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A planar solid-state potentiometric CO_2 sensor in thick-film technology for breath analysis

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Abstract:

In this work, a planar solid-state potentiometric CO_2 sensor for medical applications of the type CO_2, O_2, Au, Li_2CO_3-$BaCO_3$ | Nasicon | $Na_2Ti_6O_{13}$-TiO_2, Au, O_2, CO_2 was developed in thick-film technology. Due to an integrated screen-printed platinum heater on the rear side, the sensor can be applied without changing its working temperature of 525°C in the main flow of the respiratory air of an injured person during intubation. The sensor is insensitive to oxygen variations and its signal follows strictly and reproducible the Nernst equation. Thus, the correct installation of the endotracheal tube can be controlled by detecting the CO_2-concentration in the exhaled air.

Key words: potentiometric, CO_2 sensor, medical application, nernstian behavior, thick-film technolgy

Motivation

Solid-state potentiometric gas sensors are inexpensive in production and provide a fast sensor response behavior. They are highly selective and long-term-stable [1], [2]. Due to the fabrication in thick-film technology, small sensors can be produced with a very low weight. Hence, they may be applied in the main stream of the respiratory air of an injured person during intubation, in a way that the endotracheal tube will not be dislocated.

One way to build up a planar fast potentiometric CO_2 sensor with Nasicon as solid-state electrolyte, a carbonate mixture as sensing electrode, and $Na_2Ti_6O_{13}|TiO_2$ as reference electrode is suggested in [3]. In [4], such a sensor cell is manufactured in planar thick-film technology. According to [2], such a sensor cell system is thermodynamically well defined and the sensor characteristics are in good agreement with the theoretical considerations (Nernst behavior), especially at an operating temperature above 450°C [3].

Sensor setup

The investigated potentiometric CO_2-sensors were fully manufactured in thick-film technology as suggested by [4]. Fig. 1 shows a cross-section of the sensor structure.

On top of a bare Al_2O_3-substrate the Na^+-conducting electrolyte layer material Nasicon is screen-printed. Then, the reference electrode material $Na_2Ti_6O_{13}|TiO_2$ is printed on one side of the Nasicon film. According to Fig. 1, two gold grid electrodes are printed. Finally, the sensitive carbonate mixture $Li_2CO_3|BaCO_3$ is printed on top of the gold grid for the working electrode.

Additionally to the functional sensor layers, the sensor is also provided with an integrated heater, which is realized by a screen-printed platinum layer on the reverse side of the sensor substrate.

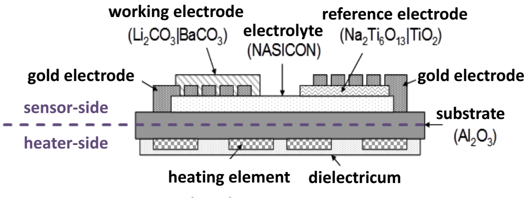

Fig. 1: Cross section through the sensor setup

Experimental

In order to construct the sensor (Fig. 2) for the medical application, it is necessary to build up miniaturized sensors with reproducible sensor signals. Therefore, the screen-printed functional sensor materials had to be examined. SEM pictures were taken to determine the thickness and the porosity of each layer. SEM pictures revealed, that the thickness of the $Li_2CO_3/BaCO_3$ layer should be at least 20 µm and the porosity of this layer should not be too high.

Fig. 2: Photographs of the sensor; a) sensor side, b) heater (rear) side with SMD connector

Furthermore, the heater structure was developed to heat up the sensor structure to operate the sensor at its optimal working temperature of 525°C. Owing to FEM modeling, an optimal heater structure was evaluated. Hence, a homogeneous temperature distribution over the whole sensor layers was obtained (Fig. 3). By using an infrared camera, the promising results could be confirmed.

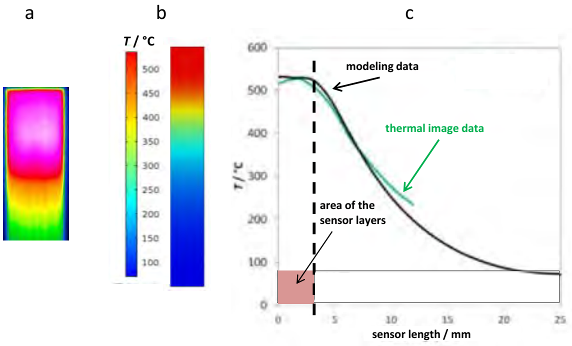

Fig. 3: Results of the temperature distribution; a) thermal image (LTTT, University Bayreuth); b) temperature distribution over the sensor substrate; c) temperature along a line from the top to the bottom of the sensor, modeling data and the data of the thermal image

Due to the known *TCR* (*TCR* = 3250 ppm/K) of the applied Pt thick film and the resistance R_0 of the platinum heater structure at room temperature, the heater-resistance at 525°C can be calculated according to eg. (1).

$$R_{525°C} = \left(R_0 \cdot TCR \cdot \Delta T\right) + R_0 \qquad (1)$$

Hence, the sensor can be heated up easily to 525°C by adjusting the heater resistance and the sensor temperature can even be kept constant, also in flowing gas atmospheres. Thus, such sensors are able to be operated as stand-alone devices for different applications. In the investigated example, it is determined to measure the CO_2 concentrations of human breath during the intubation.

