

Are Powder Aerosol-Deposited Films Appropriate for Chemiresistive NO_x Gas Dosimeters?

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Summary:

Resistive gas dosimeters based on NO_x storage materials as functional films accurately measure time-intervals like hourly mean values of small gas concentrations like NO₂ in ambient air. The gas dosimeter principle overcomes the disadvantageously low recovery times of conventional chemiresistive sensors. Typically, porous screen-printed films are used as functional films, but for detection of very low NO_x (NO₂ and/or NO) doses, almost dense powder aerosol-deposited films are investigated and their appropriacy will be demonstrated here.

Keywords: air quality monitoring; NO_x; nitrogen oxides; powder aerosol deposition; ppb detection

Background

The determination of hourly mean values, e.g. for air quality or workplace limit monitoring, requires a timely integration of the sensor signal of conventional chemiresistive gas sensors over one hour. Often, inaccuracies and long sensor recovery times might lead to large errors. In contrast, the gas dosimeter directly measures the dose or hourly mean value of a gas species since its sensor signal is proportional to the exposed analyte amount (the dose) [1].

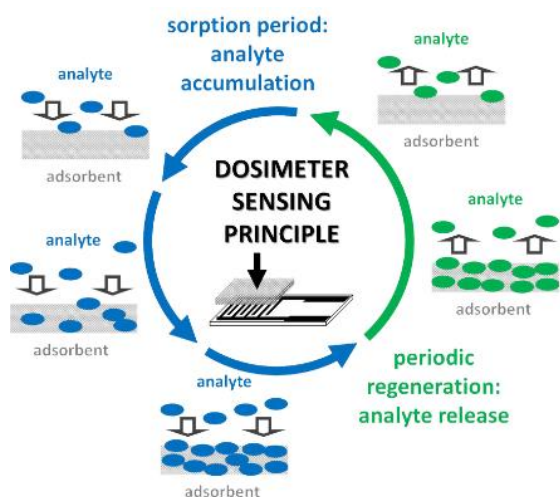


Fig. 1. Scheme of the dosimeter principle and the processes that occur in a resistive gas dosimeter during one operation cycle consisting of a long measurement (sorption) phase and a very short thermal regeneration phase (desorption). From [1], permitted by the authors.

Measuring Principle of NO_x-Dosimeter

A typical gas dosimeter consists of an alumina substrate equipped with a screen-printed platinum heating element on the backside and interdigital electrodes (IDEs). The IDE is covered by a screen-printed film (film thickness around 10 μm) of the functional material, here a NO_x storage material based on potassium and manganese impregnated on alumina powder (K/Mn-Al₂O₃). The relative resistance change, $\Delta R/R_0$, measured using impedance spectroscopy at a fixed frequency value is evaluated as the sensing signal. The optimal working temperature during sorption period is between 300 - 350 °C. In the sorption phase (Fig. 1), NO_x is sorbed in the NO_x storage material and the sensor signal changes linearly with increasing sorption time of a constant NO_x concentration. During NO_x absence, the sensor signal remains constant and is proportional to the previously dosed amount of NO_x. Additionally, the time-derivative of $\Delta R/R_0$ corresponds to the current NO_x concentration. After a certain time, the NO_x storage material is fully loaded, and a thermal initiated regeneration at 650 °C is necessary to desorb the sorbed molecules. Afterwards, a new detection cycle starts. [1]

Discontinuous Powder Aerosol Deposition

To improve the resolution limit for detection of very low NO_x concentrations in the sub-ppm range and the resulting low NO_x doses, the dosimeter properties of films prepared by discontinuous powder aerosol deposition DPAD are investigated. With DPAD, dense ceramic films can be produced at room temperature

directly from the synthesized ceramic powder. [2] Here, the resulting thicknesses of the K/Mn- Al_2O_3 films are in the range of 200 - 300 nm.

Results

The sensor signal $\Delta R/R_0$ of a porous screen-printed K/Mn- Al_2O_3 film (thickness 10 μm) at 300 °C in synthetic air atmosphere shows typical dosimeter behavior (Fig. 2). $\Delta R/R_0$ increases during exposure to NO_2 at ppb level (pulses of 50 - 300 ppb) and remains constant during dosing pauses. The dosimeter signal follows directly the timely-integrated NO_2 concentration and directly detects the total dose of NO_2 . A linear relationship between $\Delta R/R_0$ and dose of NO_2 follows. Additionally, the current NO_2 concentration can be determined by the time-derivative of $\Delta R/R_0$ (Fig. 3). $d(\Delta R/R_0)/dt$ correlates to the current concentration and increases linearly with increasing NO_2 concentration.

