Pulsed-potential method for NO_x – detection using standard zirconia-based lambda sensors

S. Fischer [a], R. Pohle [b], U. Guth [c], B. Farber [d], M. Fleischer [b], R. Moos [a]

[a] University of Bayreuth, Functional Materials
95440 Bayreuth, Germany

[b] Siemens AG, Corporate Technology
81739 Munich, Germany

[c] Kurt-Schwabe-Institute for Measuring and Sensor Technology Meinsberg,
04720 Ziegra-Knobelsdorf, Germany

[d] BJR Sensors, LLC
OH 44139 Solon, USA

Introduction

Exhaust gas aftertreatment systems equipped with exhaust gas sensors are installed in quantities of millions per year in automobiles. At least one zirconia exhaust gas oxygen sensor (lambda sensor) for the detection of the air-to-fuel-ratio is used. Generally, one lambda sensor is mounted upstream and one is mounted downstream of the three-way catalyst (TWC) [1,2]. Additionally in lean NO_x traps NO_x sensors have been added to wide-band and binary lambda sensors [3–5]. However, it is unclear whether the sensors are accurate enough for future OBD [6]. For that reason, a reliable NO_x sensor is of great interest. To date, only one type of automotive exhaust gas NO_x sensor supplied by two manufactures is on the market. It is constructed with planar zirconia technology and provides a threefold sensing function, so it not only detects NO_x, but also measures the oxygen concentration in lean exhausts and serves as a binary lambda sensor [7,8]. Because of its pumping chambers, the sensor setup is complex and the electronics must deal with extremely low currents (a few nA / ppm NO_x [3]), so that the cost is relatively high.

The classic lambda probe is known as robust and reliable systems and it is the preferred exhaust gas sensor due to its low costs [1]. Therefore it would be beneficial if its functionality could be improved to detect NO_x in the exhaust gas. Because the lambda probe act as a potentiometric solid electrolyte concentration cell ("Nernst cell") it measures the oxygen activity towards an outside air reference or in novel embodiments towards an internal pumped reference [9]. For that an yttria stabilized zirconia (YSZ) ceramic membrane with porous electrodes separates two gas chambers with the oxygen partial pressures pO_2 and pO_2^{ref} as shown in Fig. 1.

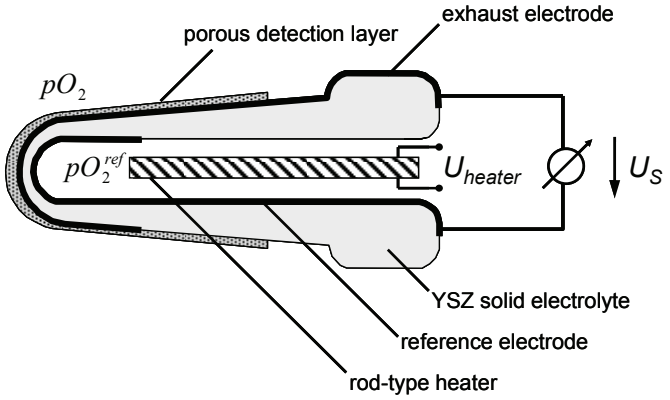

Fig. 1: Schematic depiction of a thimble-type lambda sensor

Hence, an electromotive force, U_S, can be measured in equilibrium: $U_S = \frac{k_B T}{4e} \ln \frac{pO_2}{pO_2^{ref}}$ (1).

According to the Nernst equation a voltage difference of 50 mV per decade pO_2 occurs at an operation temperature of 735 °C and with air as a reference ($pO_2^{ref} \approx 0.2$ bar).

At temperatures higher than 600 °C electrochemical devices using oxygen-ion-conducting yttria-stabilized-zirconia (YSZ) are appropriate for applications as oxygen sensor, whereas at lower temperatures the chemical reactions on the surface of metal-oxide electrodes and electrolytes compete with electrochemical reactions. Therefore other gas components like NO_x can be detected. Standard potentiometric sensors suffer under the opposite sign for the emf potential of NO and NO_2 which makes it very hard to monitor total NO_x [1]. Therefore, a wide range of complex material systems is under investigation in order to obtain reliable NO_x detection [2, 3]. A main drawback of this approach is the insufficient knowledge about the long-term stability of these systems.

