

Dielectric and DRIFTS Characterization of Ba-based NO_x Storage Materials for Radio Frequency based Dosimeters

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Summary:

A radio frequency-based approach for dosimeter-type NO_x detection using a Barium-containing NO_x storage material is demonstrated. Dielectric properties were investigated by the microwave cavity perturbation method during controlled NO_x storage. A clear linear correlation between dielectric losses and Ba-site utilization was established, demonstrating that the dielectric losses reliably reflect the stored NO_x dose. Operando DRIFTS and impedance measurements provided mechanistic insight, revealing nitrate and nitrite formation as the dominant storage species governing the electrical response.

Keywords: RF based NO_x dosimeter, Pt/Ba-Al₂O₃, Operando DRIFTS, Microwave Cavity Perturbation, dielectric properties, nitrite/nitrate formation

Motivation

Reliable detection and quantification of nitrogen oxides (NO_x) are of central importance in view of stringent air-quality regulations and the significant health impacts of NO₂. Conventional high-accuracy techniques such as chemiluminescence detectors are costly, maintenance-intensive, and only of limited suitability for widespread long-term monitoring. Classical gas sensors furthermore face challenges at low concentrations due to drift and signal noise. Gas dosimeters based on the temporal storage of NO_x going along with changes in materials properties offer clear advantages, especially for long-term measurements and direct detection of the NO_x dose. However, their applicability is often restricted by the low electrical conductivity of many NO_x storage materials. [1] Radio frequency (RF) based sensing concepts provide new opportunities, as they enable the detection of changes in dielectric properties. A detailed understanding of the relationship between NO_x storage properties and RF signal formation is therefore crucial for the development of robust RF-based NO_x dosimeters. DRIFTS investigations combined with impedance measurements provide mechanistic insights into the NO_x storage behavior.

Materials and Measurement Setup

A Barium-containing NO_x storage material with 16.9 wt.% Ba (NSC-Ba17) was prepared by impregnating a lanthanum-stabilized γ-Al₂O₃ support with an aqueous barium acetate solution. After calcination, Pt(NH₃)₄Cl₂ was added and a

reduction step in forming gas was applied to form catalytically active platinum (0.6 wt%). [2]

The dielectric properties of the NO_x storage powders were determined using the microwave cavity perturbation (MCP) technique in a resonant cavity. The scattering parameter S_{21} was evaluated using a vector network analyzer. Shifts in the resonant frequency and quality factor of a defined resonance mode were used to derive the permittivity and dielectric losses. Measurements were performed at 350 °C in defined gas atmospheres during NO_x storage (here: 400 ppm NO₂) and regeneration. [3]

For operando DRIFTS and electrical characterization, screen-printed NO_x storage films were fabricated on heated alumina transducers equipped with interdigitated gold electrodes. These sensors were operated inside a DRIFTS cell that enabled simultaneous infrared spectroscopic and impedance spectroscopic measurements under defined NO_x exposure conditions. The time-resolved detection of nitrate and nitrite species was correlated with changes in the electrical properties of the storage films, allowing chemical storage processes to be directly linked to the resulting sensor signal. [4]

Results and Discussion

The NO_x sorption behavior and the dielectric properties of NSC-Ba17 investigated in the MCP setup at 350 °C are illustrated in Fig. 1. First, the course of measured NO_x concentration downstream the NSC-powder compared to the

reference NO_x concentration shows that NO_x is stored and the powder is almost fully loaded when a concentration of 400 ppm NO_x is reached downstream. The calculated Ba-site utilization $w_{\text{Ba},\text{NO}_x}$, which describes the proportion of available Ba sites converted during NO_x storage to Ba-nitrate, increases during NO_x storage and reaches a maximum loading of approx. 35 %. When the NO_x dosing is stopped ($t = 300$ min), desorption processes occur and by thermal initiated regeneration at 600 °C the sorbed NO_x species desorbs (visible by a distinct NO_x desorption peak in c_{NO_x} and $w_{\text{Ba},\text{NO}_x}$ reaching zero). Meanwhile, the dielectric properties during NO_x loading are measured and the determined dielectric losses ϵ'' present a comparable behavior. ϵ'' increases during NO_x storage and becomes almost stable when the NSC-Ba17 is almost fully loaded with NO_x . A linear relationship between ϵ'' and the Ba-site utilization results, which is attributed to the formation of electrically more conductive nitrate and nitrite species during NO_x storage. This demonstrates that the dielectric losses provide a reliable cumulative measure of the NO_x dose, highlighting the suitability of this material for RF-based dosimeter-type NO_x sensing applications.

