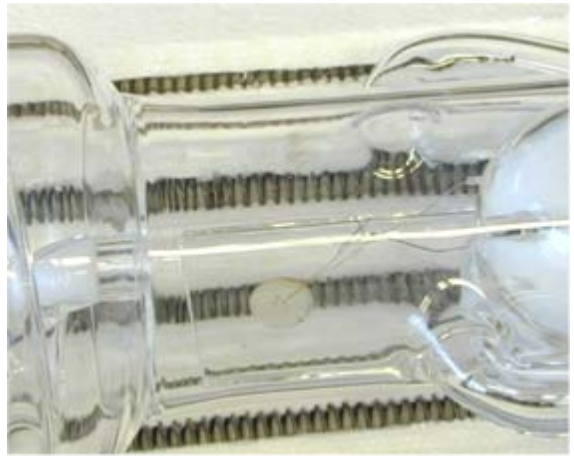
Gas Sensor Activities at Institute of Materials Research of German Aerospace Center (DLR)

Deutsches Zentrum
DLR für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

Outline



- Introduction
- Solid-state sensor principles
- Manufacturing & design of sensor
- Experimental set-up
- Experimental results

Introduction

Total NOx-Sensors

Control of functionality:

… High-Temperature NOx-Detection under Lean-burn conditions

… Control of catalyst efficiency

… Controlled reductant introduction in SCR systems

… Impedance-metric sensors

Connection to On-Board-Diagnostics (OBD):

… Feedback in Closed-Loop-System

… Malfunction-detection of the catalytic converter

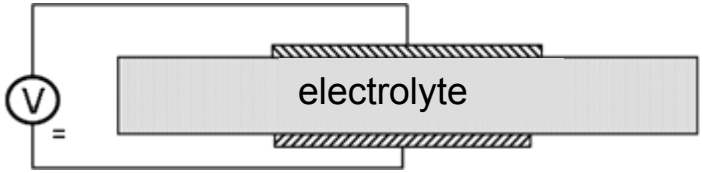
Component integration of Sensors

…. Planar design

…. Multifunctional use

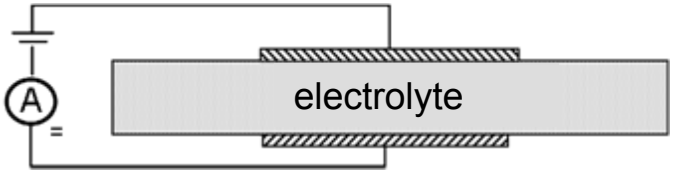
Solid-state sensor principles

potentiometric



Correlation of measured open circuit potential to the gas composition
Either the electrodes are in different atmospheres or electrodes are dissimilar

amperometric

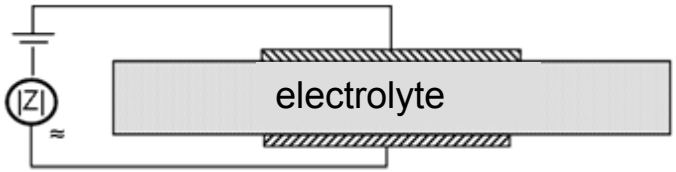


: *Sensorelektrode*

: *Referenzelektrode*

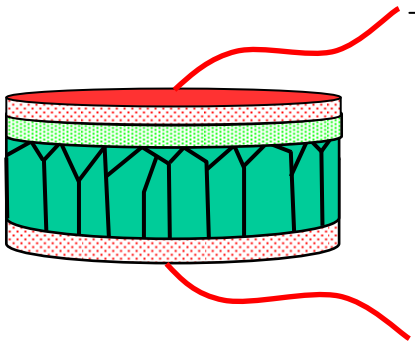
Measurement of diffusion-limited current
Isolation of oxygen from NOx through a separate pumping cell

impedancemetric



Measurement of complex impedance |Z| at a certain frequency
NO und NO_2 produces similar responses

