

Operando Investigations of Differently Prepared In₂O₃-Gas Sensors [†]

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Abstract: In this study, the electrical characteristics and surface reactions of three different kinds of In₂O₃ based gas sensors were investigated under CO exposure in dry and humid air by using DC electrical resistance measurements and Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). For the first time one gains insight into the surface reactions during the exposure to CO and humidity. The sensors show different behavior on the baseline in humidity depending on the material which is due to different kinds of OH-groups. The resistance change under CO and humidity exposure are additive and the molecules compete for the same reaction partner confirmed by the spectroscopy results. Through isotopic exchange experiments, different adsorbates could be identified.

Keywords: In₂O₃; gas sensors; SMOX; DRIFTS; operando; surface chemistry

1. Introduction

Semiconducting metal oxide gas sensors have a huge application range and many competitive advantages such as high sensitivity and stability, potential for miniaturization and low cost. In that class of materials, In₂O₃ is not as much studied as SnO₂ and WO₃ even if it shows interesting properties. It was reported that it shows good performance for the detection of CO or methane [1] but its high selectivity towards oxidizing gases (e.g., NO₂ or O₃) at low temperatures [2,3] is its most prominent and outstanding property. Although In₂O₃ has been investigated over two decades, the sensing mechanism is not fully understood. One of the few reports about the surface reaction was based on Raman spectroscopy [4]. There, the authors observed the reduction of this oxide during ethanol exposure. Because the investigation was focused on one target gas and one material, the findings are not easy to generalize. In this study, the sensing of CO and the way in which the humidity influences it was investigated on three differently prepared In₂O₃ materials. The response to CO at 300 °C was monitored in dry and humid conditions and for the understanding of the surface chemistry responsible for sensing, operando DRIFTS was used.

2. Materials and Methods

The investigated materials are: commercially available In₂O₃ from Sigma Aldrich (SA) and two home-made powders, labelled IC1 and IC2. IC1 was gained by grinding Indium(III) nitrate pentahydrate with 1 equivalent ammonium bicarbonate for 30 min. After the reaction was complete, the mixture was heated to 100 °C for 5 h and afterwards to 400 °C for 3 h [5]. To obtain IC2, indium(III) acetate was heated for 3 h at 400 °C and afterwards ground for 20 min. All three powders were made into a paste by mixing with 1,2-propandiol. The pastes were deposited onto the alumina substrates by screen printing and annealed at 400, 500 and 400 °C, for 10 min each. The DRIFTS measurements

were performed at the FT-IR spectrometer Bruker Vertex 80v at 300 °C under CO (25, 45, 100, 300 and 500 ppm), ¹³CO (500 ppm) water vapor (3%, 7% and 10%) and heavy water vapor (10%) exposure. Simultaneously, DC electrical resistance measurements were performed.

3. Results

The recorded DC resistance changes during CO exposure in dry air and 10% r.h. @ 300 °C are shown in Figure 1a. The measurements show that the influence of humidity on the baseline resistance is very different for the three materials. The largest effect is recorded for SA while IC1 shows limited changes and for IC2 the resistance change is almost negligible. What all materials have in common is that the resistances under CO exposure are not that much influenced: This is obvious in Figure 1b, where the sensor signals ($S = R_{air}/R_{CO}$) which are shown. The decrease in sensor signal is scaling with the effect of humidity on the baseline resistance: for SA the sensor signal clearly, for IC1 the effect is not that pronounced and for IC2 the sensor signal is not changed. It is like the humidity and CO effects are additive, which indicates that both have the same reaction partner at the surface of In₂O₃.

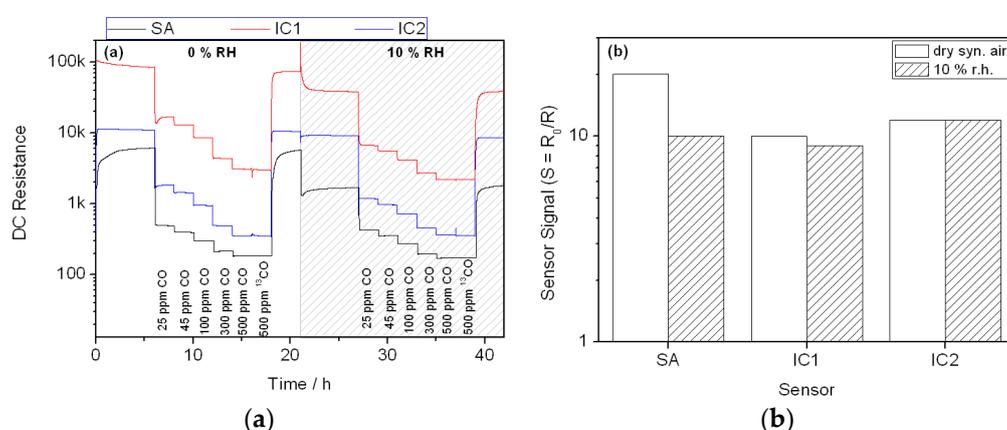


Figure 1. (a) DC resistance measurements and (b) sensor signals of SA, IC1 and IC2 under CO exposure in dry and humid air at 300 °C.

