Radio frequency-based determination of the oxygen loading of automotive three-way catalysts

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Introduction

To keep three-way catalysts (TWC) for gasoline engine exhaust gas aftertreatment in an optimal range for pollutant conversion, lambda probes monitor the oxygen partial pressure upstream and downstream of the TWC. The catalyst itself extends the operation conditions for good conversion due to an additional oxygen storage (ceria-zirconia) component. By evaluating the lambda signals upstream and downstream one can estimate the current degree of oxygen loading of the TWC [1]. This information serves as a basis for on-board diagnosis of TWCs today. Owing to transient conditions in the exhaust gas composition and influences like temperature and pressure variations, the oxygen storage state can be determined only inaccurately with this method.

Recently, it was suggested to utilize the catalyst material itself as a sensor element. The electrical conductivity of ceria-zirconia strongly depends on its oxygen loading [2]. This effect can be used for a contactless investigation of the whole catalyst by microwaves using the cavity perturbation method [3]. Depending on the electrical conductivity of the TWC, the electromagnetic waves are damped differently and provide a direct measurement approach for the oxygen loading degree of the TWC.

The catalyst canning acts as a partially filled two-port resonator and can be characterized by scattering parameters. In this work, only the reflection coefficient S_{11} is considered. S_{11} is the ratio of the complex amplitude b_1 of the wave reflected off port 1 to the amplitude a_1 of the wave impressed at the same port: $S_{11} = b_1 / a_1$. In the diagram, the magnitude of S_{11} is plotted in the form $|S_{11}|$ / dB = $20 \cdot \lg|S_{11}|$. The frequency has to be chosen with respect to the dimensions of the catalyst canning. The measurements have to be carried out above the cut-off frequency [4]. The propagation of electromagnetic waves above the cut-off frequency depends on the electrical properties of the filling, which itself strongly depends on the oxygen loading [4]. Hence, in contrast to the conventional lambda probe-based setup, this novel setup characterizes the catalyst material itself, and not the gas phase downstream of the TWC.

Experimental

The measurement setup is sketched in figure 1. Probe feeds (antennas) are installed in the canning, which can be considered as an electromagnetic circular cavity resonator at frequencies below the cut-off frequency of the exhaust gas pipes. The reflection and transmission parameters (S-parameters) are evaluated. Additional lambda-probes and thermocouples monitor the gas feed up- and downstream of the TWC. The measurements shown in this contribution are conducted at a dynamometer with temperature and mass flow-controlled exhaust gas flow at 450 °C and a space velocity of about 60,000 h^{-1}. Radio-frequency measurements are conducted by a vector network analyzer (Rohde & Schwarz ZVRE) in a frequency range of 1 to 4 GHz. Gas composition is measured upstream and downstream of the TWC.

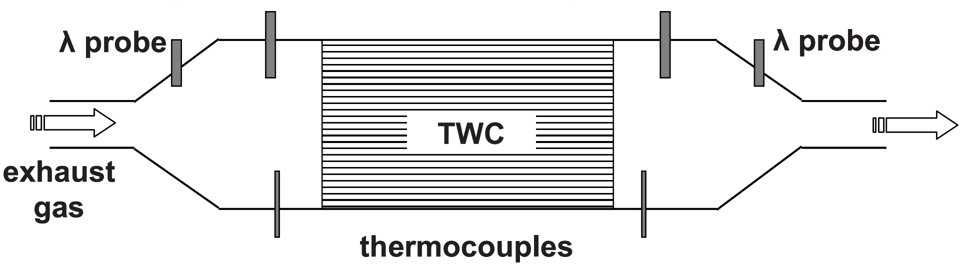

Fig. 1: Schematic setup for the radio frequency measurements of the TWC

Results and discussion

First experiments were conducted at stationary operating points of the engine. Figure 2 shows the result of a frequency sweep from 1 to 1.8 GHz under rich and lean conditions at approximately 450 °C. Resonance effects occur at about 1.25 GHz and 1.6 GHz. The catalyst is measured in a constantly rich ($\lambda = 0.95$, oxygen storage of the TWC depleted) and lean ($\lambda = 1.05$, oxygen storage filled) exhaust gas each. λ denotes the normalized air-to-fuel ratio. With an increasing amount of stored oxygen, the conductivity of the catalyst coating material decreases, the resonance dip gets more pronounced, and the position of the minimum shifts to higher frequencies.