Sensor design



5- Pt-Contact

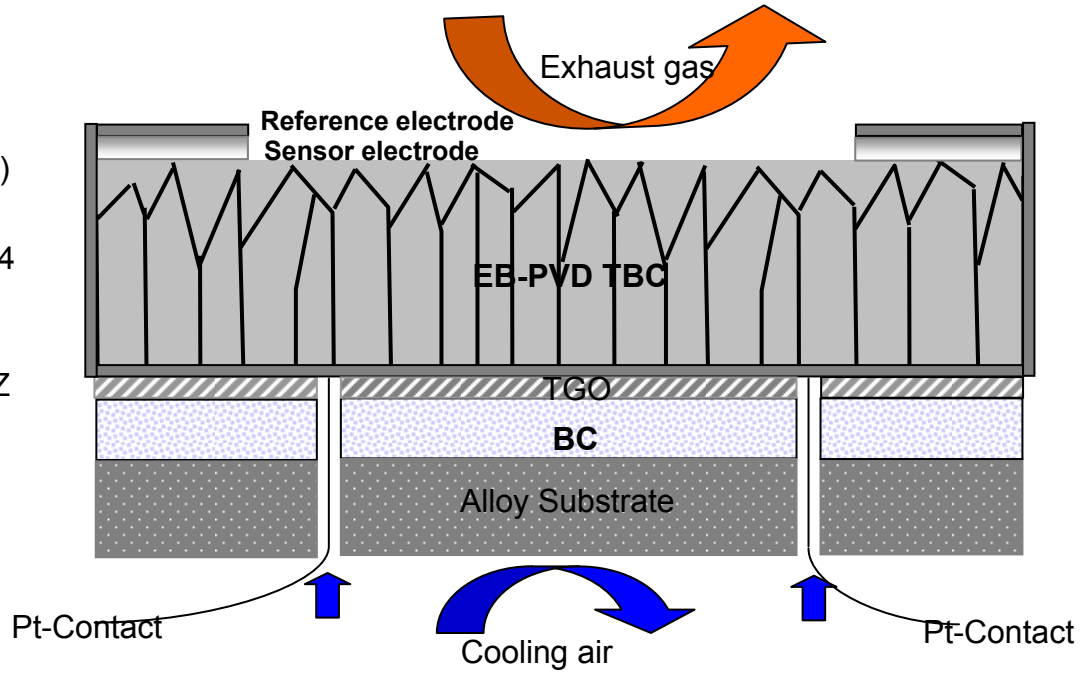
4- Collector-Electrode (Pt) 2 µm (only for $NiCr_2O_4$)

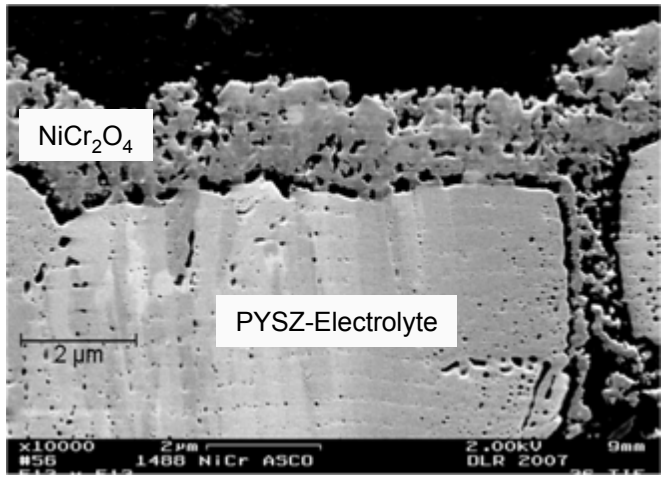
2/3- Sensor-Electrode, 2-4 µm ($NiCr_2O_4$ or NiO)