Results and Discussion

In initial measurements, it should be checked whether the output voltage of the miniaturized sensors follows the theoretical equations. The sensors were heated up in a furnace to 525 °C and the sensor voltage was measured while varying the CO_2 concentration of the test gas stepwise. The CO_2 concentration was varied in the range from 0.4 % up to 4 %. The test gas consists of the CO_2-concentrations, 20% O_2, and N_2 as a balance. The test gas, composed by mass flow controllers, is passed through the tube furnace. Fig. 4 shows the sensor signal of such a measurement.

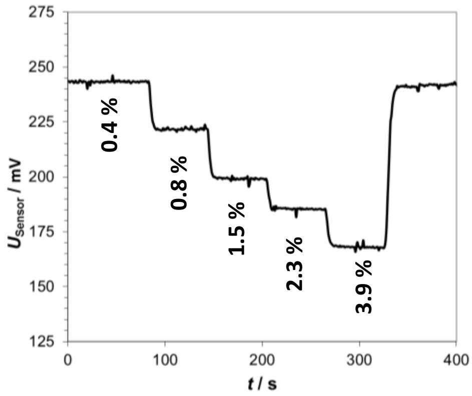

Fig. 4: Sensor signal during a calibration measurement, the CO_2-concentrations of each step are written in the graph

Fig. 5 shows the characteristic curve of the tested sensor. To evaluate the characteristic curve, the sensor voltage is plotted against the respective CO_2 concentration. Our investigated sensors show an electron transfer number about *n* = 2.1 ± 0.1. This is close to the theoretical value of *n* = 2. This proves that the sensor characteristic is in good agreement with the theoretical considerations.

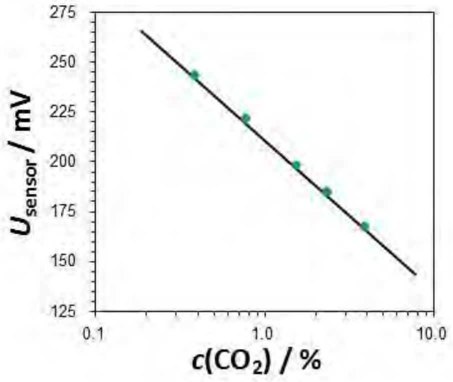

Fig. 5: Semi logarithmic representation of a characteristic curve of the tested sensor

In a next test, a person in- and exhaled a few times through a device holder (Fig. 6), in which such a potentiometric CO_2 sensor with an integrated heater on the reverse side was mounted. The CO_2 concentration of the breathing air should be measured.

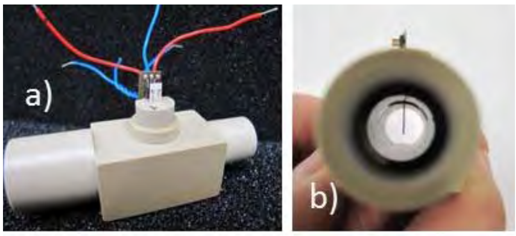

Fig. 6: a) Device holder with an integrated sensor element; b) Photography through the device holder

The sensor was heated up to 525°C. The sensor temperature was controlled to constant values with the help of the temperature-dependent platinum resistance of the heating element. During the whole test, the sensor voltages were recorded.

$$c(CO_2) = e^{\left(\frac{(E_0 - U_{sensor}) \cdot n \cdot F}{R \cdot T}\right)} \cdot 100\% \qquad (2)$$

Using a previously determined characteristic curve of the sensor, the CO_2-concentration of the human breathing air could be determined according to eg. (2) (almost 0% CO_2 during inspiration, up to 5% CO_2 during exhalation). Fig. 7 shows the measured CO_2-concentration with our investigated sensor.

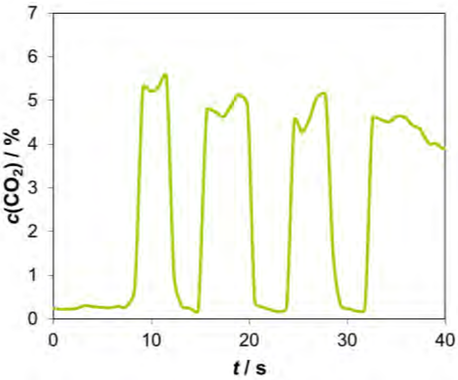

Fig. 7: Measured concentration during in- and exhaling of a test person

So, due to the fast response time ($t_{90} \approx 350$ms) of the sensor and the ability to operate the sensor as a stand-alone device, it can be used for monitoring the human breath, for instance.

Conclusion

A fast planar solid-state potentiometric CO_2 sensor with an internal heater on the reverse side was fully and reproducible manufactured in thick-film technology. We showed that the sensor characteristic agrees well with the theoretical considerations and follows the Nernst equation. The sensor can be used as a stand-alone device, for example to control the CO_2 concentration during exhaling of a person.

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