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Dielectric Properties of Materials used for a Radio-Frequency based NO_x Dosimeter

Stefanie Walter[1]*, Jaroslaw Kita*[1]*, Daniela Schönauer-Kamin*[1]*, Gunter Hagen*[1]*, Ralf Moos*[1]
[1] *Department of Functional Materials, University of Bayreuth, 95447 Bayreuth, Germany*
functional.materials@uni-bayreuth.de

Summary:
To detect low concentrations of nitrogen oxides (NO_x), a new radio-frequency dosimeter is being developed. The storage of NO_x in a functional material results in a change of its dielectric properties, that can be detected via a resonance structure. To optimize the sensor design, the dielectric properties of different sensor substrates as well as of the sensitive barium-based NO_x storage materials itself were analyzed.

Keywords: radio frequency (RF), dosimeter, dielectric properties, LTCC, NO_x storage materials

Introduction

Nitrogen oxides (NO_x) cause substantial damage to both human health and environment. To ensure air quality, monitoring of NO_x is necessary. For this purpose, a dosimeter capable of measuring average NO_x concentrations over long time periods is being developed.

Sensor Design

Many materials cannot be used for conventional resistive sensors due to their high electrical resistivity. An alternative is offered by radio frequency (RF) sensors, which can detect changes in the dielectric properties of a functional material.

The sensor setup, as shown in Fig. 1, is modified compared to a previous design in [1]. The stripline to excite the resonant structure is now shielded on both sides by a ground plane. LTCC (Low Temperature Cofired Ceramics) is used as the sensor substrate. For higher stability, the functional material can be placed in a recess in the top LTCC layer. This is necessary, since a layer thickness of several hundred micrometers is advisable for a high sensor signal.

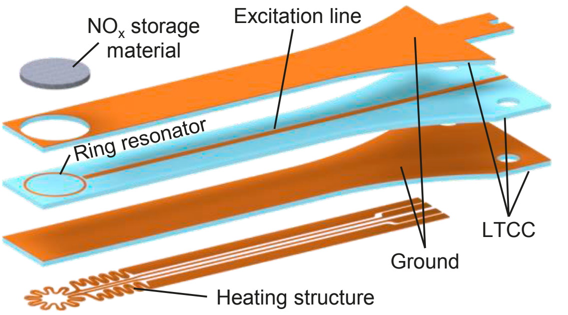

Fig. 1. Schematic setup of the planar RF-based NO_x dosimeter.

Dosimeters measure a time-integrated gas concentration. Thus, for dosimetric detection of NO_x, the functional material has to store NO_x continuously proportional to the NO_x concentration [2]. This can then be measured via the parameters of the excited resonant mode. Since the adsorption behavior of such materials is often temperature-dependent, a heating structure is implemented to vary the sensor temperature. This can also be used for sensor regeneration, as NO_x is often desorbed at higher temperatures [2].

Microwave Cavity Perturbation

To obtain an optimal sensor signal, the geometry of the resonant structure has to be designed in dependence of the dielectric properties of the LTCC substrate and the barium-based NO_x storage material. These can determined by the Microwave Cavity Perturbation (MCP), whose basic working principle has already been described in detail in [3].

By placing a sample in a cylindrical cavity, in which electromagnetic resonances can be excited, a shift of the resonant frequency Δf and of the invers quality factor $\Delta(1/Q)$ occurs. Following Eqs. 1 and 2, they can be used to infer the permittivity ε_r' and the dielectric losses ε_r'' of the material sample:

$$\Delta f \sim (\varepsilon_r' - 1) \qquad (1)$$

$$\Delta\left(\frac{1}{Q}\right) \sim \varepsilon_r'' \qquad (2)$$

However, depending on the sample properties, multiple corrections regarding the correlations in Eqs. 1 and 2 must be made as indicated in [3] in order to be able to infer the correct material properties.

Properties of LTCC

Two different types of LTCC material were analyzed: the DuPont GreenTape 951 and the DuPont GreenTape 9K7, a low-loss material optimized for radio frequency applications. According to the manufacturer's data sheet, the latter has a loss factor tan δ, which describes the ratio of ε_r'' to ε_r', of only 0.001 at 10 GHz compared with 0.014 for the LTCC 951. However, these values refer to room temperature. Since the sensor will be operated in a wide temperature range, knowledge of the temperature-dependent behaviour of the material properties is essential. The values for ε_r' and tan δ measured by the MCP in a temperature range from 20 to 600 °C are shown in Fig. 2.

