Available online at www.sciencedirect.com
ScienceDirect
Procedia Engineering 5 (2010) 139–142
Procedia Engineering
www.elsevier.com/locate/procedia

Proc. Eurosensors XXIV, September 5-8, 2010, Linz, Austria

Rare earth oxycarbonates as a material class for chemoresistive CO_2 gas sensors

A. Haensch[a], D. Koziej[b], M. Niederberger[b], N. Barsan[a], U. Weimar[a]

[a]*Institute of Physical Chemistry, University of Tübingen, Tübingen, Germany*
[b]*Department of Materials, ETH Zürich, Zürich, Switzerland*

Abstract

In this work we compare the CO_2 gas sensing properties of two new materials synthesized from rare earth hydroxide ($La(OH)_3$, $Pr(OH)_3$) precursors, with the already reported ones for neodymium oxycarbonate, which was synthesized from the corresponding $Nd(OH)_3$ precursor. In-situ XRD measurements show that by following similar thermal treatment, praseodymium hydroxide is transforming to the metal oxide while lanthanum hydroxide forms an oxycarbonate, like in the case of neodymium. The chemoresistive effects we found for the lanthanum oxycarbonate were even higher than the ones recorded for the neodymium oxycarbonate; for the praseodymium metal oxide we could not find any CO_2 sensitivity. Accordingly, we think that the condition for CO_2 sensing is the formation of the rare earth oxycarbonate.

Keywords: CO_2, gas sensor, chemoresistive, rare earth oxycarbonate

1. Introduction

For monitoring the important target gas CO_2 today's state-of-the-art sensor systems make use of electrochemical cells [1-3], capacitive sensors [4, 5] or NDIR. The disadvantages of these measurements principles span from high costs to complicated operation conditions and need for qualified operators. Easy to use chemo resistive sensors could be very useful due to their lower costs and simplicity in operation.

2. Sensor effects

As a first step towards this goal we reported in [6] that $Nd_2O_2CO_3$ is a candidate for use in chemo resistive CO_2 sensors. To understand if the sensitivity is associated to the specific formed material, namely the oxycarbonate, or to the rare earth element, we examined other rare earth metal compounds; it is also known that nearly all rare earth

1877-7058
doi:10.1016/j.proeng.2010.09.067

metals can form oxycarbonates [7,8]. Accordingly, two new rare earth tri hydroxide precursors (Praseodymium and Lanthanum) were synthesized by following the same synthesis route; the nanosized hydroxide powder was processed and screen printed onto sensor substrates and the so formed sensor element was subjected to heating to 400°C. Afterwards, the CO_2 sensor performance was assessed in a background of humid air (50% relative humidity at 25°C) and at an operation temperature of 250°C. In Figure 1 are displayed the results obtained for Lanthanum and Neodymium; the sensor signals of the Lanthanum compound spanned between a 12 times increase of resistance for exposure to 300ppm up to 20 times increase of resistance for exposure to 5000ppm CO_2, higher than in the case of the Neodymium compound. On the other side, the Praseodymium compound is not showing any sensor signals, see Figure 2.

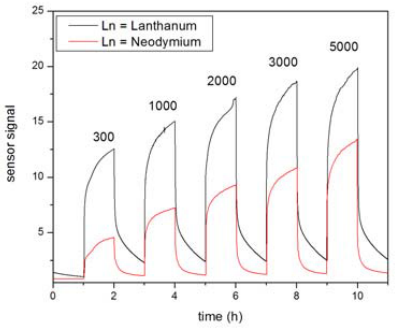

Fig. 1 Sensor signals of the neodymium and lanthanum compounds. Red line for neodymium and black line for lanthanum.

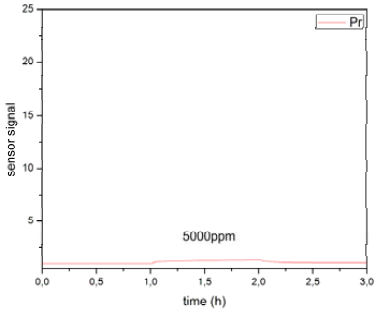

Fig. 2 : Result for a 5000ppm CO_2 pulse on the yield Praseodymium compound.

3. XRD measurements

As the signals are completely different we were analysing the crystal structures with X-Ray Diffraction by performed in-situ XRD examinations, directly on the sensors. This revealed that $Nd(OH)_3$ is forming an amorphous material during heating and, after the CO_2 exposure, crystalline $Nd_2O_2CO_3$ is formed. In Figure 3 are three XRD measurements shown. Additional peaks from the platinum electrodes and the alumina support are marked with a star. The one at the bottom corresponds to the unheated Neodymium hydroxide. After a heating over 200°C the red diffraction pattern are appearing, which shows the fortmation of an amorphous compound. During the first CO_2 exposure at temperatures over 250°C the green diffraction pattern is obtained: this corresponds to the fully crystallized oxycarbonate, which is the operating sensing material.

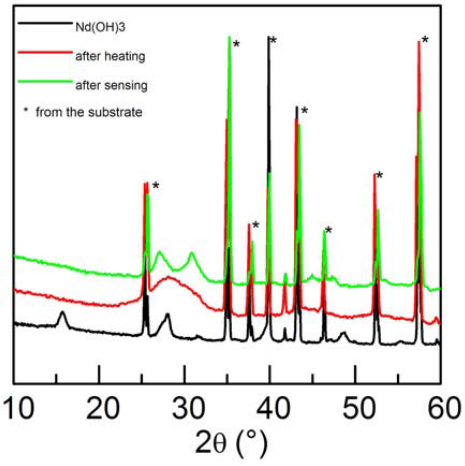

Fig. 3: XRD results for $Nd(OH)_3$ conversion: after the heating the material gets amorphous. During the first measurement with CO_2, a phase pure $Nd_2O_2CO_3$ is formed.