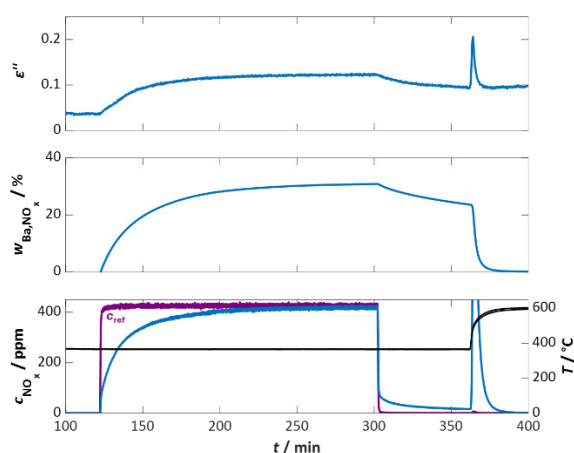


Fig. 1. Dielectric losses ϵ'' and NO_x storage behavior of NSC-Ba17 during NO_x sorption at 350 °C with calculated storage utilization $w_{\text{Ba},\text{NO}_x}$ and c_{NO_x} measured downstream of the MCP setup by FTIR.

Operando DRIFTS measurements were conducted at 350 °C to elucidate the NO_x storage mechanism of Ba-NSC-materials and its correlation with the capacitance (see Fig. 2). During exposure of a screen-printed NSC-Ba17 film to 2 ppm NO for 35 min, infrared spectra revealed the formation of both nitrite and nitrate species. The nitrite-related band (evaluated at 1220 cm^{-1}) rapidly saturates, while the nitrate band increases almost linearly throughout NO exposure. The course of the peak heights of the absorbance A of the nitrate and nitrite band clarifies this behavior. Simultaneously measured capacitance exhibited a

pronounced increase ($\Delta C \approx 4$ fF), reflecting changes in dielectric permittivity associated with nitrite and nitrate formation. After stopping NO dosing, nitrite desorption was observed, whereas nitrate species remained stable and the capacitance signal stayed nearly constant. These results demonstrate that at 350 °C nitrite and nitrate formation dominate NO_x storage in NSC-Ba17 and that more stable nitrates seem to govern the observed electrical response, highlighting its suitability for dosimeter-type sensing.

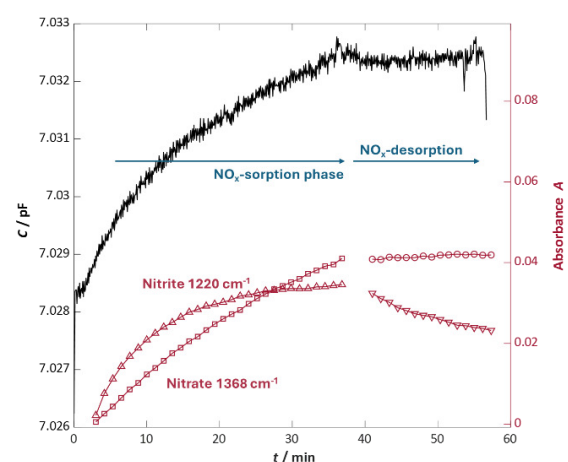


Fig. 2. Peak height of the absorbance A evaluated at 1220 cm^{-1} (denoted as nitrite) and 1368 cm^{-1} (denoted as nitrate) and the calculated capacitance C during 2 ppm NO exposure at 350 °C.

Combined RF characterization and operando DRIFTS provide consistent insights into the NO_x storage behavior of Ba-NSC-materials. Dielectric losses ϵ'' emerge as a robust, sensitive indicator of NO_x uptake, showing a clear linear correlation with stored NO_x and Ba site utilization until saturation. DRIFTS confirms formation of nitrite and nitrate species, with nitrates being stable and seem to predominantly govern the dielectric response. Overall, the results validate the dielectric properties as a reliable cumulative measure for RF-based dosimeter-type sensing.

References

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