For both LTCC materials, their permittivity ε_r' is almost independent of temperature. Therefore, a shift in resonant frequency can be attributed mainly to dielectric changes occurring in the NO_x storage material. The loss factor affects the attenuation of the electromagnetic wave during its propagation along the excitation line and in the resonance structure and therefore determines the quality of the sensor signal. For both LTCC materials, tan δ increases exponentially with temperature, however at different rate. Therefore, 951 exhibits lower dielectric losses than 9K7 at temperatures above 500 °C. Since the RF-dosimeter is intended to be operated mainly in a temperature range between 200 and 400 °C, 9K7 is still preferred as substrate for this application.

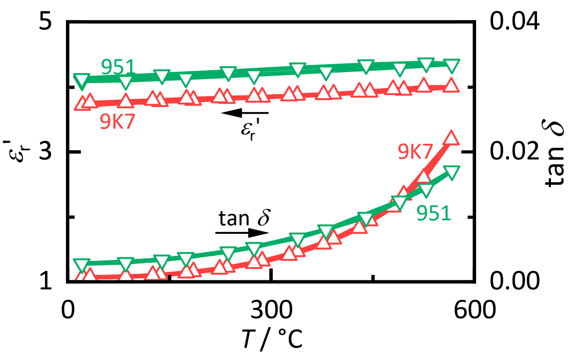

Fig. 2. Permittivity ε_r' and loss factor tan δ of different LTCC materials; red: DuPont 9K7; green: DuPont 951.

Properties of NO_x Storage Materials

To detect the NO_x loading of the functional material, it has to change its dielectric properties thereby. In barium-based materials, this is the case due to the conversion of carbonate to nitrate during NO_x storage. Such materials are commonly used in automotive storage catalysts, exhibiting significant changes in their dielectric properties during NO_x storage [4].

With the MCP the dielectric properties of barium carbonate ($BaCO_3$) and barium nitrate ($Ba(NO_2)_3$) were measured. The permittivity of the two powders differs only slightly. Therefore, only their losses - shown in Fig. 4 - are relevant for NO_x detection. The dielectric losses ε_r'' of $BaCO_3$ increase only slightly with temperature and remain below 0.05. In contrast, those of $Ba(NO_2)_3$ increase rapidly. While below 100 °C ε_r'' of both powders are in the same range, at 400 °C the losses of nitrate are already 20 times higher. Thus, operation at high temperatures would be preferable for the RF-dosimeter. However, due to the NO_x adsorption behavior, a dosimeter-like sensor behavior is only expected at temperatures up to 400 °C. In addition, the signal quality decreases with higher temperature due to higher losses of the LTCC.

Furthermore, using pure barium carbonate as the functional material seems problematic due to its slow NO_x adsorption reaction rate, as it has only a small surface area of 1.6 m²/g. Therefore in future measurements, the barium will be coated on a highly porous aluminum oxide powder to increase the reaction surface.

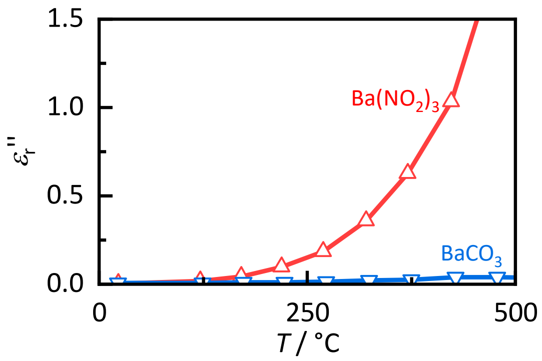

Fig. 3. Dielectric losses ε_r'' of barium-based NO_x storage materials; $BaCO_3$ in blue, $Ba(NO_2)_3$ in red.

References

[1] S. Walter, et al., Novel radio-frequency-based gas sensor with integrated heater, *J. Sens. Sens. Syst.* 8, 49–56 (2019); doi: 10.5194/jsss-8-49-2019.

[2] A. Geupel, et al., Integrating nitrogen oxide sensor: A novel concept for measuring low concentrations in the exhaust gas, *Sens. Actuators B* 145, 756–761 (2010); doi: 10.1016/j.snb.2010.01.036.

[3] C. Steiner, et al., Determination of the Dielectric Properties of Storage Materials for Exhaust Gas Aftertreatment Using the Microwave Cavity Perturbation Method, *Sensors* 20, 6024 (2020); doi: 10.3390/s20216024.

[4] S. Walter, et al., Radio Frequency-Based Determination of the Oxygen and the NO_x Storage Level of NO_x Storage Catalysts, *Top. Catal.* 62, 157–163 (2019); doi: 10.1007/s11244-018-1079-y.

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