RF-probing of Automotive Catalysts

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Introduction

In order to meet the strict emission regulations, gasoline operated vehicles are equipped with three-way catalysts (TWC) and lambda sensors are applied to control the exhaust gas aftertreatment system. Since the TWC achieves maximum conversion of hydrocarbons, carbon monoxide, and nitrogen oxides at $\lambda \approx 1$, λ is measured by lambda-probes upstream and downstream of the catalyst and is readjusted if required (λ: normalized air-to-fuel ratio). This leads to an oscillating air-to-fuel-ratio that is damped by oxygen storage components in the washcoat of the TWC (ceria-zirconia mixed oxides). These ceria-based materials store oxygen under lean atmospheres ($\lambda > 1$) and release oxygen under rich conditions ($\lambda < 1$).

In the present contribution, aspects of a novel approach to determine the oxygen loading of a TWC by a contactless measurement and in-situ with the help of radio frequency (RF) without lambda-probes is presented [1].

Theory

The conductivity σ of the TWC-washcoat component ceria-zirconia changes with the surrounding oxygen partial pressure [2]. With excess of oxygen, the trivalent cerium in Ce_2O_3 gets oxidized to Ce^{4+} (CeO_2) and vice versa in case of lack of oxygen. In simple terms, the higher the partial pressure, the higher the amount of oxidized ceria and the lower the conductivity of the washcoat.

By exploiting the interactions of the catalyst material with RF-waves, changes in the electrical properties and therefore the oxygen loading of the catalyst can be detected (cavity perturbation method [3]). The cylindrical metallic catalyst housing can be treated as a cavity resonator that guides electromagnetic waves. The resonance frequencies and the losses at these frequencies of the electromagnetic waves are dependent on the electrical material parameters of the inserted catalyst. By measuring the resonance frequencies one can determine the material parameters. A change of the conductivity of the catalyst material changes the magnitude of the electromagnetic waves [4].

Experimental

For investigating conductivity changes of the washcoat, the conductance of interdigital electrodes (IDE) coated with an almost standard washcoat has been analyzed in synthetic exhaust with changing λ in a test rig (fig. 1) [5]. In addition, monoliths with the same coating and a metallic housing have been analyzed by the RF-system at low space velocities. The schematic assembly is illustrated in fig. 2. The gas mixture as well as the catalyst have been heated to about 410°C.

In order to detect a resonance frequency shift or an attenuation of the electromagnetic wave one has to connect the cavity to an automatic vector network analyzer (VNA) via RF-cables and two antennas. Electromagnetic waves with the amplitudes a_1 and a_2 respectively are applied to the RF antennas (marked in fig. 2). The parameters b_1 and b_2 represent the amplitudes of the back-scattered waves gauged at these two ports. According to eq. 1, S parameters can be defined as reflection coefficients (S_{11}, S_{22}) or transfer functions (S_{12}, S_{21}).

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \qquad (1)$$

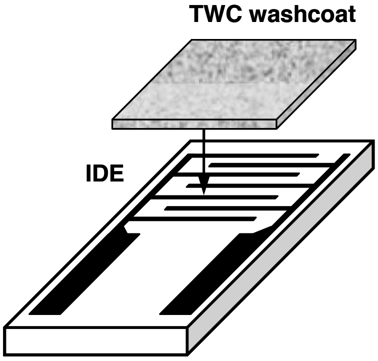

Fig. 1**:** Design of the IDE-Sensor for investigating the conductivity changes of the washcoat

One possible signal characteristic is the transfer function, S_{21}, which is defined as the relation of the energy received at antenna 2 to the power injected into port 1. Concerning the comparison of power embossed at one port and measured at the other one, the power ratio is expressed by the squared amplitude $|S_{21}|^2$. The parameters in the figures 3 and 4 are calculated and presented in dB (= 10 log $|S_{21}|^2$).

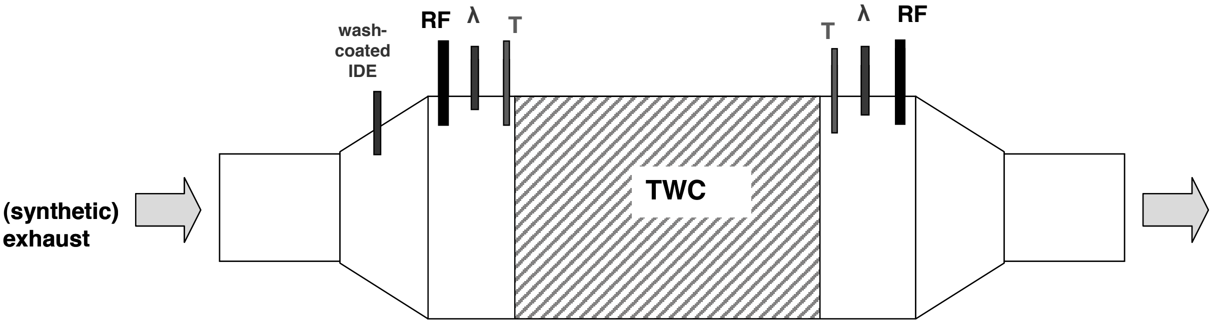

Fig. 2: Assembly of the three-way catalyst (TWC) in the test rig with RF-antennas (RF), lambda-probes (λ) and thermocouples (T)