Our approach described in this paper is to use standard lambda probes known as a robust, reliable and cost-effective system. We apply pulsed voltages to zirconia-based oxygen sensors and investigated the self discharge behavior in between the voltage pulses.

2 Experimental

Fig. 2 shows the measurement process used in this work. After applying a positive charging voltage U_0 for a defined duration t_0, the voltage supply is disconnected and the self discharge voltage U_S of the sensor is recorded for defined time t_1. This procedure is then repeated using a voltage with an opposite sign.

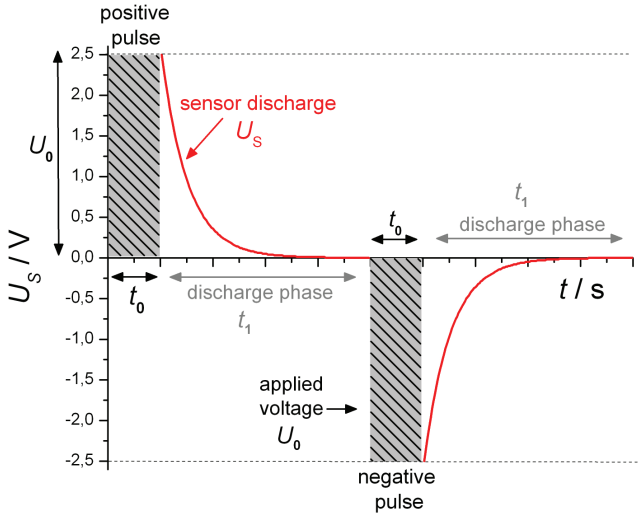

Fig. 2: Schematic depiction of the measurement approach

A positive charging voltage is defined as a higher potential of the outer exhaust electrode with respect to the inner air electrode, which is exposed to an air reference $pO_2^{ref} \approx 0.2$ bar (cf. Fig. 1). This pulse sequence with electrode polarizations of opposite signs is used permanently and the discharge curves are measured continuously. At polarization with voltage pulse duration of 100 ms and amplitude of 2.5 V the best results are achieved. The discharge curves are recorded during a time period of 10 s after this electrode polarization. After this procedure the next charging–discharging cycle follows, therefore one cycle takes 20.2 s.

In addition to this novel pulsed potential method, steady state measurements have been carried out for comparison, i.e. the voltage is measured without applied pulses (mixed potential measurement).

If not stated otherwise, gas measurements have been carried out at an oxygen concentration of 4 % and a humidity level of 3 % absolute. The total air flow was set to 1 l/min and the test gas concentrations for NO (nitrogen oxide), NH_3 (ammonia), C_2H_5OH (ethanol), and H_2 (hydrogen) are shown in Fig. 3b. In order to represent hydrocarbons in the exhaust gas, a mixture of C_2H_6 (ethane), C_2H_4 (ethene), C_2H_2 (ethylene), and C_3H_6 (propene) in equal parts was used as an additional test gas stated in the following as “HC”. The duration of the test gas pulses and the pauses between them are always 20 min.

In order to simulate a hot exhaust pipe the thimble-type lambda sensors were mounted in a furnace. At furnace temperature of 325 °C and a constant sensor heating voltage of 8 V a sensor temperature of approximately 590 °C was determined by comparing the heater resistance with respect to different external parameters [10].

3 Results and discussion

3.1 Mixed potential

The sensor voltage without applying pulses is measured to evaluate the influence of various gas concentrations (Fig. 3b) at the “normal” operational mode of the lambda probe. The measured mixed potential is illustrated in Fig. 3a.

