Solid-State Potentiometric CO_2-Sensor in Thick-Film Technology

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Abstract:

A planar solid-state potentiometric CO_2-sensor of the type

$$CO_2, O_2, Au, Li_2CO_3\text{-}BaCO_3 \mid Nasicon \mid Na_2Ti_6O_{13}\text{-}TiO_2, Au, O_2, CO_2$$

is fully manufactured in planar thick-film technology. At an operating temperature of 525 °C, the electromotive force follows the Nernst equation. An integrated heater on the backside of the sensor allows operating the sensor as a stand-alone device. Thus, it is possible to use the sensor in different applications, for example to detect the CO_2-concentration of exhaled human breathe.

INTRODUCTION

Monitoring the CO_2 concentration is useful in many applications, for example to examine the quality of the ambient air, for automotive applications or for breath analysis. Solid-state potentiometric gas sensors provide many advantages. They are inexpensive and provide a fast sensor response behavior, high selectivity, or long term-stability [1-2].

In a former study, SAHNER et al. built up a planar fast CO_2-selective potentiometric sensor, using Nasicon as sodium conducting phase, Na_2CO_3 as measuring electrode and $Na_2Ti_6O_{13}|TiO_2$ as reference electrode [3]. This system is, according to [1], a so-called type IIIa sensor-system and thermodynamically well-defined. The sensor characteristics are in good agreement with the theoretical considerations. Therefore the presented sensors follow the Nernst equation

$$emf = E_0 - \frac{R \cdot T}{n \cdot F} \cdot \ln\left(\frac{p(\mathrm{CO}_2)}{p_0}\right)$$

and due to the underlying chemical processes at the sensor electrodes, they are theoretically insensitive to a variation of the oxygen partial pressure.

Based on the promising results from SAHNER et al., the sensor principle has been optimized. Now an eutectic mixture of Li_2CO_3 and $BaCO_3$ is used as sensing electrode material. This improves the water resistance due to the low affinity of Li_2CO_3 to water vapor [4]. Furthermore, the sensor design was miniaturized and an internal heating element was printed directly on the reverse side of the sensor substrate.

EXPERIMENTAL ASPECTS AND SENSOR SETUP

The investigated potentiometric CO_2-sensors were fully manufactured in thick-film technology. Figure 1 shows a cross-section of the sensor structure. On top of a bare Al_2O_3-substrate (3.5 mm x 9.75 mm) a Nasicon layer is screen-printed. Then, the reference phase $Na_2Ti_6O_{13}|TiO_2$ is printed on one side of the Nasicon film. Two gold grid electrodes are printed according to Figure 1. Finally, the sensitive $Li_2CO_3|BaCO_3$ mixture is printed on top of one gold grid.

Additionally, the sensor is equipped with an integrated heater on the reverse side of the sensor, which is realized by a screen-printed platinum structure. Therefore, it is possible to measure the sensor as an actively heated stand-alone device. A dielectric layer covers the heating element for the protection.

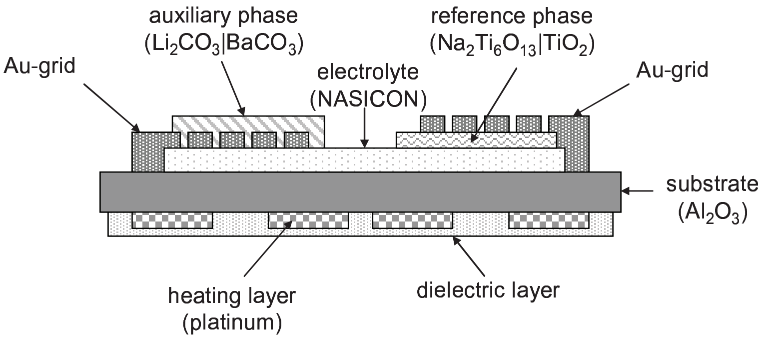

Figure 1: Sensor setup (cross section of the sensor structure)

RESULTS AND DISCUSSION

In order to obtain the characteristic curve of the sensor, the electromotive force (*emf*) has to be measured while varying the CO_2-concentration from 0.4 % up to 3.8 % in a defined synthetic gas atmosphere. The test gas consists of the varying CO_2-concentrations, 10 % O_2, 2,5 % H_2O and N_2 in balance. The test gas, composed by mass flow controllers, is passed through a tube furnace. The tube furnace, in which the sensor is located, is heated up to 525 °C.

