Development and application of a fast solid-state potentiometric CO₂-Sensor in thick-film technology

Sven Wiegärtner📌, Jaroslaw Kita📌, Gunter Hagen📌, Christa Schmausb, André Kießigb, Eckard Glaserc, Armin Bolzc, Ralf Moosa

*aDepartment of functional materials, University of Bayreuth, 95447 Bayreuth, Germany  
bSiegert electronic GmbH, 90556 Cadolzburg, Germany  
cCorscience GmbH & Co. KG, 91052 Erlangen, Germany

Abstract

A solid-state potentiometric CO₂ sensor of the type CO₂, O₂, Au, Li₂CO₃-BaCO₃ | Nasicon | Na₂Ti₆O₁₆-TiO₂, Au, O₂, CO₂ was fully manufactured in planar thick-film technology. On the rear side of the sensor substrate an integrated heater is applied. Thus, it is possible to operate the sensor as a stand-alone device. On the one hand, based on the special meander structure of the heater, a homogeneous temperature distribution on the sensor side can be obtained. And on the other hand, it is possible to operate the sensor with the ideal working temperature of 525 °C. At this temperature, the sensor signal follows the theoretical considerations and responds to the Nernst equation. That way, it is possible to use the sensor in different applications, for example to detect the CO₂ concentration of human breathing air or to monitor the air quality in closed rooms.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

Keywords: CO₂ sensor; nernstian behavior; Nasicon; potentiometric gas sensor

1. Motivation

Monitoring the CO₂ concentration is necessary in many everyday applications, for example to examine the quality of the ambient air, in automotive applications or for human breath analysis [1, 2]. Solid-state potentiometric

* Corresponding author. Tel.: +49-921-55-7401; fax: +49-921-55-7405.
E-mail address: funktionsmaterialien@uni-bayreuth.de

1877-7058 © 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

Peer-review under responsibility of the scientific committee of Eurosensors 2014

doi:10.1016/j.proeng.2014.11.337
gas sensors provide many advantages. They are inexpensive and a fast sensor response behavior, high selectivity, and long term-stability [3]. The first potentiometric CO₂ sensor based on carbonates was proposed by Gauthier et al. [4]. Several types of CO₂ sensors using a carbonate phase with a solid electrolyte like β-alumina or Nasicon are described in literature [5-7].

![Sensor setup](image)

**Fig. 1:** Sensor setup (cross section of the sensor setup; on top of the substrate there are the sensor layers and on the other side there is the heating element).

Similar as suggested in [1] or [8], planar fast potentiometric CO₂ sensors with Nasicon as a sodium conducting phase, a carbonate mixture as sensing electrode, and Na₂Ti₆O₁₃|TiO₂ as reference electrode were manufactured (see Fig. 1). Due to the low affinity of Li₂CO₃ to water vapor [9], a eutectic mixture of Li₂CO₃|BaCO₃ was used as sensing electrode material. This system (so-called type IIIa according to Weppner et al. [10]) is thermodynamically well-defined. The sensor characteristics are in very good agreement with the theoretical considerations and follow the Nernst equation (1) without cross-dependency to the oxygen partial pressure.

\[
U_{\text{sensor}} = U_0 - \frac{R \cdot T}{n \cdot F} \ln \left( \frac{p(\text{CO}_2)}{p_0} \right)
\]  

(1)

Due to the planar heater structure (see Figure 1) on the reverse side of the sensor substrate, it is possible to operate the sensor as a stand-alone device at an operating temperature of 525 °C. In the area of the functional sensor materials (upper half of the sensor substrate), there is a homogeneous temperature distribution due to the optimized heater structure.

2. Experimental

2.1. Sensor setup

The investigated potentiometric CO₂ sensors were fully manufactured in thick-film technology. All ceramic precursor powders were prepared by a mixed-oxide route, as suggested in [8]. In order to prepare screen-printable pastes, each of the prepared powders was mixed with an organic binder to form a homogeneous paste.

On top of a bare Al₂O₃-substrate (3.5 mm x 9.75 mm) a Nasicon layer was screen-printed. Then, the reference phase Na₂Ti₆O₁₃|TiO₂ was printed on one side of the Nasicon film. Two gold grid electrodes were printed according to Figure 1. Finally, the sensitive Li₂CO₃|BaCO₃ mixture was printed on top of one gold grid.

2.2. Measurements

First of all, the sensors were calibrated. Therefore, the sensors were located in a flow channel and heated up to 525 °C by the integrated heating element on the reverse side of the sensor element. Then, a synthetic gas with N₂,
15 % O₂ and varying CO₂ concentration (0.25 % - 5 %) passed through the flow channel, while the sensor voltage was measured.

In a setup for breath analysis, the flow channel was realized as an orifice, in which the sensor was mounted. It was heated up to 525 °C by the heating filament on the rear side of the sensor substrate. Then, a person inhaled and exhaled through one entry of the orifice.

Furthermore, such sensors can be used to monitor the air quality in closed rooms. For that purpose, a sensor was placed in a closed room during a seminar and heated up to its working temperature of 525 °C. The sensor voltage was recorded.

3. Results and Discussion

3.1. Characterization of the sensors

![Characteristic curve of the tested sensor; a) logarithmic scale as it is interesting from a scientific point of view; b) application-oriented linear representation. c) Measured CO₂ concentration during a few respiratory cycles of a person. The curves agree with a typical breath cycle, according to [11].](image)

Fig. 2: a) and b): Characteristic curve of the tested sensor; a) logarithmic scale as it is interesting from a scientific point of view; b) application-oriented linear representation. c): Measured CO₂ concentration during a few respiratory cycles of a person. The curves agree with a typical breath cycle, according to [11].

After the calibration of the CO₂ sensor, the characteristic curve of the sensor (see Figure 2a and 2b), which responds to the Nernst equation, is obtained ($m = 75 \text{ mV/decade } CO₂$, i.e., $n = 2.20$). Using the previously determined characteristic curve of the sensor, the CO₂ concentration of the human breathing air (almost 0 % during inhaling, up to 5 % during exhaling) could be detected (see Fig. 3). Due to the fast response time of the sensor and the ability to operate the sensor as a stand-alone device, it can be used to monitor human breathing.

3.2. Measurement in a closed room

![CO₂ concentration during a meeting in a small class room with three presentations. After ca. 35 and 50 min, the windows were opened.](image)

Fig. 3: CO₂ concentration during a meeting in a small class room with three presentations. After ca. 35 and 50 min, the windows were opened.
Such sensors were also investigated as sensors to monitor the air quality in closed rooms. Figure 3 shows data obtained in a class room during a seminar. During the presentations, the CO$_2$ concentration increased. After each presentation, the windows were opened and the CO$_2$ concentration decreased almost to the initial value. Please note that the slope after each airing is identical, since it is a measure for the number of people in the room.

4. Conclusion

A potentiometric CO$_2$ sensor with an internal heating element on the reverse side was fully and reproducibly manufactured in thick-film technology. The sensor characteristics are in good agreement with the theoretical considerations and the sensor could even be used as a stand-alone device. Due to its fast response and the good long-term stability, measurements with real breathing air and measurements to control the air quality in closed room are possible.

Acknowledgement

This work was supported by the Bavarian Research Foundation (Bayerische Forschungsstiftung; AZ-879-09)

References