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NO detection by pulsed polarization with Pt interdigital electrodes on yttria stabilized zirconia

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Summary:
Pulsed polarization measurements were performed on Pt | YSZ sensors. These consist of four interdigital electrodes (IDEs), two on the upper and two on the lower side of the YSZ-substrate. IDEs with an electrode gap and width of 150 and 300 µm were tested. The sensors were operated one-sided and double-sided. It was found that the sensors operated on one side showed a significantly better symmetry in the signal path. This symmetry, in turn, makes it possible to halve the measuring time. In general, the sensitivities were very similar in all operating modes and show no dependency on the investigated gap.

Keywords: pulsed polarization, Pt | YSZ, NO detection, interdigital electrodes, exhaust gas sensor

Motivation

Pulsed polarization is a new method to measure nitrogen oxides without a reference. In contrast to common measuring principles such as potentiometry or amperometry, this method uses a signal that depends not only on the concentration of the analyte gas but also on time. This method is therefore comparable to cyclic voltammetry [1] or the thermo-cyclic operation of sensors [2], meaning it is a dynamic method.

The pulsed polarization technique has mainly been tested for operation with planar Pt|YSZ|Pt sensors and lambda probes so far [3–5]. A less considered field is the use on sensors with interdigital electrodes [6]. On the one hand, the effect of the spatial proximity of both electrodes is interesting, since the polarization creates a strongly oxidizing as well as a strongly reducing local surrounding at the electrodes. On the other hand, interdigital electrodes have the advantage that both electrodes can be produced in one step, resulting in more symmetrical with the same morphology.

Experimental

A pulsed polarization cycle is schematically shown in Fig. 1. The sensor is periodically and alternately polarized with a constant voltage U_{pol} for a fixed duration t_{pol}. Since this voltage does not correspond to the thermodynamic behavior, the sensor subsequently discharges to its state of equilibrium. This self-discharge of the sensor is significantly accelerated in the presence of NO. This is utilized in pulsed polarization by measuring the self-discharge $U_{discharge}$ of the sensor between alternating polarization pulses. If this self-discharge is accelerated, lower voltages are reached earlier. By evaluating these voltages at fixed times, a sensor signal can be generated (U_{signal}).

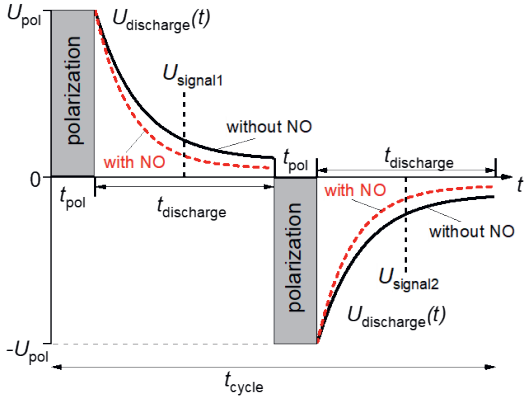

Fig. 1 Overview of a pulsed polarization cycle

For the pulsed polarization measurements, the sample is polarized for t_{pol} = 0.5 s with a voltage of U_{pol} = 1 V. The sensor discharges for $t_{discharge}$ = 10 s between the alternating polarizations.

Sensor elements have been fabricated using 300 µm thick yttria stabilized zirconia substrates and screen printed platinum interdigital electrodes on both sides as depicted in Fig. 2. The distance between the finger electrodes as well as the line width was 150 and 300 µm.

The sensor elements were placed in a tube furnace and heated up to 400 °C in base gas consisting of 10 % O_2 and 2 % H_2O in N_2 at a gas flow of 200 ml/min. NO concentrations in the range from 5 ppm up to 50 ppm were admixed stepwise with base gas.

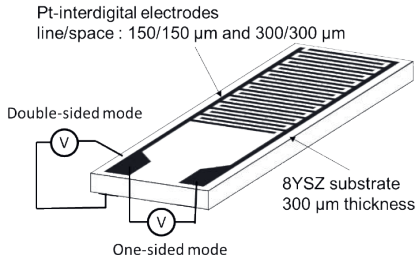

Fig. 2 Sensor layout with IDEs on both sides

Results and discussion

Fig. 3 shows the accelerated discharge 0.5 seconds after positive (solid) and negative (dashed) polarization. The voltage values in the base gas at this time serve as a reference. In the one-sided mode, the sensors show a very symmetrical signal for both electrode distances. Thus the voltage differences for the positive and the negative polarization are almost identical. Also among each other, both measurements show only very small differences (a)(b). In contrast, the sensors operated on both sides show differences in the discharge after positive and negative polarization (c)(d). However, the sensitivity of the double-sided operated sensor after negative polarization is higher than that of the one-sided operated sensors.

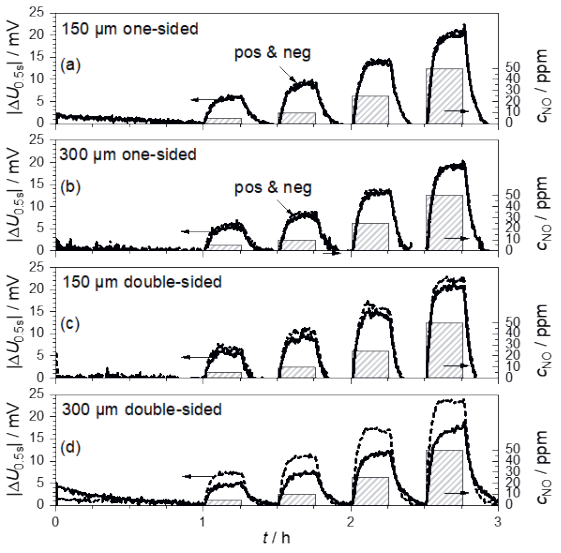

Fig. 3 Voltage differences $|\Delta U_{0.5s}|$ between a discharge in the base gas and in 5, 10, 25 and 50 ppm NO, measured 0.5 s after positive (solid) and negative (dashed) polarization. U_{pol}=1 V, t_{pol}=0.5 s, $t_{discharge}$=10 s

Impedance spectroscopy measurements before and after pulsed polarization operation (not shown here) show electrolyte resistances of 600 to 1000 Ω for the double-sided 150 µm sensor and the single-sided 300 µm sensor, respectively. The almost doubling of the electrolyte resistance and the small influence on the sensitivity show that the electrolyte resistance seems to have only a small influence on the sensor effect. The electrodes seem to have the greater effect. This can be concluded in particular from the very symmetrical signals of the IDE electrodes with positive and negative polarization. No difference can be seen between the 150 µm and the 300 µm interdigital electrodes. Possibly, the electrode distances are still too large to influence each other.

However, the symmetrical signals allow to use both polarization directions ($U_{signal1}$ and $U_{signal2}$ in Fig. 1) for the concentration evaluations by using the absolute values. This allows for halving the measuring time.

Outlook

It could be shown that the interdigital electrodes do not influence each other at the minimal distance of 150 µm. The next step would therefore be a further reduction of the electrode distance. On the one hand, this would allow a miniaturization of the sensor, on the other hand it would possibly provide a better insight into the sensing mechanism.

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