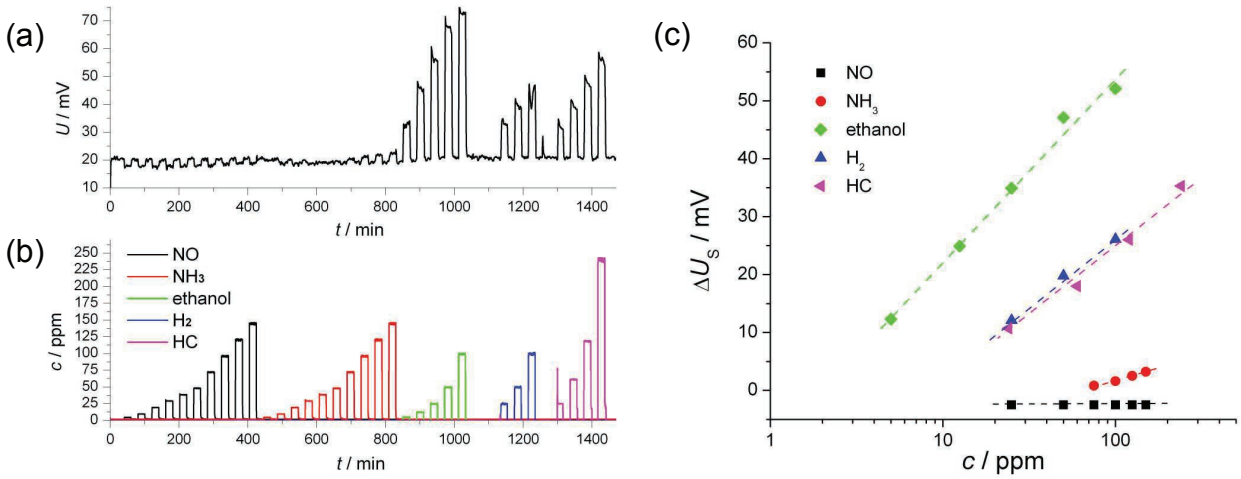

Fig. 3: a) Mixed potential
b) Gas concentration profile; gases were added to a base gas of 4 % O_2, 3 % H_2O in N_2
c) Characteristics $\Delta U_S = \left| U_S (c_{gas}) - U_S (0\ ppm) \right|$

The base voltage of 20 mV is achieved by Nernst behavior and is nearly consistent to the oxygen content of 4 % at this temperature range. The sensor response to ethanol is most prominent, followed by HC and H_2 with similar sensitivities; in contrast to that a concentration independent voltage with opposite sign (- 5 mV) is measured in NO. In ammonia-containing atmosphere the sensor voltage is influenced by test gas only at concentrations above 75 ppm. Comparing the sensitivities to various gas components, the voltage differences between test-gas containing atmosphere (with defined concentrations c_{gas}) and N_2 (c_{gas} = 0 ppm) atmosphere are evaluated; the characteristics $\Delta U_S = \left| U_S (c_{gas}) - U_S (0\ ppm) \right|$ of investigated gases are shown in semi-logarithm plots (Fig. 3c).

3.2 Pulsed potential methoe

3.2.1 Discharge curves

The great benefit of the new pulsed potential method is becomes obvious from the following results. After evaluating the NO sensitivity in detail, the influence of other exhaust gases is pointed out.

