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Detection of NO by pulsed polarization of Pt I YSZ

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ABSTRACT

Pulsed polarization is a measurement technique based on alternating voltage pulses with intermediate pauses for self discharging. The possibility of NO detection by this dynamic measurement technique using conventional lambda sensors is shown in prior investigations. The discharging after polarization depends strongly on NO content in the low ppm range. Due to faster discharging at NO containing atmosphere compared to base gas, the voltage difference between the discharge curves can act as a characteristic value; this voltage change shows a logarithm dependency on NO concentration. The feasibility of NO sensing by use of a planar, more cost-effective sensor (Pt electrodes on yttria stabilized zirconia) is evaluated in detail. The optimum range for NO detection is found at 400 °C by comparing the NO sensitivities at temperatures from 300 °C up to 550 °C.

1. Introduction

Smog and acid rain are serious environmental problems and NO_x as a precursor of both has to be reliably detected in the low ppm range in order to control vehicle or turbine emissions. In this interesting field, much research is conducted, as shown in recent reviews of the materials used for NO_x gas sensors, e.g. [1,2]. Different sensor principles including potentiometric, impedancemetric, and amperometric sensors are presently under study. Most sensors utilize the mixed potential principle that consist of mixed oxide electrodes on oxygen ion conducting yttria-stabilized zirconia (YSZ) [3–5]. Also novel concepts for measuring low NO_x contents are under investigation like solid-state gas dosimeters that determine the accumulated amount of total NO_x in exhausts [6].

Novel automotive aftertreatment concepts to reduce NO_x emissions rely on NO_x sensors [7] which have been added to wide-band and binary lambda sensors [8,9]. However, it is unclear whether the existing or proposed NO_x sensors are accurate enough for future OBD [10]. Two YSZ-based NO_x sensors with a relatively complex setup are on the market. Owing to their two-pumping-cell setup, extremely low currents occur (a few nA/ppm NO_x) leading to high costs for electronics and sensor manufacturing.

Commercial thimble type lambda probe is installed in quantities of millions per year in automotive exhaust aftertreatment systems and can be operated reliably over 100,000 mile automotive exhausts [11]. Therefore, in previous initial investigations we used well-known thimble type lambda probes but operated them in a pulsed polarization mode. This leads to excellent sensitivities and a good selectivity towards total NO_x even at low concentrations [12,13].

For cost reduction reasons, an even more simplified sensor design without air reference electrode is preferred. Pt applied on oxygen ion conducting YSZ as used by lambda probes provides well-known catalytic electrodes. The promising measurement results regarding NO_x sensing thimble type lambda probes by applying pulsed polarization suggest the assumption that a simpler planar setup using the polarization technique also yields a good NO_x response without the need of air reference electrodes. The feasibility of this planar sensor concept is the subject of this study.

2. Experimental

For the planar sensor design, Pt electrodes (5 mm × 6 mm) were screen-printed on both sides of an 8 mol% Y_2O_3-stabilized ZrO_2 thick-film substrates (YSZ) with a thickness of 300 μm and fired. Pt wires (∅100 μm) were bonded onto the Pt electrodes by a drop of the Pt paste, leading to a setup as depicted in Fig. 1. Hence, both electrodes had a symmetrical setup with a distance of the thickness of the YSZ substrate (300 μm).

This setup is called "sensor" in the following. The sensor is placed in a tube furnace, in a way that both electrodes are completely exposed to the applied gas atmosphere. Care has been taken that the electrodes did not have any contact with the tube of the furnace. A premixed gas flow of 0.5 l/min with 20% oxygen at a humidity level of about 3 vol.% is applied, unless otherwise stated. To investigate the NO sensitivity, small amounts of NO were added, leading to NO concentrations in the low ppm range from 2.5 ppm to 30 ppm. The sensor is heated only by the furnace, since in this early stage no additional heater was added. For evaluation of the optimum operating point for NO detection, temperatures between 300 °C and 550 °C were used and the sensors' sensitivities are compared under various conditions.

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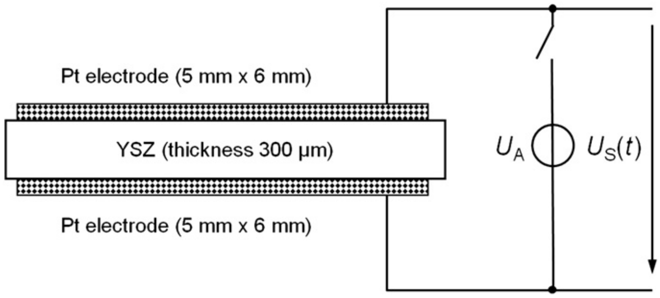

Fig. 1. Scheme of the planar sensor design: symmetric Pt electrodes on YSZ.

The pulsed polarization technique is based on the self-discharge of the electrodes measured after alternating voltage pulses according to prior investigations on lambda probes [12–14]. Fig. 2 shows this dynamic measurement method in detail.

After applying a voltage pulse of defined amplitude U_A for a defined time duration t_0, the switch was opened and the self-discharge voltage $U_S(t)$ was recorded for a defined duration t_1. Subsequently, this voltage pulse was repeated with an electrode polarization of opposite sign and with the same voltage amplitude, polarization duration and pause duration for discharging. This procedure, consisting of alternating pulses with equal pulse parameters, was repeated permanently.