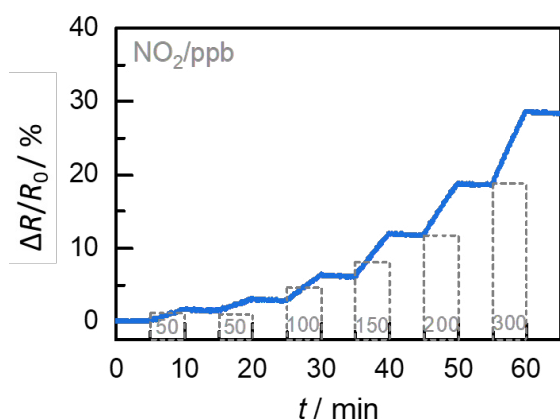


Fig. 2. Relative resistance change $\Delta R/R_0$ of a typical gas dosimeter at 300 °C during exposure to NO_2 (50 - 300 ppb) directly proportional to the integrated NO_2 concentration or total dose of NO_2

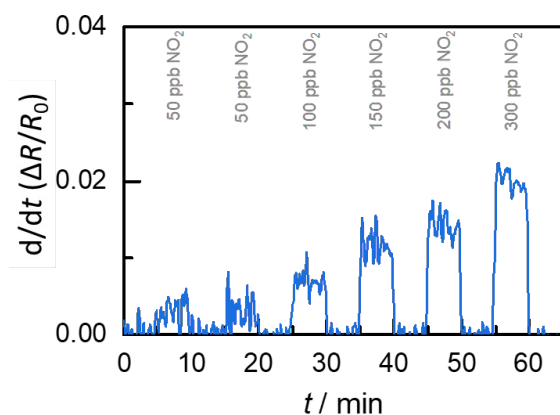


Fig. 3. Timely derivative $d(\Delta R/R_0)/dt$ of the dosimeter signal correlating with the current NO_2 concentration

The results demonstrate the advantages of a NO_x dosimeter like very fast recovery times, but also show the detection limit at very low NO_x concentrations (below 50 ppb) and small NO_x doses, especially directly at the beginning of the

sorption period. The investigation of dense and thinner PAD films as functional film for the NO_x dosimeter provides advantages over thicker screen-printed porous films, shown in Fig. 4.

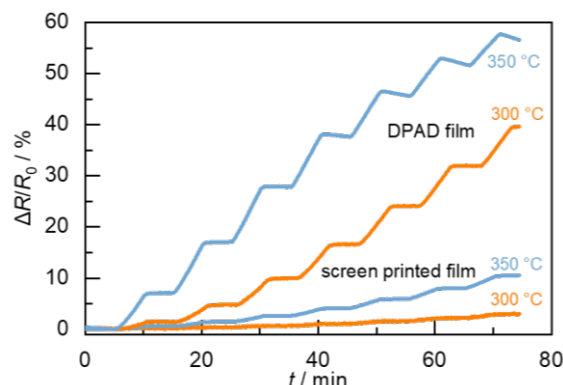


Fig. 4. Comparison of the dosimeter signal $\Delta R/R_0$ of a screen-printed film and a powder aerosol-deposited film during exposure to pulses of 100 ppb NO at 300 and 350 °C.

$\Delta R/R_0$ during exposure to seven pulses of 100 ppb NO was determined at 300 and 350 °C for a DPAD film and a screen-printed film (both prepared from the same starting powder, K/Mn- Al_2O_3). It is clearly recognizable that the DPAD film provides a higher sensor signal than the screen-printed layer. In particular, the first NO pulse can also be resolved quite well whereas it is almost impossible to detect it with the screen-printed film. The DPAD layer shows very good dosimeter behavior up to approx. 40 - 50 minutes. Afterwards, desorption effects become apparent, i.e. the sensor signal decreases during NO_x dosing pauses, and the thermal regeneration phase is necessary. In contrast, the screen-printed film still shows a smaller sensor signal, but no desorption effects are visible.

It is possible to detect low ppb- NO_x concentrations with a dense and thin DPAD film, but the regeneration must be started earlier than with the screen-printed film. With the thicker and porous screen-printed film, it is more difficult to detect lowest NO_x concentrations, but the sorption phase is significantly longer. Therefore, it is possible to detect higher NO_x doses or over a longer time without regeneration.

References

- [1] I. Marr, A. Groß, R. Moos, Overview on Conductometric Solid-State Gas Dosimeters, *J. Sens. Syst.*, 3, 29-46 (2014); doi:10.5194/jsss-3-29-2014
- [2] M. Linz, J. Exner, J. Kita, F. Bühner, M. Seipenbusch, R. Moos, Discontinuous Powder Aerosol Deposition: An Approach to Prepare Films Using Smallest Powder Quantities, *Coatings* 11, 844 (2021); doi: 10.3390/coatings11070844