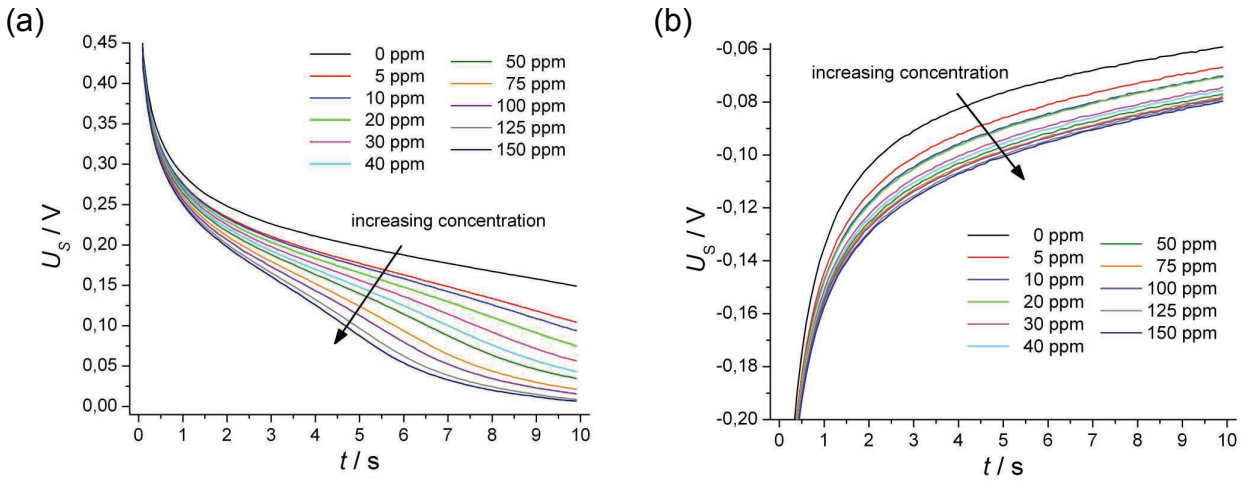

Fig. 4: Time behaviour of the sensor voltage during the discharge phase at changing NO concentrations [10]
Reprinted with Permission of Elsevier
a) after a positive pulse of 2.5 V and 100 ms
b) after a negative pulse of 2.5 V and 100 ms

Fig. 4 illustrates the discharge curves at N_2 base gas (black) compared to NO concentrations in the range of 5 ppm (red) to 150 ppm (dark blue). The drop of voltage from the applied pulse voltage of 2.5 V to approximately 500 mV occurs in a few milliseconds and is therefore not displayed. For both positive (Fig. 4a) and negative (Fig. 4b) pulses the discharge curves show a strong and monotonic dependency on the concentration of NO and differ in NO-behavior. With changing concentrations the curves are shifted, so that the lambda probe discharge faster compared to base gas after positive pulse and discharge slower after alternating polarization. Furthermore the curves show additional changes in the overall shape, which are more evident for the positive pulse. Even at the lowest investigated concentration level of 5 ppm a clear response to NO can be observed. The detection of NO is possible over at least two decades of concentrations, because a further shift of the discharge curves is evident at NO concentrations up to 150 ppm.

As already shown in [10] the discharge curves of the lambda probe correlates with total NO_x in the range from 10 to 2000 ppm, independently if NO or NO_2 is dosed to test gas. Additionally, the curve shapes exhibit an individual character for different gases like NH_3, ethanol, H_2 and HC, which leads to the conclusion that the influence of several gas species could be separated. The response to CO as a relevant exhaust gas is negligibly.

Table 1 summarizes the sensitivities in mV / decade by using different methods, the pulsed-polarization one in contrast to continuous readout (mixed potential measurement).

Tab. 1: gas sensitivities in mV / decade using different methods

	NO	**NH_3**	**ethanol**	**H_2**	**HC**
mixed potential	-	7.5	31.5	23.0	24.0
positive pulse	110	125	60	6.0	29.0
negative pulse	9.5	13.5	27.0	13.0	20.5

Towards NO, only a negligible response was obtained in the mixed potential mode (Fig. 3), which is in strong contrast to the pulsed discharge method with positive voltage, where the response to NO is the most prominent one compared to other gases. The sensitivity towards NH_3 is higher compared to NO (cf. Tab.1), but the voltage differences after positive pulses are at a higher lever [10]. By polarization with negative pulses, the response to reducing gases is comparable to the mixed potential measurement, while the response to NH_3 and NO is slightly increased (Tab. 1). In contrast, the response to ethanol is similar for the continuous readout method and for the evaluation of the discharge curve after negative pulses, respectively.

3.2.2 Oxygen influence on NO-sensitivity

According to (1) the output voltage of Lambda probes depends strongly on oxygen content, so that a theoretical sensitivity of 43 mV / decade reveals at a determined temperature of 590 °C. To evaluate the influence of oxygen to NO response, the voltage response (without voltage pulses) of the sensor is measured at various oxygen contents in the range of 1 % to 20 % O_2 first. At the measurement conditions (heat voltage of 8 V, gas temperature of 325 °C with a humility level of 3 % absolute) a sensitivity towards oxygen of 34 mV / decade is received. This result does not agree exactly with the Nernst equation (1) at a temperatur of 590 °C, but is on a similar level.