To check this idea, DRIFTS measurements were performed under exposure to CO and ¹³CO in dry and humid conditions (Figure 2a) as well as under exposure to H₂O and D₂O vapors (Figure 2b). The parameter represented in the figures is the absorbance, which is calculated from the single channel (SC) spectra corresponding to the respective single gases:

$$A = -\log((SC_{testgas})/(SC_{reference})) \quad (1)$$

Exposure to CO in dry synthetic air, for all materials, reduces the intensity of the In-O bands which are located between 1560 and 1000 cm⁻¹. This indicates a reduction of the surface. The same effect is also observable under CO exposure in 10% r.h., but the decrease is less than in dry air. Over 3000 cm⁻¹ the decrease of the concentration of the hydroxyl groups is observed for all materials. CO is oxidized on the In₂O₃ surface to CO₂, whose characteristic gas phase absorption bands are visible around 2349 cm⁻¹. To differentiate between carbon related and non-carbon related surface species, ¹³C is used. This will replace ¹²C by ¹³C which causes a shift in the spectra to lower wavenumbers. Between 1500 and 1300 cm⁻¹ the two home-made materials show adsorbed carbonate species, which are missing for SA.

During water vapor exposure one can observe the formation of hydroxyl group for all materials over 3000 cm⁻¹. To get more information about which hydroxyl groups already exist and which one are newly formed, 10% heavy water vapor was used in an isotopic exchange experiment. This will cause the replacement of the preexisting O–H groups by O–D groups with a shift in the spectra of about 0.74 [6]. On all sensors surfaces hydroxyl groups are present indicated by the decreasing O–H bands and increasing O–D bands. The non-shifting bands of IC1 and IC2 indicate that these are

formed additionally to the already existing O–H groups. However, the hydroxyl groups are very different in nature and concentration. For IC1 and IC2 the spectra indicate interacting terminal and rooted hydroxyl groups by the broaden ones at lower wavenumbers. For SA one finds isolated terminal hydroxyl groups. The effect of water on In–O bands at lower wavenumbers, which indicates surface reduction, is observable for all materials.

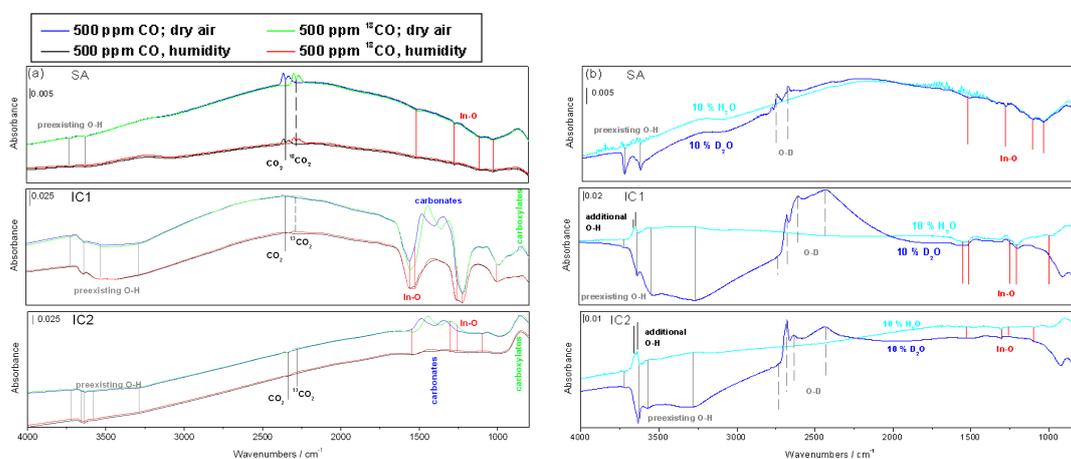
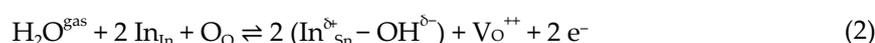


Figure 2. Absorbance spectra of SA, IC1 and IC2 (a) under 500 ppm CO/¹³CO exposure in dry syn. air and humidity and (b) under 10% water and 10% heavy water vapor at 300 °C; reference spectra: dry synthetic air.

4. Discussion

The experimental results are confirming the hypothesis drawn from the sensing performance evaluation: indeed, CO and water vapor compete for the same reaction partners, namely surface oxygen. That means that in the presence of humidity, depending on how strong its reducing effect is, the effect of CO exposure will be, correspondingly, decreased. It is important to note that the chemistry of water is different for the different sensitive materials because the nature and the relative weight of the different water related surface species differ: the rooted hydroxyl groups seem not to be present in the case of SA while for IC1 they seem to be dominant. It is also very interesting that there does not seem to be any carbonates in the case of SA but a lot of them for IC1 and IC2; in future experiments we will have to find out if those carbonates are reaction intermediates from CO to CO₂ or are due to the adsorption of the resulting CO₂ like in the case of SnO₂ [7]. Anyways, in the presence of humidity their concentration decreases.

The quasi-chemical equations that describe the effect of humidity can be the ones proposed by Heiland and Kohl [8] and Wicker et al. [9] for the case of tin oxide, adapted here for In₂O₃, namely:



For SA, Equation (1) seems to be appropriate while for IC1 and IC2 all reactions seem to be possible so Equations (1)–(3) need to be considered. For the case of CO the respective quasi-chemical equation is:



5. Conclusions

It was shown that, depending on the synthesis route, water vapor has different electrical effect on the baseline of In₂O₃. Likely, this is caused by different OH-groups which could be identified by DRIFTS. The results showed an additive effect of CO and water vapor on the resistance which could

be confirmed by DRIFTS. This seems to be a property of this metal oxide, since all three materials showed the same effect. These results demonstrate that it is possible to manipulate the impact of humidity depending on the synthesis route and the potential of DRIFTS to identify surface species.

Conflicts of Interest: The authors declare no conflict of interest.

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