Both the resonance frequency and the absolute value of the reflection coefficient S_{11} at the resonance frequency are an appropriate signal feature from which the oxygen loading of the TWC can be inferred. This dynamometer measurement reproduces results generated in the lab test bench with synthetic exhaust. Therefore, this system is suitable for monitoring a TWC during operation in harsh environments.

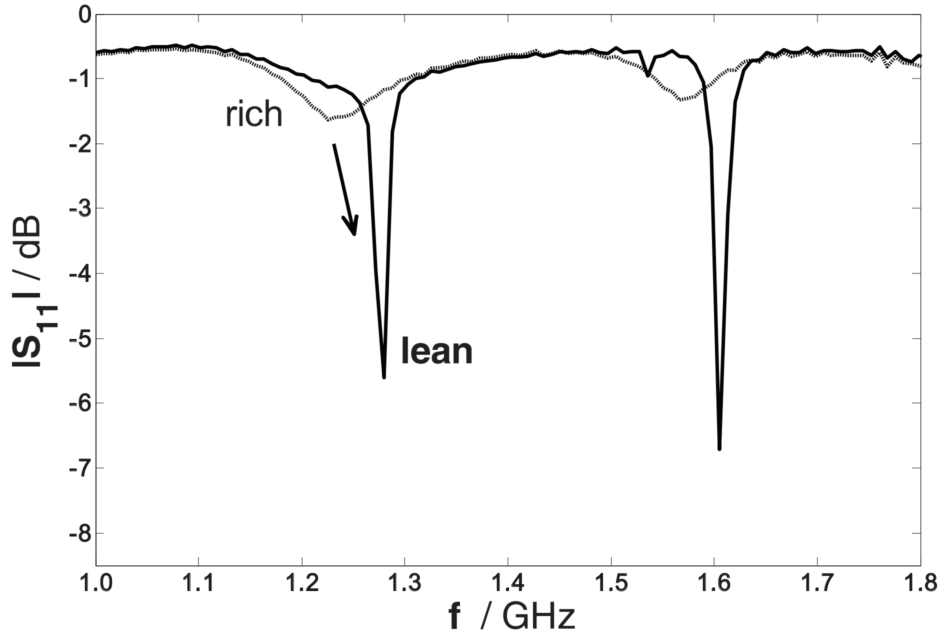

Fig. 2: Measured frequency dependence of the reflection coefficient magnitude $|S_{11}|$ of a canned TWC at approximately 450 °C

For monitoring the operation state of the catalytic converter during changes in the gas composition, the position of the minimum of the first resonance dip at about 1.25 GHz is evaluated. This represents the resonance frequency f_{res}.

Figure 3 shows the response of the radio frequency (RF) measurement system during periods of constant λ of the engine exhaust. The upper diagram shows signals of the lambda probes up- and downstream of the catalyst. Starting with lean operation mode, the λ-value of about 1.05 of both lambda probes indicates that the catalyst is completely filled with oxygen. At $t = 10$ s, the engine switches to rich and the lambda probe upstream shows a value of 0.95. Due to the stored oxygen that is consumed in rich gas, the lambda probe downstream shows stoichiometric conditions until there is no more oxygen in the catalyst and the rich atmosphere can be detected downstream as well at about $t = 18$ s. Obviously, the downstream lambda signal is significantly lower than the signal upstream. This is caused by hydrogen, which is produced by the water-gas shift reaction in the TWC [5]. Due to its very fast diffusion coefficient, the lambda probe is strongly cross sensitive to hydrogen. Therefore, the output of the lambda probe downstream of the catalyst is shifted to lower values [6]. From about $t = 48$ s, the engine is operated in a lean mode again and the oxygen storage can be detected by the lambda probes analogously to the oxygen depletion shown before. At about $t = 55$ s, the TWC is entirely oxygen-loaded again.
To obtain information on the current level of oxygen loading of the TWC, it is necessary to evaluate the differences of the lambda values up- and downstream. By integrating this information over time the oxygen loading can be deduced.

