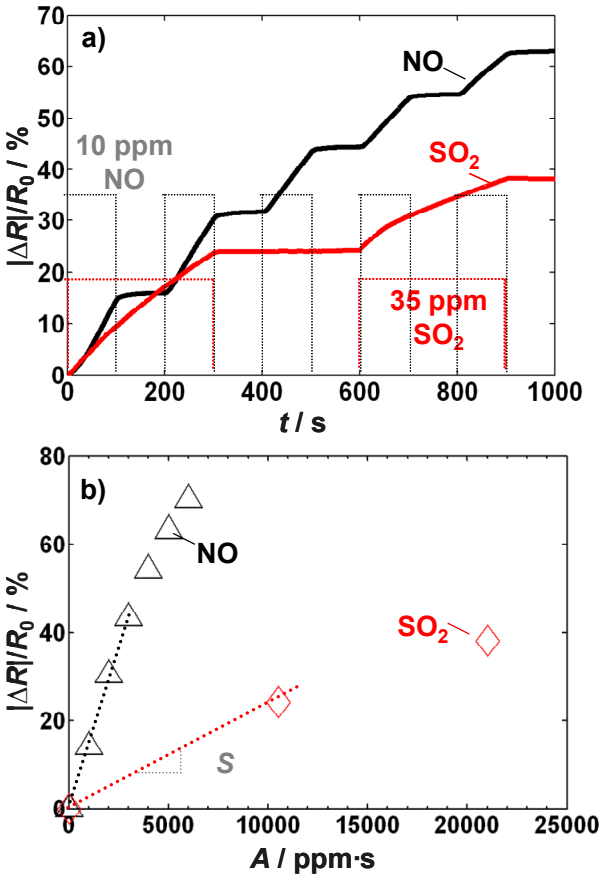

Fig. 2. Effect of sulfur poisoning on the integrating NO_x sensor signal: a) cyclic dosing of NO or SO_2 results in a stepwise increase of $|\Delta R|/R_0$, b) characteristic lines linear up to ~ 30 %, $S_{NO} \approx 6.5\ S_{SO2}$ (in applied gases).

Fig. 2 compares the effect of cyclic exposure to NO and SO_2 at 350 °C on the sensor response of the presented NO_x sensor. 10 ppm NO alternating with 0 ppm for 100 s each (NO-program: 10 ppm NO, 10 % O_2, 3 % CO_2, 50 % N_2 humidified with a water bubbler, rest N_2)

resulted in a stepwise increase in $|\Delta R|/R_0$ (Fig. 2a). This sensor response is in agreement with the theory of the integrating sensing principle since the signal increases linearly in the presence of NO but remains constant in between (holding capability). This indicates accumulation of NO_x in the sensitive layer. An integrating behavior was also observed for SO_2 (SO_2-program: 35 ppm SO_2 in compressed air): Linearity of the increase of $|\Delta R|/R_0$ in SO_2 and a constant response in the absence of SO_2 indicating successive sulfate formation. To account for the different amounts of NO and SO_2 offered to the sensitive device, the corresponding characteristic lines are shown in Fig. 2b. Up to about 30 % the correlations are linear for both gases, but the sensitivity to NO, S_{NO}, which is the slope of the characteristic line, is enhanced by about a factor of 6.5.

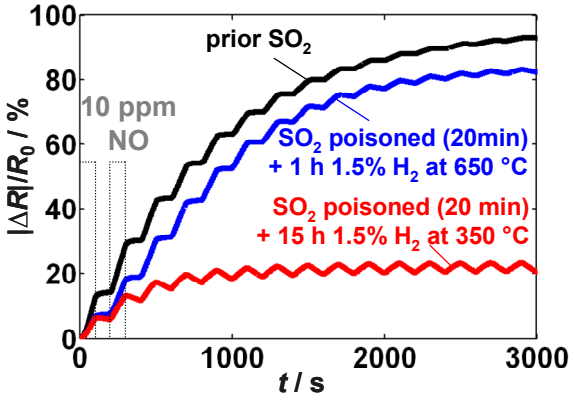

Fig. 3. Sensor response to 15 times 10 ppm NO for 100 s each after H_2 desulfation at 350 °C and 650 °C compared to the signal prior to SO_2 exposure.