To investigate the oxygen influence towards NO sensitivity for the pulsed potential method, various NO concentrations (5 ppm to 150 ppm) are dosed in pulses to base gas for 20 min. each at different oxygen levels (2 %, 4 % and 6 % O_2). Fig. 5 illustrates the results by analyzing the discharge curves at different times after the pulse voltage was switched off. The red curve illustrates the discharge voltage which is measured 0.5 s after each polarization pulse, whereas the pink curve depicts the voltage behavior at the end of discharging phase (10 s).

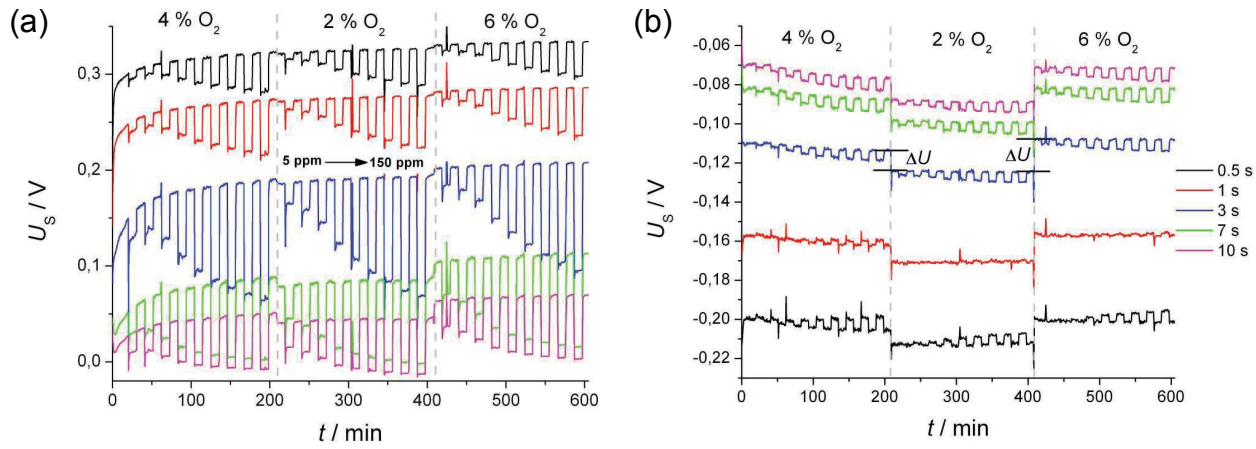

Fig. 4: influence of oxygen variation towards NO response
NO gas pulses (20 min.) at concentrations from 5 to 150 ppm at different evaluation times
(a) after positive pulses
(b) after negative pulses

In agreement with Fig. 4a and 4b the sensor signal is different at various evaluation times. At all evaluation times each concentration of dosed NO is clearly recognizable for both positive and negative pulses of 2.5 V. The voltage differences between a defined NO concentration and base gas differ at shown evaluation times of 0.5 s, 1 s, 3 s, 7 s and 10 s and are clearly higher after positive pulses. Furthermore for all evaluation times the voltages are on a higher level after positive pulses (base voltage of about 300 mV at an evaluation time of 0.5 s after positive polarization versus 200 mV after negative pulses).

Sensor voltage at various oxygen contents in the background of NO changes to more negative or positive direction according to the Nernst equation. The influence on discharge curves is different for positive and negative pulses. After polarization with positive voltages the influence of oxygen increased with evaluation time. The oxygen step from 4 % to 2 % (or from 2 % to 6 %) O_2 is clearly noticeable in a voltage step at evaluation times above 3 s, whereas just a few mV are measured at this oxygen variation at shorter discharging times. Fig. 4b shows the oxygen influence after alternating polarisation with negative pulses. The denoted voltage steps ΔU at oxygen variation are independent of evaluation time, which leads to the conclusion that the overall discharge curve is only shifted according to Nernst equation.

Comparing the NO sensitivities at various oxygen atmospheres the voltage differences for positive pulses $|\Delta U_S = U_S(c_{NO}) - U_S(0\text{ppm})|$ are shown in semi-logarithm plots (Fig. 5).