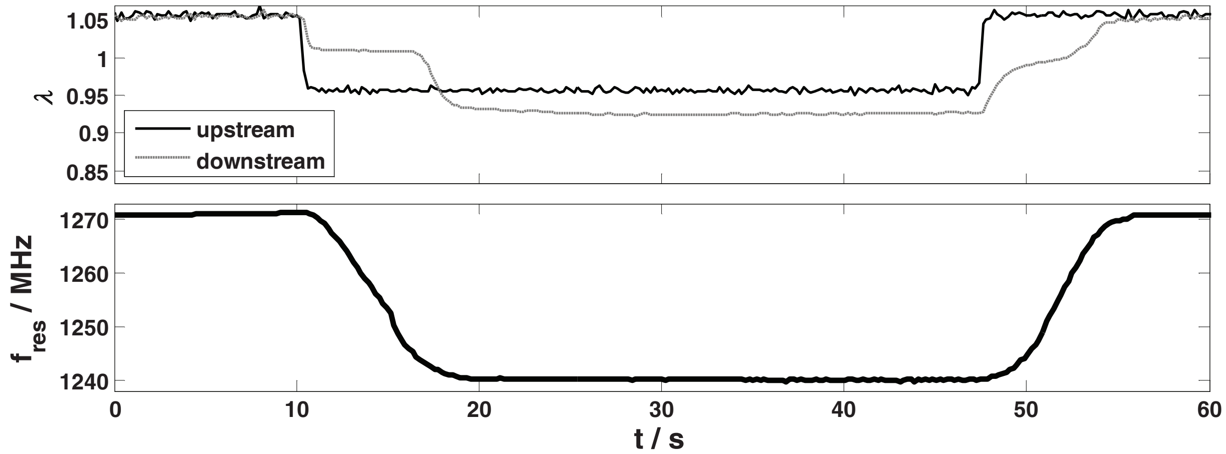

Fig. 3: Measured lambda and resonance frequency f_{res} extracted from the reflection coefficient S_{11} at the dynamometer at approximately 450 °C

The diagram at the bottom of figure 3 shows the RF signal feature f_{res} during this test. In the constantly lean phase, the resonance frequency remains constant at about 1.272 GHz. When the engine was switched to rich, the resonance frequency starts to decrease. Simultaneously with the constant lambda value indicated by the lambda probe downstream of the TWC, the resonance frequency reaches a stationary level, here at about 1.239 GHz. The two steady-state resonance frequencies indicate the completely oxidized and the completely reduced catalyst, respectively, at the temperature of 450 °C. When the exhaust got lean again, the oxygen storage sites of the TWC were filled up and the resonance frequency increases again to its initial value.

During the oxygen depletion or filling, there is an almost linear change in f_{res}. This highlights the major advantage of the RF measurement system, since the current oxygen loading state of the TWC can be measured directly at each single point during operation. With calculating the oxygen loading by integrating the lambda signals deviations from the real loading state can occur easily [7]. Therefore, the new system utilizes the catalyst material itself as the sensor material and the direct measurand is its oxidation (=oxygen storage) state. The actual oxygen loading of the TWC can be measured without the detour of evaluating the oxygen concentration in the gas phase upstream and downstream of the catalyst.