Results

The result of the measurement is shown in fig. 3. The parameter is plotted in dB. Several spectra of $|S_{21}|$ in the range of 1 to 2 GHz are presented, that are taken during oxygen storing in the TWC. Starting at rich (reducing) conditions (mark 1), oxygen is added to N_2 base gas till the ceria is oxidized completely (mark 2). There is a significant change at the resonance peaks in the amplitude as well as in the resonance frequency position. Considering the peak at about 1.27 GHz, the transmission increases with the oxygen stored in the washcoat and the resonance frequency shifts towards higher frequencies. The better transmission is in good agreement with the decreasing conductivity while ceria gets oxidized.

In general, the penetration depth of electromagnetic waves depends primarily on the electrical conductivity. So the wave propagation is affected stronger at higher washcoat conductivity. The more oxygen is stored in the catalytic converter, the more the washcoat conductivity decreases. Hence, the electromagnetic waves are damped less and the transmission increases.

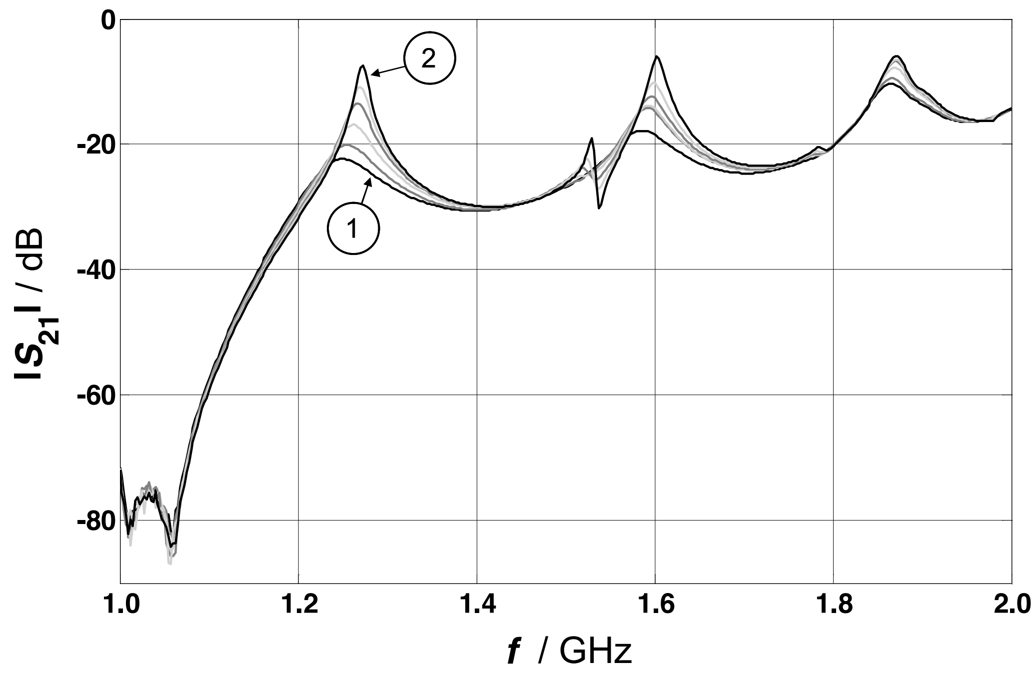

Fig. 3: Spectra of $|S_{21}|$ in a frequency range from 1 to 2 GHz at different points in time during oxygen storage in the TWC. Lines consecutively numbered from reduced (1) to oxidized (2) condition.

Based on this data, a fixed frequency can be selected to evaluate the transmission signal during gas atmosphere changes.

