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Dosimeter for Low-Level NO_x Detection – Influence of the Deposition Method of the NO_x Storage Film

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Abstract:

The detection of low-level NO_x concentrations and the dose of NO_x for air-quality monitoring (AQM) is still a huge task and a widely discussed topic. Dosimeter-type NO_x sensors detect directly the NO_x dose and are advantageous considering mean value detection, linearity of sensor responses, and drift phenomena. The electrical properties of a NO_x storage film, here potassium permanganate impregnated on alumina powder, depend linearly on the amount of sorbed NO_x. The electrical resistance correlates very well with the amount of formed nitrate and nitrite species. The influence of the deposition method of the sensitive NO_x storage material on the characteristic behavior of the dosimeter-type sensors is investigated. Aerosol-deposited dense films (ADM films) behave like porous thick-films, but typical sensor characteristics like detection limits and relative resistance changes seem to be different.

Key words: NO_x detection, gas dosimeter, sub-ppm, Aerosol deposition (ADM), NO_x storage material

Introduction

Nitrogen oxide (NO_x) emissions in urban areas are in focus since they cause risks for human health. For air-quality (AQ) control of the exposure limits (given as average annual value or hourly mean value) of NO_x, AQM stations and mobile AQ units including NO_x gas sensors are essential tools [1]. Besides metal-oxide-based and electrochemical NO_x sensors, which detect the NO_x concentration, novel sensor principles like dosimeter-type sensors, which measure directly the dose of NO_x are investigated [2]. In [2], a NO_x dosimeter based on potassium permanganate ($KMnO_4$) is suggested. At 350 °C, the resistance of the sensor decreases linearly with the amount of NO_x. This can be explained by the formation of nitrates and nitrites [3]. In NO_x-free phases, the resistance remains constant. After reaching a pre-defined loading state of the sensor film (e.g. a relative resistance change $\Delta R/R_0$ of 40 %), the sensor is regenerated to release the adsorbed species. A new loading cycle starts. Here, the influence of the deposition method of the sensitive film on the sensing properties are investigated: screen-printing for porous thick films and aerosol-deposition method (ADM) for thin dense layers without high temperature firing process [4,5].

Experimental

Different alumina powders with slightly varying particle geometries and BET-surface areas are impregnated by incipient wetness impregnation with an aqueous solution of $KMnO_4$. The powders were dried and calcined at 650 °C. For sensors with screen-printed thick films, a paste was printed on an alumina substrate with gold interdigital electrodes (IDE 100/100 µm) and fired at 650 °C resulting in porous films with a thickness of 15 µm. To deposit thinner and almost dense films, the calcined powders were used for ADM [4,5]. The resulting films provide thicknesses around 1.9 µm and are dense.

The sensors were placed in a quartz-tube furnace heated to 350 °C. A gas flow consisting of 20 % O_2, 2 % H_2O and N_2 balance with varying NO_x concentrations was added. Before each measurement, the sensors were heated to 650 °C for release of adsorbed species. The complex impedance $|Z|$, determined by impedance spectroscopy, is the NO_x depending sensor signal. $\Delta R/R_0$ is calculated assuming an $R||C$ electrical circuit. The NO_x dose is determined by a chemiluminescence detector.

Results and Discussion

The complex impedance decreases during exposure to NO_x linearly with the dose of NO_x. Fig. 1 shows the characteristic behavior of a dosimeter-type thick-film sensor at 350 °C. Three NO_x concentration steps of 390 ppb NO_x are added. A very good correlation between $\Delta R/R_0$ and the calculated dose of NO_x in ppm·s is visible until $\Delta R/R_0$ reaches a value of around

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40 %. The non-linearity above 40 % results in a decreasing sensor signal during NO$_x$ absence due to saturation and desorption effects. At around 125 min, the thermal regeneration starts and all stored NO$_x$ is released.