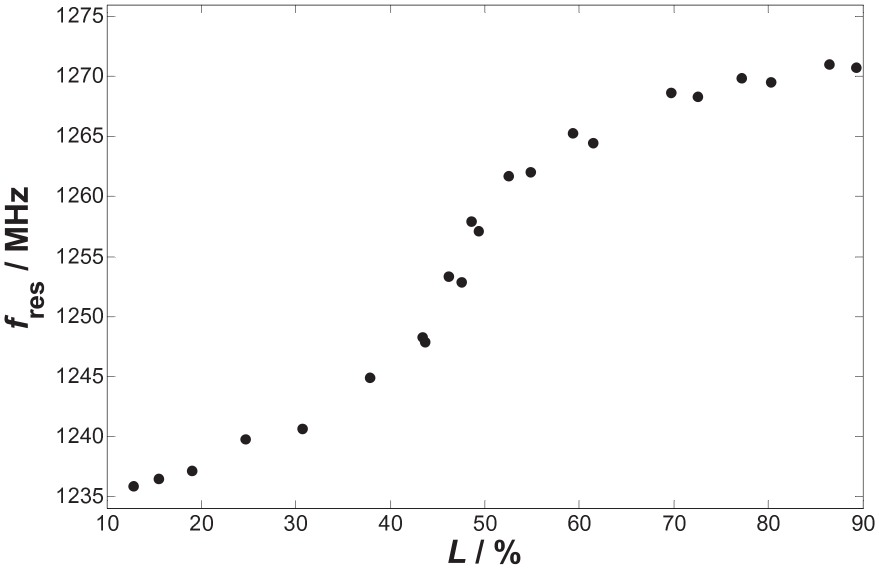

Fig. 4: Characteristic curve of the RF parameter f_{res} as a function of the TWC loading L at 450 °C

Measurements at the engine test bench with a gas analysis upstream and downstream of the TWC allow to balance oxygen and to calculate the oxygen loading of the TWC. The integration of the oxygen excess difference between upstream and downstream analysis yields the oxygen loading degree, L, of the TWC. The functional relationship $f_{\mathrm{res}}(L)$ with the resonance frequency f_{res} extracted from the dip position in $|S_{11}|$ represents the characteristic curve of the measurement system (Fig. 4). It shows an S-shaped but monotonic behavior, with a pronounced increase around 50 % oxygen loading.

Conclusion and outlook

With this novel measurement technique, the instantaneous oxygen loading state of the catalyst can be determined at any time during operation. This could provide a major advantage for engine control. While the lambda probe indicates only a break-through of lean or rich gas downstream of the TWC, now the condition for optimal conversion can be detected directly. This enables engine control strategies without a break-through of lean gas, for instance. In addition, this system has the capability to reduce the precious metal loading of the TWC as well as the catalyst volume and mass.

Cross sensitivities like changes in the gas flow rate (space velocity), or CO_2 or water content in the gas flow are found to be negligible [8]. Further research deals with the temperature dependency, the detection of the cold start state of the TWC, and the establishment of a control strategy for gasoline engines based on the oxygen loading degree information.

Acknowledgement

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References

[1] R. Möller, M. Votsmeier, C. Onder, L. Guzzella, J. Gieshoff, Is oxygen storage in three-way catalysts an equilibrium controlled process?, Applied Catalysis B: Environmental, 91, 30-38 (2009)

[2] S. Reiß, M. Wedemann, R. Moos, M. Rösch: Electrical In Situ Characterization of Three-Way Catalyst Coatings. Topics in Catalysis, 52, 1898-1902 (2009)

[3] R. Moos, M. Spörl, G. Hagen, A. Gollwitzer, M. Wedemann, G. Fischerauer, TWC: lambda control and OBD without lambda probe - an initial approach, SAE paper 2008-01-0916 (2008)

[4] G. Fischerauer, M. Spörl, S. Reiß, R. Moos, Mikrowellengestützte Aufklärung elektrochemischer Vorgänge in Katalysatoren und verwandten Systemen, Technisches Messen, 77, 419-427 (2010)

[5] J. Barbier, D. Duprez, Steam Effects in 3-Way Catalysis, Applied Catalysis B: Environmental 4, 2-3, 105-140 (1994)

[6] K. Saji, H. Kondo, T. Takeuchi, I. Igarashi, Voltage Step Characteristics of Oxygen Concentration Cell Sensors for Nonequilibrium Gas Mixtures, Journal of The Electrochemical Society 135, 7, 1686-1691 (1988)

[7] M. Votsmeier, L. Mussmann, D. Lindner, J.-M. Richter, E. Lox, T. Kreuzer, Verfahren zum Betreiben eines Dreiweg-Katalysators, welcher eine Sauerstoff speichernde Komponente enthält, Europäische Patentschrift EP1227231B1, 19.12.2001

[8] S. Reiß, M. Wedemann, M. Spörl, G. Fischerauer, R. Moos, Effects of H2O, CO2, CO, and Flow Rates on the RF-based Monitoring of Three-Way Catalysts. Accepted for publication in Sensor Letters (2010)