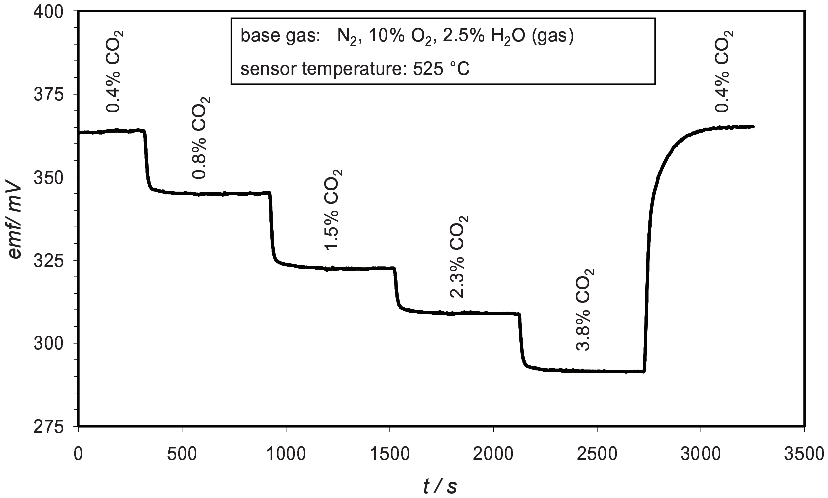

Figure 2: Electromotive force of a planar potentiometric CO_2 gas sensor with $Li_2CO_3|BaCO_3$ as the auxiliary phase at different CO_2-concentrations

To line up the characteristic curve of the sensor, the measured *emf* values of each adjusted CO_2-concentration are plotted against each other. So the characteristic curve, shown in Figure 3, results. The left graph is plotted in a semi-logarithmic scale as it is interesting form a scientific point of view and the right one is given in an application-oriented linear representation.

According to [3] and [5], the semi-logarithmic representation *emf* = f(log(c(CO_2)) is used to evaluate the sensor performance. With the slope m of this plot, the electron transfer number n of the electrochemical reaction can be calculated according to the Nernst equation with p_0 = 1013 mbar, as shown below.

$$emf = E_0 - \frac{R \cdot T}{n \cdot F} \cdot \ln\left(\frac{p(\mathrm{CO_2})}{p_0}\right) = E_0 - \underbrace{\frac{R \cdot T \cdot \ln 10}{n \cdot F}}_{m} \log\left(\frac{p(\mathrm{CO_2})}{p_0}\right)$$

Our investigated sensors show an electron transfer number about *n* = 2.10, which is near the theoretical index value of *n* = 2, which is given by the electrochemical cell reactions. This proves that the sensor characteristic is in good agreement with the theoretical considerations.

As the characteristic curves of all tested sensors show also the same slope and offset parameters, we can point out a high reproducibility in fabrication.

