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NO_x-Detection by Pulsed Polarization of Lambda Probes

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Abstract:

Conventional thimble type lambda sensors combined with a pulse discharge technique were used for NO_x detection in a simulated combustion exhaust gas with varying oxygen and moisture levels. Open circuit discharge characteristics after defined polarization pulses with alternating polarity show strong dependencies on NO_x (112 mV / decade) in the lowest ppm range (0.5 – 50 ppm). Increase in NO_x concentration accelerates sensor discharge, whereby the discharge curves following negative pulses are more affected by the NO_x content compared to positive pulses. The sensitivities to NO and NO_2 are equal and measurement of total NO_x is possible. The discharge curves are affected by the oxygen and the water content. An increase in O_2 concentration results in a shift of the discharge curves to negative voltages. Additionally a decreased sensor response to NO_x is obtained for both polarization polarities. The water concentration has the opposite effect. All discharge curves are shifted to positive voltages with increasing H_2O content. As a result, the sensor response increases strongly. The voltage shifts due to O_2 and H_2O are expected from Nernstian behavior of a lambda probe, whereby moisture influence is stronger compared to O_2. The feasibility of the method as an exhaust gas total NO_x measurement system is confirmed.

Key words: polarization, self discharge, Pt|YSZ, lambda probe, NO_x sensor, exhaust gas

Introduction

Lambda probes are appropriate for applications as oxygen sensors at high temperatures and in harsh environments. The conventional thimble type lambda sensors consist of an oxygen ion conducting solid electrolyte (yttria-stabilized zirconia YSZ) and two porous platinum electrodes, whereby one of the electrodes is exposed to reference gas atmosphere with a constant oxygen partial pressure pO_2^{ref}. The second electrode is in contact to the exhaust gas with a varying $pO_2^{exhaust}$. The resulting potentiometric solid electrolyte concentration cell measures the oxygen activity of the exhaust gas. A potential difference U can be measured in equilibrium according to Nernst equation:

$$U = \frac{k_B T}{4e} \ln \frac{pO_2^{exhaust}}{pO_2^{ref}} \qquad (1)$$

with Boltzmann's constant, k_B, the absolute temperature, T, and the elementary charge, e [1], [2].

Our approach is to combine a well-known classic thimble type lambda probe (robust, reliable and cost-effective sensors) with a pulse discharge technique for NO_x detection. Pulsed voltages are applied to zirconia-based oxygen sensors and the open circuit self-discharge characteristics in between the voltage pulses with alternating polarities are investigated. A strong dependency of the discharge behavior on NO_x concentration with a high selectivity is found [4]. As consequence, a total NO_x sensor can be realized by using a conventional lambda sensor.

In order to investigate the influence of main combustion exhaust gas components on the discharge characteristics, the lambda probe is exposed to varying oxygen, moisture and carbon dioxide levels. The resulting discharge curves after alternating polarization pulses are measured and analyzed in dependence on the gas composition. Relevant or critical interfering gas components for selective NO_x detection can be determined. Additionally the contribution of these gases to the sensing mechanism can be analyzed.

Experimental

The pulse discharge technique is based on measurements of the open circuit discharge curves between the sensor electrodes following

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polarization with voltage pulses of opposite polarity but equal amplitude [3].

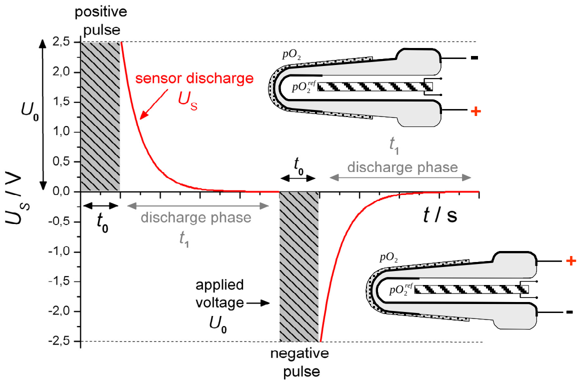

Fig. 1. Schematic of pulsed polarization and discharge technique with polarity of the pulses.

Fig. 1 shows schematically the pulsed discharge technique with the polarities of the polarization pulses as related to the design of a conventional thimble type lambda sensor. Discharge curves were continuously recorded during the pauses (pause duration 10 s) between the polarizing voltage pulses with the amplitude of 2.5 V and duration of 1 s. NO_x sensitivity was measured in a simulated combustion exhaust with oxygen concentration varying from 0 – 25 %, H_2O from 0 – 10 % and NO or NO_2 from 0 – 50 ppm.

NO_x sensitivity

Fischer et al. [4] showed that the discharge characteristics depend strongly on NO level and the sensor response is related to the overall NO_x concentration. A very selective NO_x sensor response was found.

