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# CO<sub>2</sub> sensing with chemoresistive Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> sensors - Operando insights

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## Abstract

In this work the sensing of Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>-based chemoresistive CO<sub>2</sub> sensor was investigated combining DRIFT and DC-resistance measurements. Besides the already reported effect of CO<sub>2</sub> exposure, we found that exposure to CO determines comparable effects and that the presence of oxygen in the background is not important. The humidity significantly influences the response for both gases. The spectroscopic results reveal that the exposure to both CO and CO<sub>2</sub> consumes the water-related surface species – the rooted-hydroxyls being the electrically active one – and increases the concentration of carbonates; the decrease of the rooted-hydroxyls is probably the cause of the resistance increase.

Keywords: gas sensor; CO; CO<sub>2</sub>; metal carbonate, operando, FTIR

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## 1. Introduction

CO<sub>2</sub> is one of the most relevant target-gases for applications spanning from air quality control to emissions monitoring. State-of-the-art detection relies on expensive solutions, mostly based on NDIR systems. The interest to develop cheap, easy to use chemoresistive sensors is very high. Recently we reported very interesting results based on Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> as sensitive-material [1]: we have shown that under exposure to CO<sub>2</sub> the resistance increases considerably. Here, we attempt to understand the sensing-mechanism by simultaneously performing DC resistance and DRIFT measurements while exposing the sensor to 300ppm of CO and CO<sub>2</sub> in a background of dry and humid air as well as in low oxygen containing atmosphere. The reason for combining electrical and spectroscopic investigations at the same time (operando approach), is the need to correlate the changes in the concentration of surface species with changes in the sensor-resistance and identify the species responsible for the sensing.

Besides CO<sub>2</sub>, as the main target gas of this investigation, it was decided to study also the effect of CO. The reason to use both CO and CO<sub>2</sub> as probing gases is the fact that both are known [2, 3] to build up surface carbonates, which could have an influence on the resistance of the sensor.

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The various backgrounds were used to understand the importance of the gases that are normally present in gas sensing applications ( $O_2$  and  $H_2O$ ; for the latter the effect of exposure to humidity is a huge decrease of the sensor resistance).

## 2. Setup

For measuring DC sensor resistance and simultaneously acquire infrared spectra, a homemade sensor chamber was installed in a modified Bruker Vertex 80v spectrometer. The whole spectrometer, except the sensor chamber and the gas line, was evacuated during all measurements to reduce optical influences of atmospheric gases like water and  $CO_2$  and increase overall optical throughput. For the resistance measurements, which are in the GOhm range, a Keithley EMM 617 electrometer was used.

The sampling intervals of the infrared measurements is indicated by the dashed rectangles in Figure 1 and 2. A reference spectrum was recorded right before the injection of the test gas and the sample spectrum was recorded in the last 15 minutes of the test gas pulse. During the measurements in low oxygen a constant background of approximately 150ppm  $O_2$  was present.

## 3. Material Characterization

From the electrical point of view, very less is known about the properties of rare earth oxy carbonate compounds. To clarify the conduction mechanism of the material, electronic or ionic, we performed AC impedance measurement in the range from 50 mHz to 1 MHz. No ionic contribution was identified in this experiment, so we think that the conduction is mainly of electronic nature. This finding is in line with what it is known about the structurally-similar A-type rare earth binary oxides, which are n-type semiconductors [4]. Both compounds contain hexagonal ( $Nd_2O_2^{2+}$ ) layers; in  $Nd_2O_3$  they are interconnected through  $O^{2-}$  groups, in the  $Nd_2O_2CO_3$  through  $CO_3^{2-}$  groups. This suggests that also the oxy carbonate shows n-type semiconducting character. Moreover,  $Nd_2O_3$  obtained by heating of  $Nd_2O_2CO_3$ , shows the same trends for resistance changes under gas exposure albeit with a much lower sensitivity and baseline resistance.