In order to obtain a direct characteristic value that correlates in a certain way with the NO concentration, the voltage difference between the discharge curve at base gas and at a defined NO concentration is defined as

$$\Delta U_{t*} = U_{\text{base gas}}(t*) - U_{\text{c\_NO}}(t*) \tag{1}$$

where c_NO being the NO concentration, and was evaluated for a defined discharge time t^* (with $t^* \leq t_1$). Thus, ΔU_{t^*} is denoted as the sensor responses. It can be compared for different conditions.

3. Results and discussion

Different NO concentrations in the low ppm range were investigated to evaluate the polarization technique for the planar Pt|YSZ system. To find the best temperature range for NO sensing, the gas temperature was varied in the range from 300 °C up to 550 °C.

3.1. Discharge curves and influence of NO

Due to the symmetric sensor design, the curve shape of the discharge voltage U_S is the same after both polarization signs. This is in strong contrast to the results obtained for the thimble type oxygen sensor in [12,13], where one electrode is always exposed to a defined air reference. The voltage drops very fast after the potential pulses and the sensor voltages halves compared to the applied voltage U_A only 100 ms after the polarization pulse. Since the resistance of the YSZ decreases with higher temperatures, this parameter has a big influence on the discharging behavior, so that the voltage drops faster with increasing temperature. This dependence is studied later in detail.

The fundamental influence of NO on the sensor discharge voltage $U_S(t)$ is the accelerated discharging compared to that of base gas, which is identical for both polarization signs due to the symmetric sensor design. Fig. 2b depicts schematically the influence of NO on the discharge curves. If NO is in the gas phase, the discharge curves are shifted to lower voltage values after a positive pulse, which is equal to a faster discharge. After opposite potential (the so-called negative voltage pulses), the NO curves are on a higher potential level, which conforms to an accelerated voltage drop after polarization, too.

This effect is completely different from a sensor that follows the classical mixed potential principle, because there is no offset voltage above both curves of opposite polarization signs but rather the discharge time is affected by the gas components. Because the curve shapes are equal for both polarization signs, only one polarization sign is displayed in the following.

Fig. 3 shows the discharge curves at base gas (20% O_2 in N_2 at a humidity level of about 3 vol.%) compared to different NO concentrations in the range of 2.5 ppm to 30 ppm after applying a voltage pulse of $U_A = 2.5$ V for $t_0 = 100$ ms. The discharge voltage is recorded for $t_1 = 3.0$ s after each voltage pulse at a temperature of 400 °C. Due to fast discharging

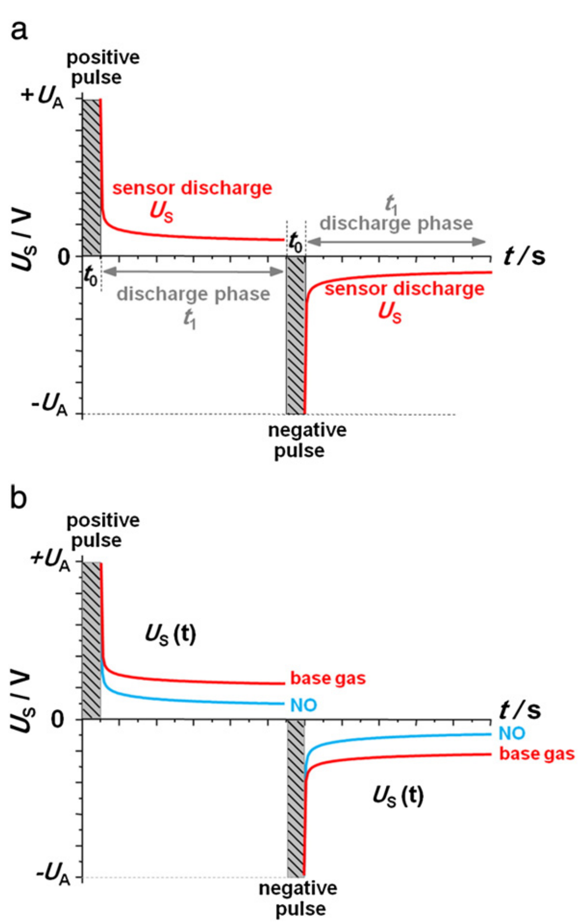

Fig. 2. Scheme of one cycle of the pulsed polarization technique (a). Scheme of NO nfluence on discharging curves: accelerated discharging at NO containing atmosphere compared to that at base gas at both polarization signs (b).

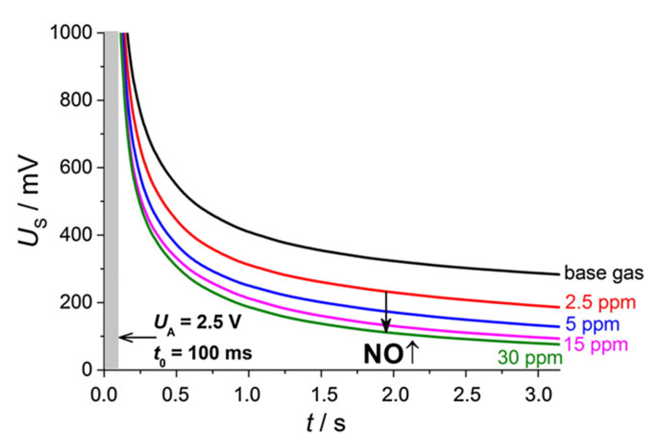

Fig. 3. Discharge curves at different NO concentrations added to the base gas. $T = 400$ °C, $U_A = 2.5$ V, $t_0 = 100$ ms, $t_1 = 3$ s, $c_{O_2} = 20\%$, $c_{H_2O} = 3$ vol.%.

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