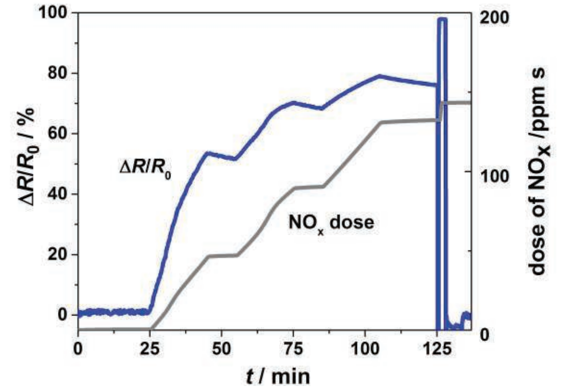

Fig. 1. Relative resistance change $\Delta R/R_0$ of thick film sensor and dose of NO$_x$ vs. time at 350 °C. Added are three steps of 390 ppb NO$_x$ each.

For application, a linear characteristic curve is advantageous. Therefore, the thick film sensor is investigated at lower NO$_x$ doses with 25 ppb NO$_x$ steps (Fig. 2). The sensor can even detect 25 ppb NO$_x$ with $\Delta R/R_0$ around 2 % for each NO$_x$ step. Here, $\Delta R/R_0$ is below 40 % resulting in a very good correlation between sensor response and NO$_x$ dose.

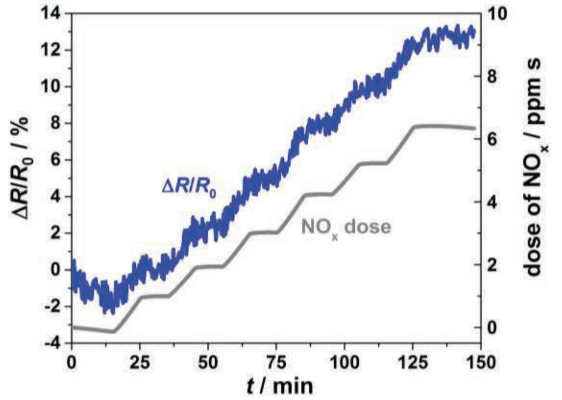

Fig. 2. $\Delta R/R_0$ of thick film sensor and dose of NO$_x$ vs. time at 350 °C. Added are six steps of 25 ppb NO$_x$.

Sensors with higher film thicknesses are not able to detect such low NO$_x$ concentrations and NO$_x$ doses. Since it is interesting for AQM to detect NO$_x$ concentrations even below 25 ppb sensors with thinner films are prepared by ADM. In contrast to the porous screen-printed films, the resulting films are almost dense with a thickness of 1.9 µm. Initial measurements show that even these thin dense films show a NO$_x$ depending dosimeter-type sensor response at 350 °C (Fig. 3).

Here, NO$_x$ concentration steps between 0.5 and 1.6 ppm are added, resulting in higher NO$_x$ doses. Fig. 3 illustrates the sensor behavior of two sensors, prepared from two different alumina powders with the same KMnO$_4$ loading.

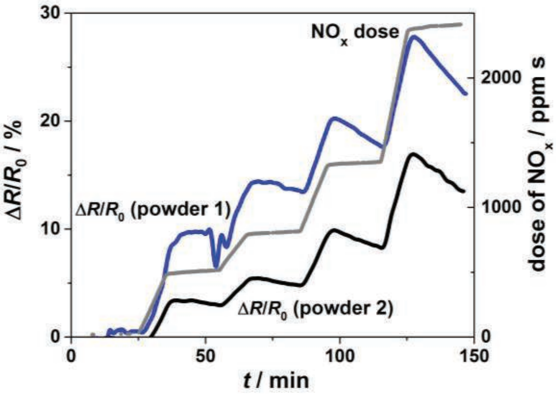

Fig. 3. $\Delta R/R_0$ of two AD-prepared sensors (film thickness 1.9 µm) and dose of NO$_x$ vs. time at 350 °C.

$\Delta R/R_0$ increases linearly during NO$_x$ exposure and stays at the beginning almost constant during NO$_x$ absence. At higher doses, saturation effects are visible. Interestingly, it seems that the thinner but dense ADM film shows smaller values of $\Delta R/R_0$ and behaves linearly at higher NO$_x$ doses. Slower diffusion processes inside the film could explain this behavior. It is assumed that nitrate and nitrite species are formed only on the surface of the film resulting in lower $\Delta R/R_0$ values.

Conclusion

All investigated dosimeter-type NO$_x$ sensors behave as expected with differences between the preparation methods. Even the AD-films behave like a dosimeter, but the characteristics need to be investigated in more detail.

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