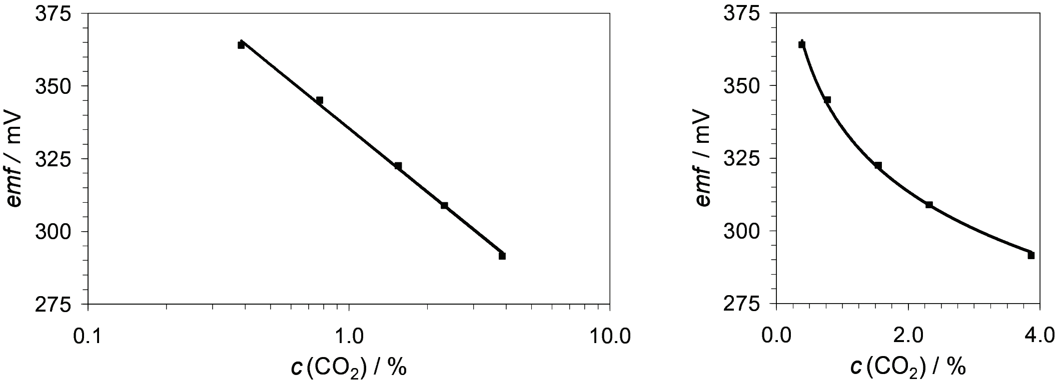

Figure 3: Characteristic curve of the sensor (*n* = 2.11);
***left*: logarithmic scale as it is interesting from a scientific point of view;**
***right*: application-oriented linear representation**

Since the sensor is equipped with the integrated heating element on the reverse side, the sensor can be heated up to a desired operating temperature. Because of the temperature-dependent resistance of platinum, the sensor temperature can even be kept constant, actually in flowing gas atmospheres. Therefore, the produced sensors can be used for different applications. For example, it is possible to measure the CO_2-concentration of human breath during inhaling and exhaling.

In an initial test, a person in- and exhaled a few times through a tube, in which such a sensor was mounted. The sensor was heated up to 525 °C and the electromotive force was measured. Using the characteristic curve of this sensor, it is possible to calculate the prevailing CO_2-concentration, according the following equation.

$$c(CO_2) = e^{\left(\frac{(E_0 - EMF)\cdot n \cdot F}{R \cdot T}\right)} \cdot 100\%$$

Figure 4 represents the measured CO_2-concentrations. During the exhalation, the sensor showed concentrations up to 5 % CO_2. Throughout the inhalation steps with ambient air, the measured concentration falls down to nearly 0 % CO_2 every time. These results agree with the expected values.

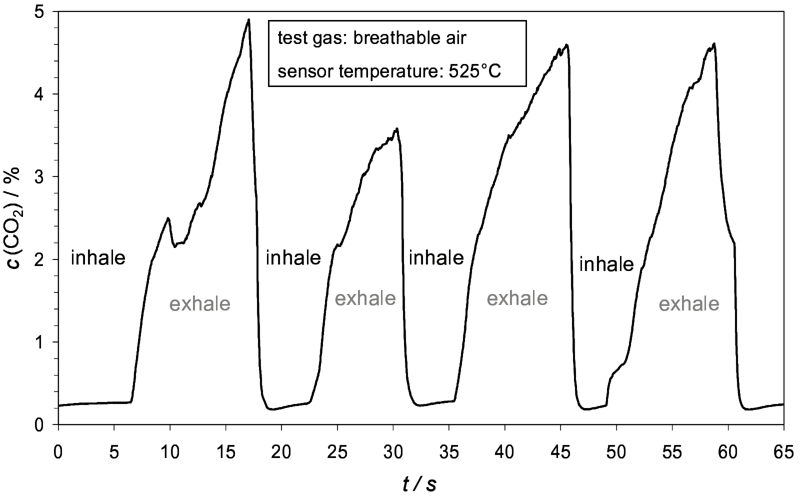

Figure 4: Measured CO_2-concentration during the in- and exhaling process of a human

CONCLUSIONS AND OUTLOOK

A potentiometric CO_2-sensor with an internal heating element on the reverse side was fully and reproducible manufactured in thick-film technology. We proved that the sensor characteristics are in good agreement with the theoretical considerations and that the sensor even could be used as a stand-alone device.

For further works, it would be interesting to miniaturize the sensor setup in order to reduce the power input, which is necessary for the sensor heating. This will lead to other interesting application fields.

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