After exposure to 35 ppm SO_2 for 20 min, the sensor sample was treated in a rich, H_2 containing atmosphere (1.5 % H_2, 3 % CO_2 in N_2, humidified) since H_2, amongst reducing gases, is reported to show the best efficiency for desulfation [8]. The subsequent sensor response to cyclic dosing of 10 ppm NO in Fig. 3 revealed that the sensing properties are severely reduced compared to the original performance prior to the SO_2 treatment: lower sensitivity (about half in the first NO step), declined holding capability (decrease of $|\Delta R|/R_0$ at 0 ppm NO) and reduced saturation level (at about 22 % signal changes compared to over 90 % prior to SO_2). This diminished NO storage capacity, expressed by the low saturation level and the lower sensitivity, is most likely caused by highly stable K_2SO_4 occupying the storage sites and constraining KNO_3 formation. Additional desulfation at 650 °C in the rich gas composition for 1 h recovers about 72 % of the original NO-sensitivity. Besides incomplete desulfation, sintering effects of LNTs at elevated temperatures are known to lead to a decrease in the catalytically active surface area [8] and may also contribute to a loss in sensitivity of the integrating NO_x sensor after long-term desulfation at 650 °C.

Fig. 2 demonstrates that sulfur poisoning affects the NO_x sensing properties and that the presented sensor setup could be also applied to detect the amount of SO_2 (in NO_x free atmospheres) with a lower sensitivity to SO_2 compared to NO_x.

Dependency of the sensor performance on the thickness of the sensitive layer

The integrating sensing principle bases on a chemical accumulation of analyte molecules in the sensitive layer. In the case of the presented integrating-type NO_x sensor, the NO_x storage in the K-based LNT layer is essential. Therefore, it can be expected that the number of accessible storage sites and consequently the thickness of the sensitive layer affects the sensor performance.

To investigate the influence of the thickness of the LNT layer on the sensor characteristics, sensitive layers with various thicknesses were obtained by multiple screen-printing of the prepared LNT-paste.

The values of the thickness *d* of the resulting LNT layers were estimated from cross-section micrographs. Thereby, *d* was found to correlate linearly with the number of screen printings used to accumulate the film. Unfortunately, the roughness of the surface increases with each printing step complicating the analysis of the measurement results.

The resistance of the samples in the unloaded state (after regeneration) increases with 1/d which is in accordance to theoretical considerations (same electrode geometry and same material composition).

Additionally, the influence of the thickness of the sensitive layer on the sensing properties of the integrating NO_x sensor was investigated. The exposure to alternately NO and NO_2 reveals, that the integrating behavior itself is not affected by the thickness of the sensitive layer. $|\Delta R|/R_0$ increases during accumulation of NO_x with a slope which is dependent on c_{NOx} indicating linearity and the holding capability is expressed as a constant signal in the absence of NO_x. But the sensitivity *S*, which is the slope of the characteristic line, was found to correlate with 1/d and the magnitude of the response on the same NO_x amount decreases the thicker the layers. The effect of the thickness can be attributed to the enhanced ratio of unoccupied storage sites to the amount of formed nitrate for

the thicker coatings when exposing both to the same amount of NO_x.

The analysis of the measurement data shows that the sensitivity and consequently also the linear measurement range of the integrating NO_x sensor are dependent on the thickness of the sensitive accumulating layer. This has the benefit that by variations of the thickness of the LNT coating the sensor performance (sensitivity and measurement range) can be adapted to the requirements of the individual sensing applications (e.g. for monitoring of the exhaust aftertreatment system or urban air quality measurements [1]).

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