Fig. 2 shows discharge curves at different NO concentrations from 0 to 50 ppm. Sensitivity to NO is much higher for the discharge curves following negative pulses as compared with positive pulses.

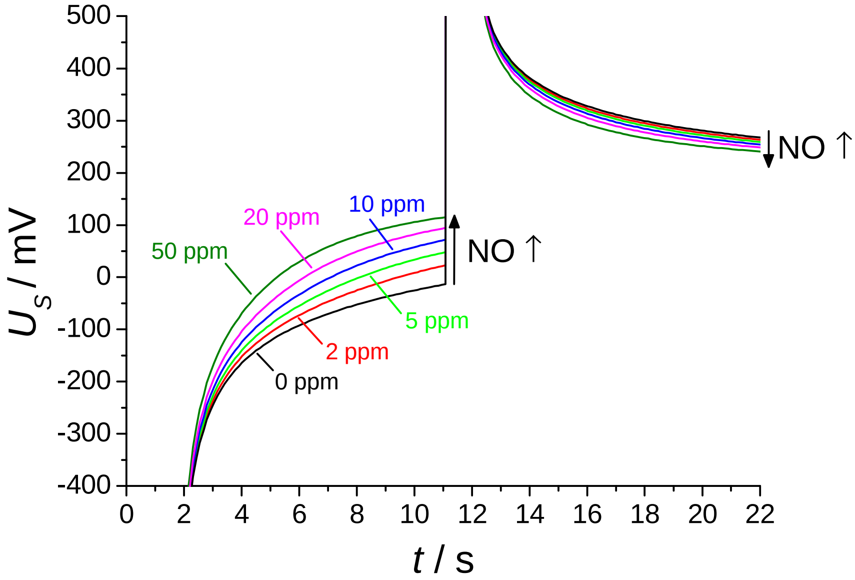

Fig. 2. Discharge curves U_s after negative and positive polarization pulses at different NO concentrations

Using a signal processing algorithm, developed in [3] and [4], sensor response to pulses of NO were measured and shown in Fig. 3. Even at the lowest NO concentrations of 0.5 ppm, the sensor response amounts to 20 mV and reaches 150 mV at 12.5 ppm, which corresponds to a sensitivity of 112 mV / decade. In addition, the lambda probe exhibits short response time and a steady baseline. This result is especially astonishing when one keeps in mind that a conventional lambda probe serves as a very sensitive NO_x sensor.

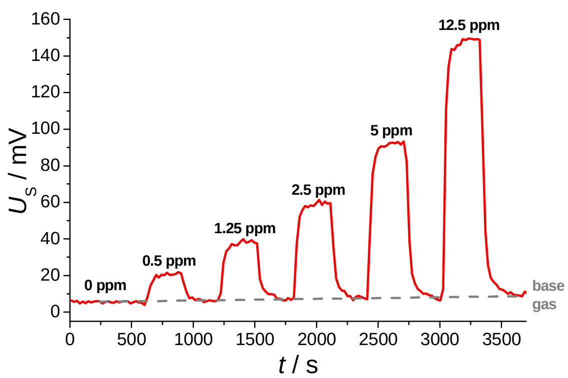

Fig. 3. Sensor response at different NO contents in the concentration range of 0.5 to 12.5 ppm.

O_2 influence on discharge curves

The influence of different O_2-concentrations in the range of 0 to 25 % on the discharge curves at base gas and at 50 ppm NO_2 are compared in Fig. 4 for negative and positive polarizing voltage pulses. With increasing oxygen content, all curves are shifted towards negative voltages, as expected from the Nernstian response of a lambda sensor. Changes in oxygen concentration do not significantly change the shape of the discharge curves. The effect to NO is stronger after negative voltage pulses, but minor after positive pulses.

