Solid-State Potentiometric CO₂-Sensor in Thick-Film Technology

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Abstract:
A planar solid-state potentiometric CO₂-sensor of the type

\[
\text{CO}_2, \text{O}_2, \text{Au, Li}_2\text{CO}_3|\text{BaCO}_3 \mid \text{Nasicon} \mid \text{Na}_2\text{Ti}_6\text{O}_{13} \mid \text{TiO}_2, \text{Au, O}_2, \text{CO}_2
\]

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 CO₂-concentration of exhaled human breathe.

INTRODUCTION

Monitoring the CO₂ 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 CO₂-selective potentiometric sensor, using Nasicon as sodium conducting phase, Na₂CO₃ as measuring electrode and Na₂Ti₆O₁₃TiO₂ as reference electrode [3]. This system is, according to [1], a so-called type IIA 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

\[
emf = E_s - \frac{R}{n \cdot F} \cdot \ln \left( \frac{p(\text{CO}_2)}{p_s} \right)
\]

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 Li₂CO₃ and BaCO₃ is used as sensing electrode material. This improves the water resistance due to the low affinity of Li₂CO₃ 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 CO₂-sensors were fully manufactured in thick-film technology. Figure 1 shows a cross-section of the sensor structure. On top of a bare Al₂O₃-substrate (3.5 mm x 9.75 mm) a Nasicon layer is screen-printed. Then, the reference phase Na₂Ti₆O₁₃TiO₂ is printed on one side of the Nasicon film. Two gold grid electrodes are printed according to Figure 1. Finally, the sensitive Li₂CO₃|BaCO₃ 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.

RESULTS AND DISCUSSION

In order to obtain the characteristic curve of the sensor, the electromotive force (emf) has to be measured while varying the CO₂-concentration from 0.4 % up to 3.8 % in a defined synthetic gas atmosphere. The test gas consists of the varying CO₂-concentrations, 10 % O₂, 2.5 % H₂O and N₂ 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.

To line up the characteristic curve of the sensor, the measured emf values of each adjusted CO₂-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 from 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 \( p_0 = 1013 \text{ mbar} \), as shown below.

\[
emf = E_s - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{p(CO_2)}{p_i} \right) = E_s - \frac{R \cdot T}{n \cdot F} \cdot \ln_{10} \left( \frac{p(CO_2)}{p_i} \right) \]

\[
\ln_{10} x = \frac{\ln x}{\ln 10} = \frac{\ln x}{2.30258509299} = \frac{\ln x}{2.3026}
\]

\[
elef = E_s - \frac{R \cdot T}{n \cdot F} \cdot \frac{\ln \left( \frac{p(CO_2)}{p_i} \right)}{2.30258509299} = E_s - \frac{R \cdot T}{n \cdot F} \cdot \frac{\ln \left( \frac{p(CO_2)}{p_i} \right)}{2.3026}
\]
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.

\[
c(\text{O}_2) = e^{(\frac{(E_{\text{th}}-\text{EMF}) n F}{R T})} \cdot 100\%
\]

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.
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.

REFERENCES