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Investigation of the pulsed-polarization sensor mechanism in YSZ-based gas sensors

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Abstract:
The pulsed polarization method is a new method to detect nitrogen oxides. It uses differences in the depolarization behavior but the mechanism has not yet been fully understood. Therefore, different sensor geometries and materials are investigated to provide a better insight into the sensing mechanism.

Key words: pulsed polarization, Pt | YSZ, NO_x detection, interdigital electrodes, exhaust gas sensor

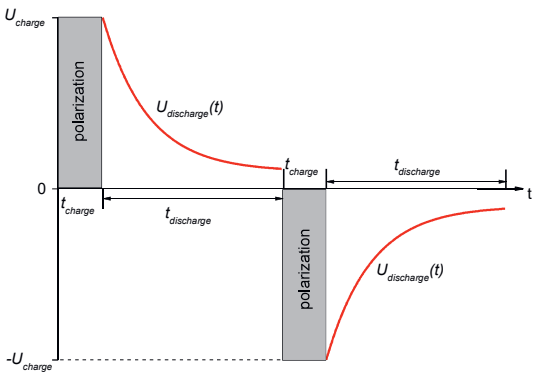

Fig. 1 Principle of the pulsed polarization method, based on [1].

Pulsed polarization method

Most sensors for nitrogen oxides (NO_x; NO and NO_2) are based on potentiometric (equilibrium and non-equilibrium), amperometric, or impedancemetric principles to detect the concentration of NO_x in the atmosphere [2]. All these methods have in common that they reach a steady state value at a constant atmosphere after certain time.

In contrast, the pulsed polarization method is a dynamic method and that utilizes the well-known Pt|YSZ-system. The dynamic method itself consists of four measuring phases [1]. First, the sensor is polarized by a defined voltage U_{charge} for a defined duration t_{charge}. Second, the voltage supply is disconnected and the self-discharge of the Pt|YSZ device is recorded for a duration $t_{discharge}$ as the open circuit voltage (OCV). In the next step, the sensor is polarized with opposite polarity $-U_{charge}$ and the discharge curve is recorded again. A complete cycle is schematically shown in Fig. 1.

Fischer et al. have shown for thimble type lambda probes a correlation between the depolarization voltage and the concentration of NO_x in the gas atmosphere at a certain sensor temperature [1]. Further tests showed that no reference atmosphere is needed for this effect [3]. Consequently, simple planar sensors with Pt-electrodes, screen-printed on both sides of an 8YSZ-substrate were investigated without reference atmosphere, i.e., both electrodes are exposed to the same gas atmosphere [4]. They also showed a clear change in depolarization behaviour if NO_x is present.

Finally, interdigital electrodes were tested. They were screen-printed on a 150 µm YSZ-substrate [5] and on a YSZ-layer, deposited on top of an Al_2O_3-substrate by screen-printing and by aerosol deposition [6]. Both sensor types also showed a faster depolarization in presence of NO_x. Fig. 2 shows the depolarization of a sensor with planar Pt electrodes on 8YSZ-substrate, after polarization with a potential U_{charge} of 1.0 V for 1 s. It is obvious that the depolarization is faster with increasing NO concentration. U_{1s} represents the depolarization voltage in base gas and base gas with NO, measured 1 s after polarization. The voltage curve of U_{1s} is shown in Fig. 3. This increased depolarization could be observed for both, NO and NO_2 [6]. Therefore, U_{1s} might be used as sensor signal for total NO_x. An application as exhaust gas sensor was recently presented by Pohle et al. [7].

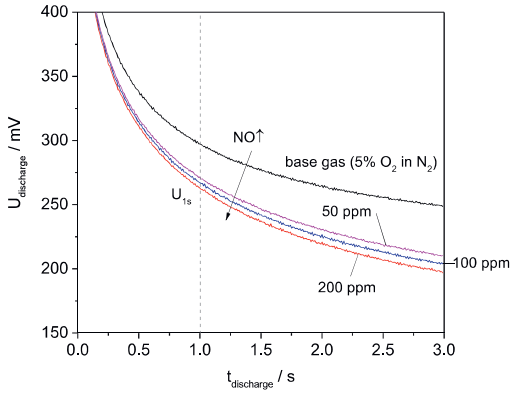

Fig. 2 Time-dependent sensor voltage $U_{discharge}$ during self-discharge in base gas and under NO exposure. Here the sensor consists of an 8YSZ-substrate and screen-printed platinum electrodes on both sides.

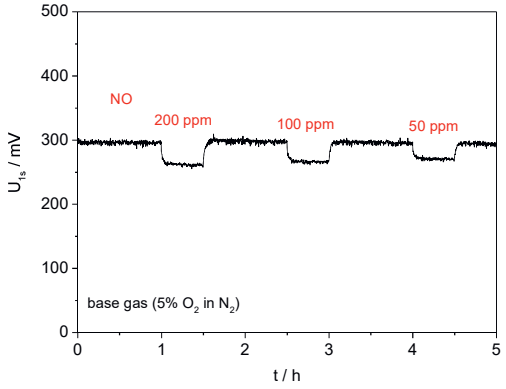

Fig. 3 Depolarization voltage U_{1s}, measured 1 s after positive polarization.

Sensor model

A first model approach to explain the sensing mechanism was published by Fischer et al. [8]. One aspect of this initial model is the difference in the oxygen partial pressures between both electrodes. Generally, the voltage between both electrodes is related to the oxygen partial pressures at both electrodes (pO_2^{I}, pO_2^{II}) by the Nernst equation (1):

$$U_{nernst} = \frac{RT}{4F} \ln \frac{pO_2{}^{I}}{pO_2{}^{II}} \qquad (1)$$

If 1 V polarization voltage is applied at T=400°C, this equation leads to a difference in oxygen partial pressure in the order of $\frac{pO_2^I}{pO_2^{II}} \approx 10^{30}$ between the electrodes in the same atmosphere. Therefore, at the electrode with higher oxygen partial pressure (positive potential), platinum oxides will be formed on the electrode and the NO/NO_2 equilibrium will be shifted to NO_2. At the electrode with lower oxygen partial pressure (negative potential), previous platinum oxides will be reduced and the NO/NO_2 equilibrium is shifted locally to NO. It is suggested, that especially these changes of the NO/NO_2 equilibrium are responsible for the increased depolarization of the sensor.

Effects of the sensor design and materials

One interesting aspect of the pulsed-polarization principle is the role of the electrode geometry. A signal amplification with interdigital electrodes, compared to planar electrodes [5] was found. The reasons for this are still unclear. Therefore, different electrode geometries will be tested with variations in electrode size and distance. Another key point is the material aspect. This includes both, the electrodes and the solid electrolytes. Thus, Pt, Au and perovskite [9] will be used as electrode materials with different electro-catalytic activities. Different solid electrolytes will be used on the one hand, to vary the ionic conductivity at a constant temperature and, on the other hand, to vary the temperature and keep the ionic conductivity constant. This may provide a better insight into the sensing mechanism.

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