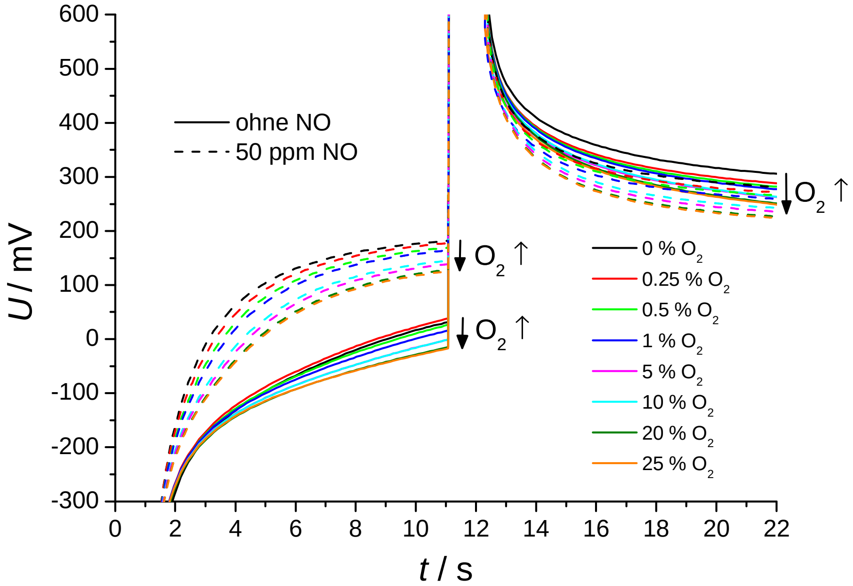

Fig. 4. Influence of oxygen on discharge curves at base gas and 50 ppm NO_2

A minor reduction in the sensitivity to NO_x is found with increasing oxygen content. This can be seen in Fig. 4 as the slightly reduced difference in the discharge curve of NO_2 containing atmosphere compared to that of the base gas.

The O_2 influence on NO_2 sensor response is more pronounced than expected from Nernstian O_2 effect. It can be assumed that O_2 is involved in the sensor mechanism and affects the polarization phenomena, also during NO_x exposure. It is well known that O_2 is an active species at the Pt|YSZ-interface of lambda probes. The formation of platinum oxide is discussed in dependency of polarization parameters and O_2 concentration [5, 6]. The correlation between O_2, PtO_x formation and NO_x sensitivity is currently under investigation.

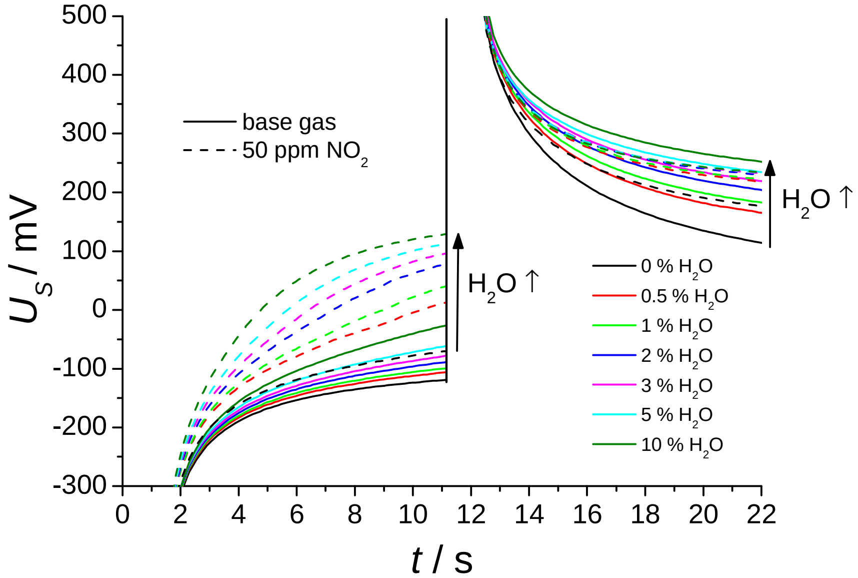

Fig. 5. Influence of water content on discharge curves at base gas and 50 ppm NO_2.

H_2O dependency of discharge curves

There is a broad range of water content in exhaust gases. To cover this issue, water-concentration dependency of the sensor output was investigated in the range of 0 – 10 %. For both polarization polarities, the voltage is shifted towards positive voltage with increasing moisture content as can be expected from Nernstian behavior. The H_2O content influences the NO_2 sensor response as well (see Fig. 5). An increase in moisture strongly enhances the sensor response. The NO_2 response is marginal without H_2O.

H_2O seems to be a promoter for NO_2 sensitivity. The H_2O dependency in base gas corresponds to Nernstian behavior. With NO_2, the H_2O influence increases and promotes the NO_2 sensitivity. It is assumed that H_2O catalyzes the reactions involving NO_2 and affects the sensing mechanism.

In contrast to the O_2 dependency, the effect of varying water concentration is much stronger in the investigated range.

Summary

The main result of this investigation is the demonstrated high NO_x sensitivity on discharge curves in all atmospheres with different water and oxygen concentrations. O_2 and especially H_2O have strong effects on the discharge curves. Especially the voltage shifts due to O_2 and H_2O at NO_x exposure are enhanced compared to Nernstian behavior in base gas.

In summary the feasibility of a pulsed mode operated lambda probe as a NO_x sensor for exhaust gas measurements is confirmed.

For further understanding of the sensing mechanism the investigation of processes and reactions at the Pt|YSZ interface during polarization and discharging is necessary. Reactions taking place at a Pt I YSZ model system should also occur at thimble-type lambda probes during pulsed polarization method and are assumed to be responsible for sensor effect.

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