YSZ THICK FILM OXYGEN GAS SENSOR USING THE DIRECT IONIC THERMOELECTRIC EFFECT

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Introduction

The introduced thick-film sensor determines the oxygen partial pressure by measuring the thermopower over an oxygen ion conductor. The measurand is a voltage, which means that the sensor signal is independent on geometry. That is advantageous for long-term stability because the influence of aging effects like cracks or sintering is low. Another advantage of this method compared to the measuring of a Nernst voltage (e.g. in a λ -probe) is that no reference atmosphere is needed. So, the sensor setup can be designed easier.

In the proposed sensor set-up, a temperature gradient is applied over an YSZ thick film, and the resulting thermovoltage V_{meas} is measured between two platinum electrodes. If the temperature difference ΔT is known, the thermopower (also known as Seebeck coefficient) of the YSZ-based thermocell, ε , can be determined:

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_{Pt} - \frac{V_{meas}}{\Delta T} \tag{1}$$

Here, ϵ_{Pt} denotes the Seebeck coefficient of the electrode material.

Since ε depends on the pO_2 of the surrounding gas atmosphere [1], the oxygen concentration can be measured.

Experimental

The sensor was prepared in thick-film technology, similar to the method presented in [2], where an electronic semi-conductor was used as the gas sensitive phase. Fig. 1 shows a top view. The gold and platinum electrodes form two thermocouples to measure the temperature difference ΔT . The thermovoltage of the cell is mesured between the two platinum leads. The Pt/YSZ cermet electrode promotes the equilibrium between the YSZ film and the gas phase. The temperature difference was achieved by a screen-printed platinum heater on the backside of the sensor to which a sinusoidal voltage was applied. Between the sensor and the heater, a platinum film is applied that serves as an equipotential layer (see Fig. 2). This equipotential layer minimizes electrical interferences as shown in [3].



Fig. 1: Top view of the sensor setup



Fig. 2: Sensor set-up

For sensor testing, the sensor was mounted onto a sample holder and inserted in a tube furnace to reach the measuring temperature. Different O_2/N_2 ratios were applied to adjust a defined oxygen partial pressure, pO_2 . For cross sensitivity tests, a variety of other gases were added.

Results and discussion

The measured thermovoltage V_{meas} as a function of the temperature gradient ΔT is shown in Fig. 3 for an oxygen partial pressure of 0.1 bar. For each pO_2 , 200 measurement points are plotted and fitted by linear regression. The slope of the fitted graph is directly proportional to the Seebeck coefficient ε at this particular oxygen partial pressure.



Fig. 3: Measured thermovoltage for different temperature differences at T = 700 °C and $pO_2 = 0.1$ bar

The oxygen sensor characteristics of the thermoelectric sensor device at 700 °C is presented in Fig. 4. Each point in this curve was calculated from the slope values at one specific pO_2 as described above. It can be seen that the sensor characteristic is semilogarithmic as expected from literature [1].



Fig. 4: Sensor characteristic of the YSZ film at T = 700 °C

The cross sensitivity to other gases (CO, CO₂, NO, C_3H_8 , H_2 and water vapour) was low, as shown in [4]. Furthermore, the temperature dependance of the thermoelectric sensor was investigated. As can be seen in Fig. 5, the sensor signal is nearly independent of the temperature in the investigated temperature range. This behaviour is expected from literature, where only a very small temperature dependence of the thermopower of YSZ was observed [5].



Fig. 5: Temperature dependence of the thermopower for two different oxygen partial pressures

Conclusion

The introduced thermoelectric sensor, based on YSZ, was successfully operated as an oxygen sensor. Its main advantages are a very low cross sensitivity to many other gases and a negligible temperature dependence of the sensor signal.

Literature

- C. Wagner, The thermoelectric power of cells with ionic compounds involving ionic and electronic conduction, *Progress in Solid State Chemistry*, 7, (1972), pp 1-37
- [2] F. Rettig, R. Moos, Direct thermoelectric hydrocarbon gas sensors based on SnO₂, *IEEE Sensors Journal*, 7, (2007), pp 1490-1496
- [3] F. Rettig, R. Moos, Direct thermoelectric gas sensors: design aspects and first gas sensors, *Sensors and Actuators B: Chemical*, 123, (2007), pp 413-419
- [4] U. Röder-Roith, et al., Thick-film solid electrolyte oxygen sensors using the direct ionic thermoelectric effect, *Sensors and Actuators B: Chemical*, in press
- [5] H. Yoo, J. Hwanga, Thermoelectric behavior of single crystalline ZrO₂(+8mol Y₂O₃), *Journal of Physics and Chemistry of Solids*, 53, (1992), pp 973-981