Selective mixed potential ammonia exhaust gas sensor for harsh environments

Daniela Schönauer, Ralf Moos
Universität Bayreuth
Lehrstuhl für Funktionsmaterialien
95440 Bayreuth, Germany

Kerstin Wiesner, Maximilian Fleischer
Siemens AG
CT PS 6
81739 München, Germany

Abstract

An ammonia exhaust gas sensor for harsh environments enables to control the NH_3 emission downstream an SCR (selective catalytic reduction) catalyst, which is used to reduce the NO_x emissions of diesel engines and industrial plants. A novel mixed potential NH_3 exhaust gas sensor for selective NH_3 detection showed in synthetic exhaust a very good correlation between sensor voltage and NH_3 concentration with a marginal NO_x cross interference. First tests in real exhaust gas to proof the applicability showed promising results.

Introduction

Minimizing the emissions of vehicles and plants is a huge concern of the society. More stringent NO_x emission standards result in the application of exhaust gas aftertreatment systems like the SCR-system. NO_x is reduced by addition of NH_3 or NH_3-forming substances to the exhaust pipe and a following selective reduction reaction at the catalyst to H_2O and N_2. An ammonia sensor would enable to measure the NH_3 slip and therefore would provide a closed-loop control system and an active OBD (on board diagnosis). Consequently, an increasing NO_x conversion rate could be achieved [1, 2]. In this work, the sensor characteristic of a novel NH_3 sensor is described including the influence of important cross sensitivities like nitrogen oxides and the air-to-fuel ratio λ. Additionally, initial engine test bench results are discussed.

Experimental

The schematic sensor setup in ceramic multi-layer technology is described in Fig. 1. The sensor consists of two alumina substrates. One substrate is the heater substrate including a platinum heater structure and a dielectric protection cover, both realized in thick film technology. The second substrate is the sensor substrate: First, a solid electrolyte layer (yttria stabilized zirconia, YSZ) is screen-printed. On top, two porous gold electrodes are applied, whereas one electrode is covered afterwards by an additional porous catalytic active film. As a catalyst material, commercially available materials with proven long-term stability in the exhaust and known catalytic behaviour are examined. In this contribution, the properties of V_2O_5-WO_3-TiO_2 as coating material are characterized. Tests are conducted at a sensor temperature of 550 °C in a gas composition near $\lambda = 2$ (10% O_2, 6.5% CO_2, 7% H_2O, N_2 balance) with different NH_3 and NO_x concentrations.

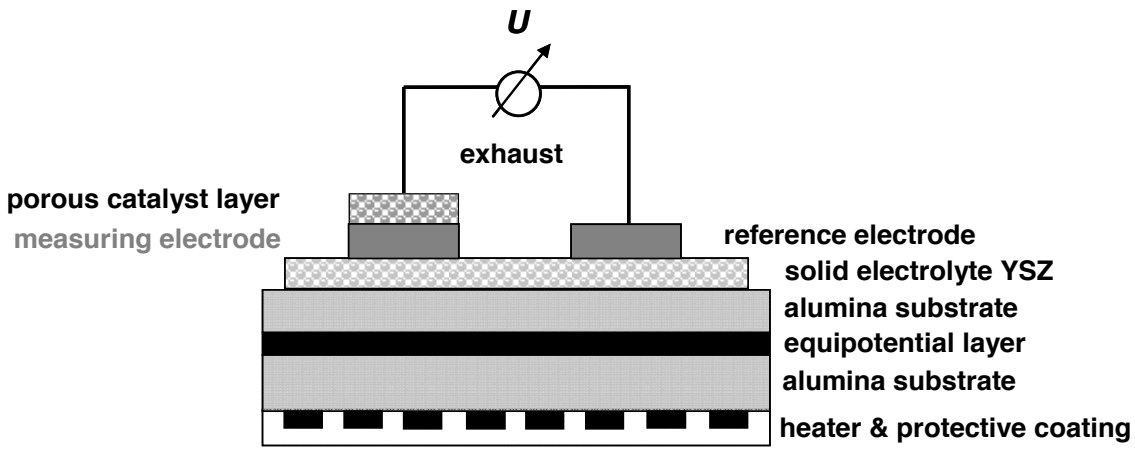

Fig. 1 Sensor setup in ceramic multi-layer technology

Results and Discussion

The $U(c_{NH3})$ sensor characteristic curve (Fig. 2) shows a semi-logarithmic behaviour with a slope of 88 mV per decade NH_3. The sensor shows its highest sensitivity at low NH_3 concentrations and the detection limit of the sensor is against 1 ppm NH_3. The calculated slope is in good accordance with the mixed potential ammonia sensor presented in [3] (80 mV/decade NH_3).