The carbonate groups of  $Nd_2O_2CO_3$  are referred in the following text as lattice-type carbonates. They show 4 specific stretching vibrations which - for free ions - according to [5] are labelled  $\nu_1$  ( $1063\text{ cm}^{-1}$ ),  $\nu_2$  ( $879\text{ cm}^{-1}$ ),  $\nu_3$  ( $1415\text{ cm}^{-1}$ ) and  $\nu_4$  ( $680\text{ cm}^{-1}$ ).

Onto the used comb platinum electrode structure and heated at  $300^\circ\text{C}$  the sensors show a very high resistance of about 120 GOhms in dry conditions and about 20 GOhms in 50%rel. humidity.

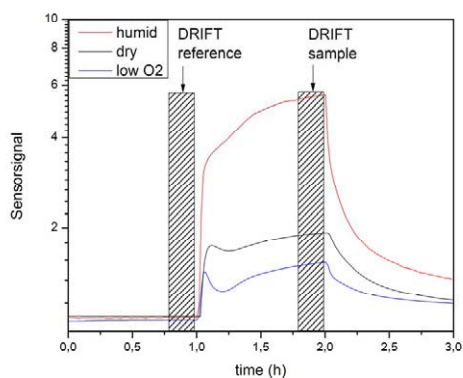


Figure 1: Sensor signals at  $300^\circ\text{C}$  / 250ppm  $CO_2$  in nitrogen (low oxygen), dry synthetic air and humid synthetic air.

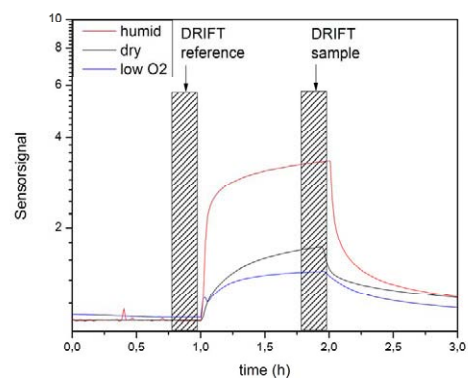


Figure 2: Sensor signals at  $300^\circ\text{C}$  / 250ppm  $CO$  in nitrogen (low oxygen), dry synthetic air and humid synthetic air.

Figures 1 and 2 show the sensor signals corresponding to exposures to 250 ppm CO<sub>2</sub> and CO. First of all, one observes that the sensor signals in 50% relative humid air are more than double than in dry conditions. Furthermore, a change of the carrier gas from air (20,5% Oxygen) to almost pure nitrogen is not affecting the sensitivity too much. The small differences in the sensor signals between both carrier gases indicate that oxygen is not needed for the sensing. Moreover, a comparison between the resistance in dry air and in nitrogen shows that the material is not ionosorbing oxygen, which would change the resistance of the material. This is unexpected, keeping in mind what is generally known about metal oxides. [6].

The DRIFT (Diffuse-Reflectance-Infrared-Fourier-Transformed) quasi-absorbance-spectra (Figures 3 and 4) have been calculated by dividing the spectra acquired during the “DRIFT-sample” period by the one acquired during the “DRIFT-reference” period (see Figures 1 and 2). Consequently, the spectra show changes of surface-species determined by the exposure to the test gases.

The spectra in Figure 3 show two main changes. The first is a dramatic “consumption” of the hydroxyl-groups, see the wavenumber region between 3750 and 2500 cm<sup>-1</sup>. The hydroxyl absorptions are coming from stretching vibrations of terminal OH groups (sharp bands) and rooted hydroxyls (broad bands). At the other end of the spectrum a “generation” of carbonates is visible. Two lattice-type carbonate absorption bands are centered at  $\nu_1$  (1059cm<sup>-1</sup>) and  $\nu_2$  (861cm<sup>-1</sup>) [5]; they are in line with the literature data [7, 8]. Another broad band ( $\nu_4$ ) is located between 1700 and 1230cm<sup>-1</sup> and is disturbed by an overlap with the negative band corresponding to the delta-vibrations of the terminal hydroxyl groups, whose amount decreases during exposure to CO<sub>2</sub> (compare with the sharp negative band of stretching OH-vibrations). This overlap results in a quasi-splitting of the carbonate band and changes the intensities in a way that makes it difficult to distinguish between possible surface carbonate groups or carboxylates and lattice-type carbonates. Nevertheless, we think that the main product on the surface is a lattice-type surface carbonate group because of the increase of the other the lattice-type vibrations carbonates of Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> ( $\nu_1$  and  $\nu_2$ ).