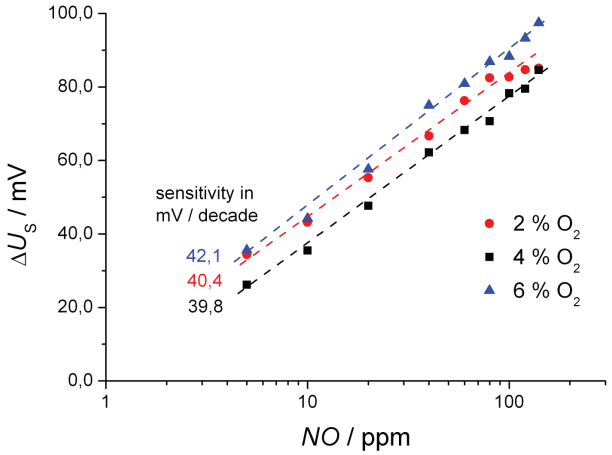

Fig. 5: NO characteristic $\Delta U_S = |U_S (c_{NO}) - U_S (0\text{ ppm})|$ after positive pulses at an evaluation time of 7 s

Because the characteristics are received by subtracting the voltage at NO pulses towards base gas with the same oxygen content, the voltage shift at oxygen variation is nearly suppressed, so that the influence of oxygen can be neglected. Therefore the NO sensitivity is nearly independent of oxygen content.

4 Conclusion, summary and outlook

In contrast to most mixed potential sensors, the signal response obtained by the self-discharge method shows a good correlation to the NO_x concentration, independently if NO or NO_2 is dosed. The new pulsed polarization technique enables the detection of NO_x in the concentration range from 5 to 2000 ppm, which is a suitable range for exhaust gas measurements. Furthermore the sensitivity to NO prevails significantly compared to other investigated gases like H_2, ethanol or hydrocarbons.

The cross sensitivity toward oxygen is the most prominent one, because the lambda probe usually act as oxygen sensor. A variation of oxygen in a range of 2 % to 6 % can be neglected, because the discharge curves are only shifted according to Nernst equation and therefore the voltage differences at NO pulses are nearly the same.

If one aims to install such a sensor in automotive exhausts, the cross sensitivity to water and carbon dioxide has to be investigated as well as the influence of the sensor and the exhaust temperature. All in all the investigation of the self-discharge characteristic is a promising approach for detection of NO_x in exhaust gas using potentiometric standard lambda sensors.

References

[1] J. Riegel, H. Neumann, H. M. Wiedenmann, Exhaust gas sensors for automotive emission control, Solid State Ionics 152–153 (2002) 783–800.

[2] R. Moos, A brief overview on automotive exhaust gas sensors based on electroceramics, Int. J. Appl. Ceram. Technol. 2 (2005) 401–413.

[3] N. Kato, K. Nakagaki, N. Ina, Thick film ZrO_2 NO_x sensor, SAE Paper 960334 (1996).

[4] A. Waltner, et al., 27th International Vienna Motor Symposium (2006).

[5] U.G. Alkemade, B. Schumann, Engines and exhaust after treatment systems for future automotive applications, Solid State Ionics 177 (2006) 2291–2296.

[6] Y.W. Kim, M. Van Nieuwstadt, Threshold monitoring of urea SCR systems, SAE Paper 2006-01-3548 (2006).

[7] H. Zhang, C. Pfleger, B. Lemire, Integration eines smart NO_x-sensors im Abgasstrang für die Benzindirekt-einspritzung 21st Intl. Engine Symposium, Vienna (2000) pp. 288–310.

[8] H. Sasaki, D. Scholl, M. Parsons et al., Development of an Al_2O_3/ZrO_2-Composite High-Accuracy NO_x Sensor, SAE Paper 2010-01-0041 (2010).

[9] T. Baunach, K. Schänzlin, L. Diehl, Sauberes Abgas durch Keramiksensoren, Phys. J. 5 (2006) 33–38.

[10] S. Fischer, R. Pohle, B. Farber, R. Proch, J. Kaniuk, M. Fleischer, R. Moos, Method for detection of NO_x in exhaust gases by pulsed discharge measurements using standard zirconia-based lambda sensors, Sensors and Actuators B 147 (2010) 780-785.