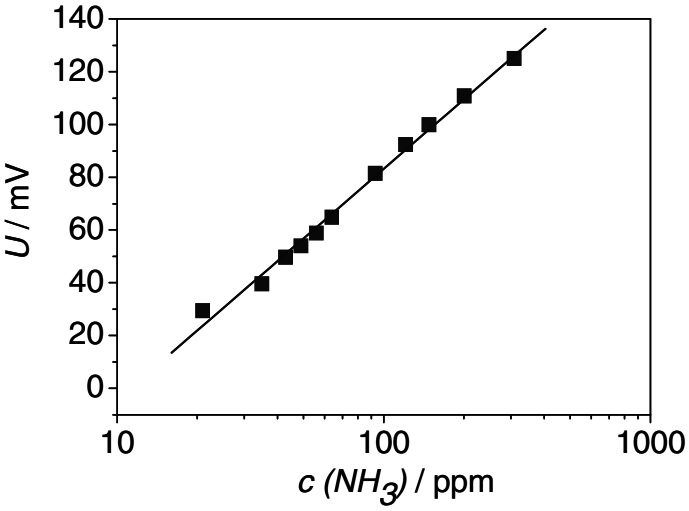

Fig. 2 Characteristic sensor response curve in dependence of the ammonia concentration

The influence of NO_x on the NH_3 signal, presented in Fig. 3, is the most interesting point concerning the sensor application in SCR systems. In Fig. 3, ΔU is plotted semi-logarithmically against the NH_3 concentration for a background gas containing 0 or 160 ppm NO_x (NO/NO_2 = 1). The signal behaves almost independent from the background gas composition. Comparing both curves illustrates that the NO_x influence on the NH_3 sensitivity is marginal for NH_3 concentrations above 20 ppm. For low NH_3 concentrations, a small influence in the range of 5 mV is visible in the inset graph of Fig. 3. Depending on the working point, a slightly higher measured ammonia concentration value in the range of 4 ppm NH_3 is

the consequence. The NO_x cross interference on the NH_3 signal decreases with decreasing NO_x and especially with decreasing NO_2 concentration [4].

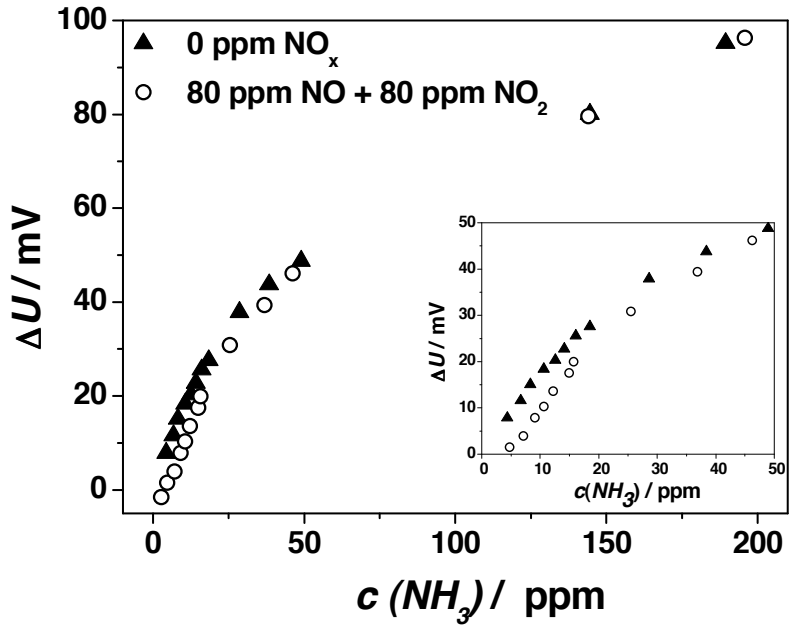

Fig. 3 NO_x influence on the NH_3 sensor

Another crucial point is the dependency of the sensor signal on λ fluctuations. λ was varied in lean atmosphere from 1.9 (10% O_2, 6.6% CO_2, 7% H_2O, N_2) to 1.05 (0.93% O_2, 12.1% CO_2, 13% H_2O, N_2) by adjusting the concentrations of O_2, CO_2 and H_2O. The dependency of the sensor signal on λ is demonstrated exemplary in Fig. 4 for λ = 1.86 and 1.047.