$La(OH)_3$ transforms easily to $La_2O_2CO_3$ only by heating in the oven at 400°C in air. In Figure 4, two XRD spectra are shown, before and after heating together with the reference XRD spectra for the hydroxide and the oxycarbonate. Before heating, the spectrum is the one of

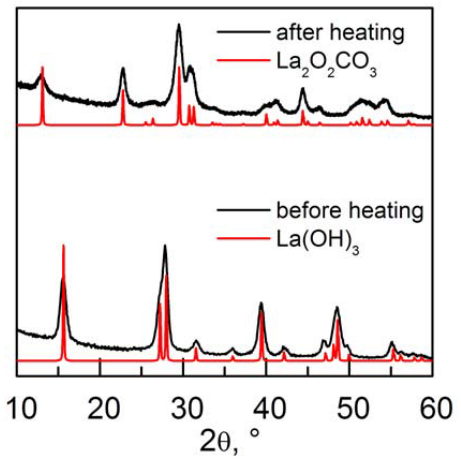

Fig. 4: XRD of $La(OH)_3$: Lanthanum compound is transformed directly to the oxycarbonate.

praseodymium oxide. The resulting material was identified to be Pr_9O_{16}. For comparison, the praseodymium dioxide and oxycarbonate references are also displayed. This result suggests that the oxycarbonate formation is needed for the CO_2 sensing, most probably because the metal oxide does not have sufficient surface basicity to bind CO_2.

4. Conclusion

We found a new rare earth oxycarbonate which shows even a higher sensitivity towards CO_2 than the initial neodymium oxycarbonate. Additionally we could demonstrate that the CO_2 sensing is linked to the formation of the oxycarbonate phase.

the hydroxide with broadened peaks because of the small crystallite size of the measured material. In the upper part of the figure the results corresponding to the post heating situation are displayed; the measured XRD spectrum fits quite well to the oxycarbonate. This result shows that the Lanthanum oxycarbonate can be synthesized only by heating the hydroxide over 400°C in air and proves that the lanthanum tri hydroxide is more easily converted to the oxycarbonate than the neodymium one. Interestingly also the sensor signals of the lanthanum compound are higher. This fact fits to the general properties inside of the lanthanide elements: Lanthanum is the element that shows the highest lewis-basicity and the basicity is getting smaller if one moves in the right direction in the periodic table. [9]

The question is now, why the praseodymium compound is not showing any sensor effects. We found that the praseodymium tri hydroxide prepared by the same synthesis route is not converted to $Pr_2O_2CO_3$. as proven by the results displayed in Figure 5; one can observe that as soon as the material is heated over 200°C it converts directly to a

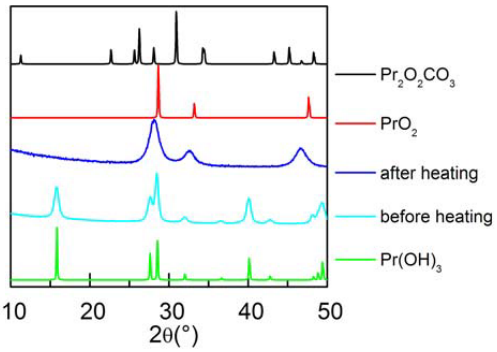

Fig. 5: The $Pr(OH)_3$.is forming a non stoichimetric oxide.

Acknowledgements

Alexander Haensch, Nicolae Barsan and Udo Weimar thank the DFG for supporting this work under the DFG

References

[1] T. Kida, Y. Miyachi, K. Shimanoe, N. Yamazoe, Nasicon thick film-based CO2 sensor prepared by a solgel method, Sensors and Actuators B: Chemical 80 (2001) 28–32.
[2] I. Lee, S. A. Akbara, P. K. Dutta, High temperature potentiometric carbon dioxide sensor next term with minimal interference to humidity, Sensors and Actuators B: Chemical 142 (2009) 337–341.
[3] M. Morio, T. Hyodoa, Y. Shimizu, M. Egashira, A high temperature potentiometric CO2 sensor mixed with binary carbonate and glassy ceramic oxide, Sensors and Actuators B: Chemical 139 (2009) 563–569.

[4] T. Ishihara, K. Kometani, Y. Nishi, Y. Takita, Improved sensitivity of CuO—BaTiO3 capacitive-type CO2 sensor by additives, Sensors and Actuators B: Chemical 28 (1995) 49–54.
[5] S. Matsubara, S. Kaneko, S. Morimoto, S. Shimizu, T. Ishihara, Y. Takita, A practical capacitive type CO2 sensor using CeO2 / BaCO3 / CuO ceramics, Sensors and Actuators B: Chemical 65 (2000) 128-132
[6] I. Djerdj, A. Haensch, D. Koziej, S. Pokhrel, N. Barsan, U. Weimar, M. Niederberger, Neodymium dioxide carbonate as sensing layer for chemoresistive CO2 sensing, Chemistry of Materials 21 (2009) 5375-5381.
[7] Turcotte, Sawyer, Eyring, Rare earth dioxymonocarbonates and their decomposition, Inorg. Chem. 6 (1969) 238-246
[8] Olafsen, Fjellvag, Synthesis of rare earth oxide carbonates and thermal stability of Nd2O2CO3 II, J. Mater. Chem. 9 (1999) 2697-2702
[9] Cotton, Hoboken, Lanthanide and actinide chemistry, Wiley, 2006.