The effect of CO is very similar (see Figure 4): A large amount of rooted and terminal hydroxyls is consumed and lattice-type carbonates are produced. The general reaction seems very similar, but there are some differences in the weight of the specific hydroxyls. One possible explanation is that CO needs more hydroxyls to form carbonates.

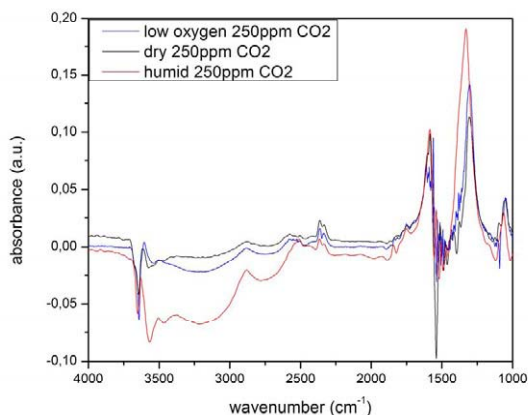


Figure 3: operando DRIFT spectra after exposing the sensor for 60min to 250ppm CO<sub>2</sub> in nitrogen (low oxygen), dry synthetic air and humid synthetic air.

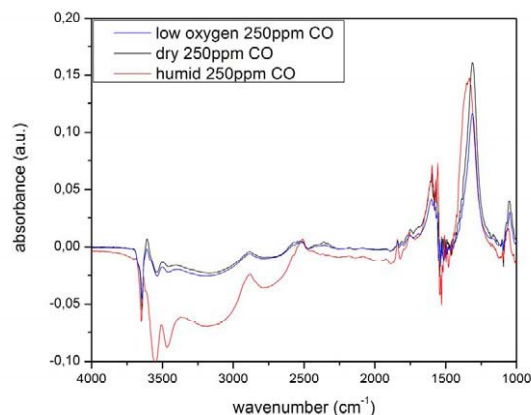
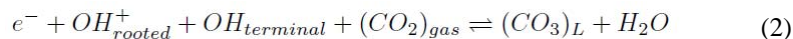
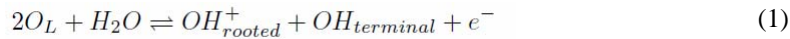


Figure 4: operando DRIFT spectra after exposing the sensor for 60min to 250ppm CO in nitrogen (low oxygen), dry synthetic air and humid synthetic air.

#### 4. Sensing mechanism

For the assessment of the electrical impact of the surface chemistry, one needs to take into consideration the net charge of the, produced or destroyed, surface groups. It is known that this net charge changes the conductance of the material by trapping from or releasing to the bulk free charge carriers.

We think that the rooted hydroxyl groups, formed by the reaction with water vapor, are behaving as donors - see equation (1). This is leading to the observed resistance decrease in humid conditions. On the other hand, we think that surface carbonate groups are replacing these donor sites – see equation (2). It is, therefore, the interplay between the generation of carbonate and of hydroxyl groups that delivers the observed resistance change.



The mechanism can also explain why the presence of humidity increases the sensor effect: there is a higher concentration of reaction partners for CO/CO<sub>2</sub>, therefore a larger amount of donors is removed.

#### 5. Conclusion and Outlook

The present work proposes a mechanism for the CO and CO<sub>2</sub> sensing with Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>-based sensors, which relies on the electron donor character of rooted hydroxyl groups. The latter concentration is changed by the reaction with CO and CO<sub>2</sub>, which results in the build-up of lattice like surface carbonate groups. Also, most probably the presence of atmospheric oxygen is not relevant to CO<sub>2</sub> sensing. In order to deepen the understanding, additional operando investigations are performed.

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