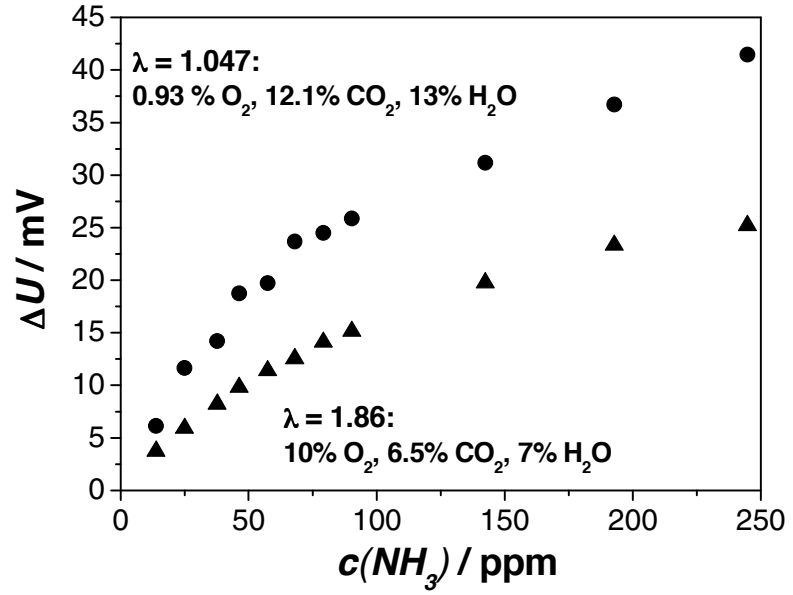

Fig. 4 λ-dependency of the NH_3 sensor signal

The NH_3 sensor signal increases with a decreasing λ (O_2-changes from 10% to 0.93%) around 10 mV. To specify if the cross interference is due to O_2, CO_2 or H_2O changes, tests with only one changing gas component proofed the expectation that the NH_3 sensor signal depends on the oxygen concentration.

More specified measurements showed that the NH_3 signal is nearly constant until reaching an O_2 concentration of around 4% [4]. A lower O_2 concentration or smaller λ leads to an increasing NH_3 signal. It is noteworthy to mention that the O_2 or λ cross interferences can be neglected in lean atmospheres with $c(O_2) > 4\%$.

An initital real exhaust gas measurement at steady state engine test bench operation is illustrated in Fig. 5. The measured ammonia sensor signal and the ammonia concentration determined by Laser diode spectroscopy (LDS) are plotted over the measuring time. The trend of the curves agree very well. The characterized NH_3 sensor provides a stable ammonia signal and the response curve follows the measured NH_3 concentration instantenously.

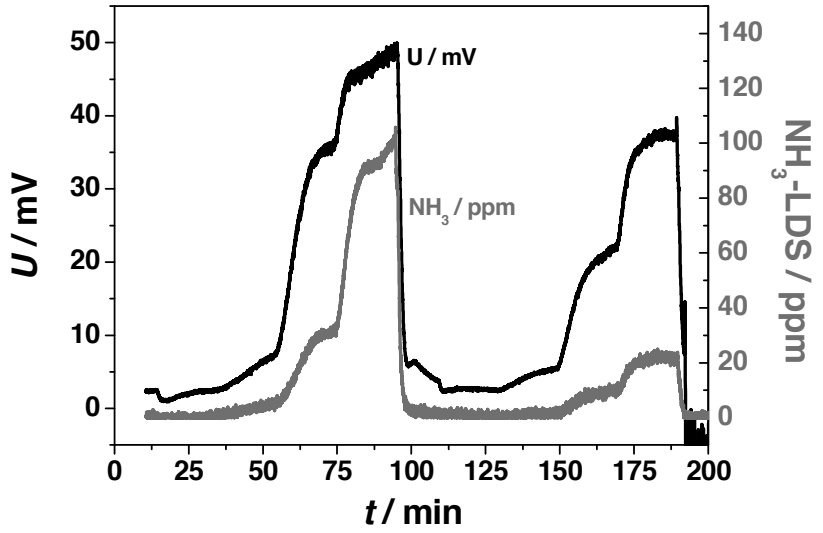

Fig. 5. Engine test bench result for steady state operation
black: ammonia sensor signal in mV, grey: LDS-NH_3 concentration in ppm

Conclusion

The presented ammonia exhaust gas sensor shows promising results for the detection of NH_3 in harsh environments. The slight NO_x interference on the ammonia signal is combined with a marginal λ dependency at $\lambda > 1.1$. Engine test bench measurements showed promising results. The novel sensor setup provides the possibility to optimize the electrode configuration independently from the catalyst material. As catalyst material also electrically insulating materials can be characterized, because they only have to provide catalytic activity and long-term stability. Optimizing both electrode layers separately offers a method to develop designing selective, sensitive and long-term stable sensors.

References

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4. Schönauer et al., Sensoren im Automobil 2009, expert Verlag, in press.