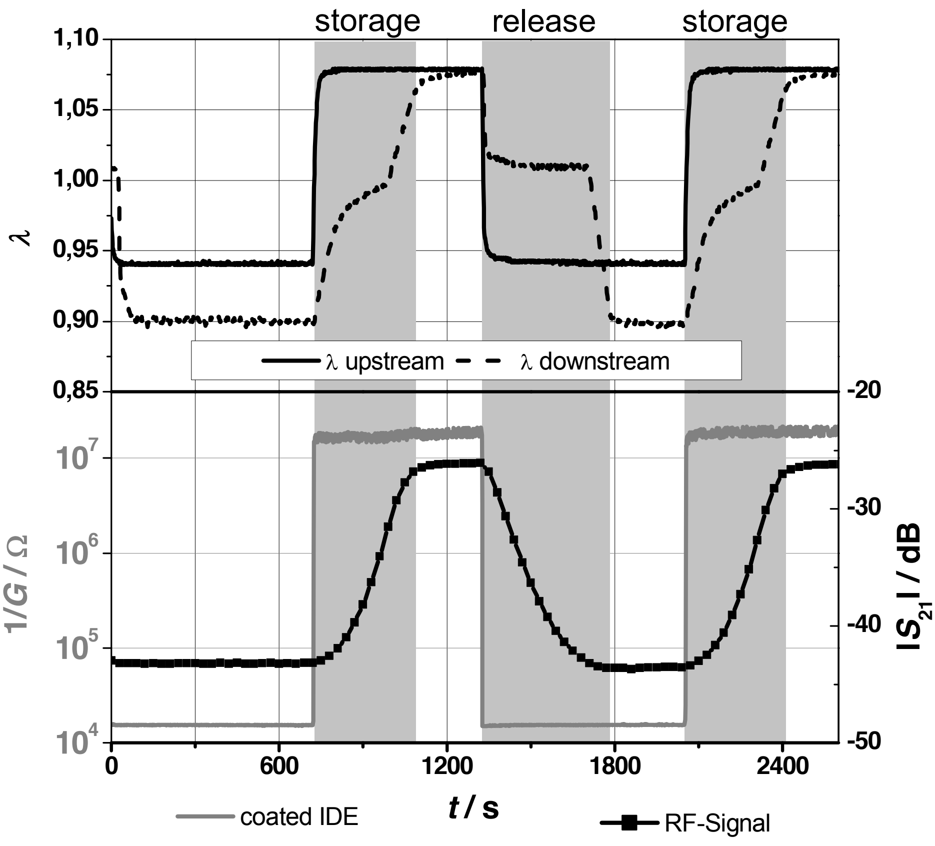

Fig. 4: RF-Signal ($|S_{21}|$ at 1272.5 MHz) compared to the signal of lambda-probes up- and downstream of the catalyst and the inverse conductance of a coated IDE. Oxygen storage and release phases of the catalyst are highlighted in grey.

Fig. 4 shows the chronological sequence of the transmission amplitude at a fixed frequency. On top of the diagram, the signal of a lambda-probe upstream of the catalyst (solid line) and downstream (dashed line) is displayed. At the bottom of the diagram, the signal of a coated IDE (left, grey) placed upstream of the catalyst in the preheated gas and the RF-Signal (right) can be seen. In this case, the transfer function magnitude $|S_{21}|$ is evaluated in dB. When changing the atmosphere from rich ($\lambda<1$, oxygen deficient) to lean ($\lambda>1$, oxygen rich), λ downstream changes slowly to $\lambda\approx1$, because oxygen is stored in the catalyst (ceria gets oxidized). As soon as the catalyst is "filled" with oxygen, λ downstream changes to lean values (deviations between λ-values in lean and rich exhaust after catalyst breakthrough are due to the high sensitivity of λ-probes towards H_2 which is produced in the catalyst converter because of the catalytically activated water-gas shift reaction). When changing the atmosphere to rich, λ downstream again changes slowly to $\lambda\approx1$, at first since the previously stored oxygen is released.

The conductance G of the coated IDE changes by about three decades between rich and lean atmospheres. The RF-Signal shows a gradient as long as the catalyst is storing or releasing oxygen and constant values as long as the catalyst is in a constant state. These results suggest that it is possible to infer from a RF-signal to the instantaneous oxidation state of the catalyst.

Conclusion

By investigating RF-signals measured at three-way catalysts, changes of the catalyst oxidation state can be detected. The analysis provides an integral measurement of the device, so that a control of the catalyst is possible. Compared to λ-probes this could be advantageous with regard to future on-board-diagnostics (OBD) for better monitoring of exhaust aftertreatment components. The effect of changing transmission coefficients could be reproduced and is a reliable indication of the oxygen storage in the TWC.

Outlook

Further measurements concerning reproducibility, especially the stability of the resonance frequency positions are conducted. The temperature-dependency as well as cross-sensitivities towards several gases of the system are currently under investigation.

Furthermore, measurements in an engine test bench are in preparation to proof the applicability in real exhaust conditions.

Besides TWC characterization, the transfer to other catalyst types such as lean NO_x traps opens up a wide spectrum of possible OBD applications.

References

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