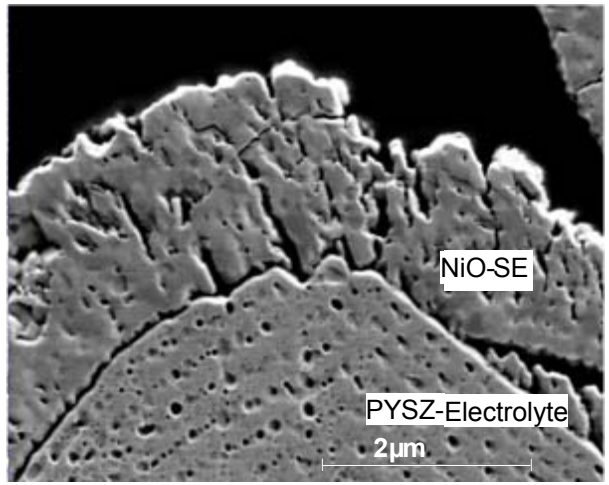
1- Electrolyte PYSZ/FYSZ 500 µm

4- Pt-Electrode, 2-3 µm

5- Pt-Contact

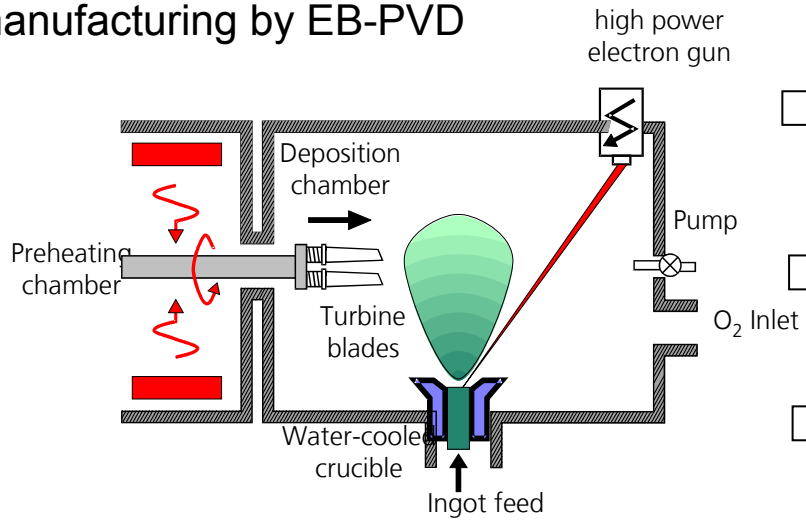




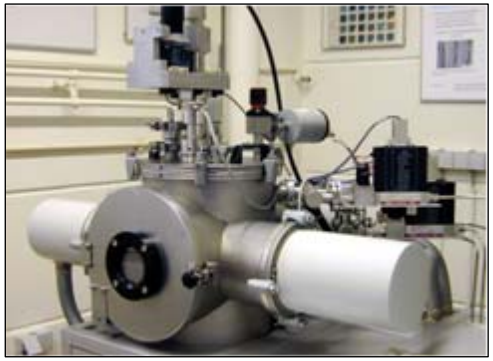


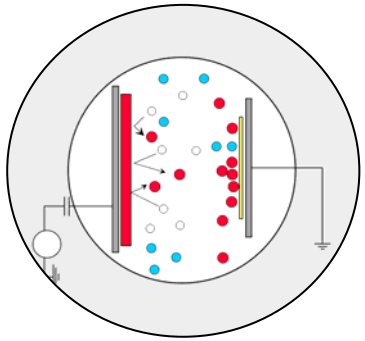
Sensor manufacturing

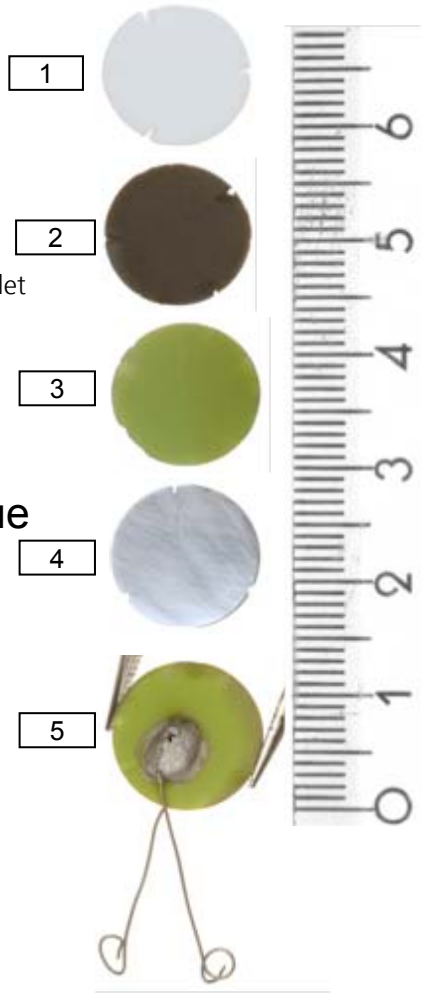
1 Electrolyte (PYSZ und FYSZ) manufacturing by EB-PVD



2 Coating of sensor electrode via RF-Reaktive Magnetron-Sputter technique







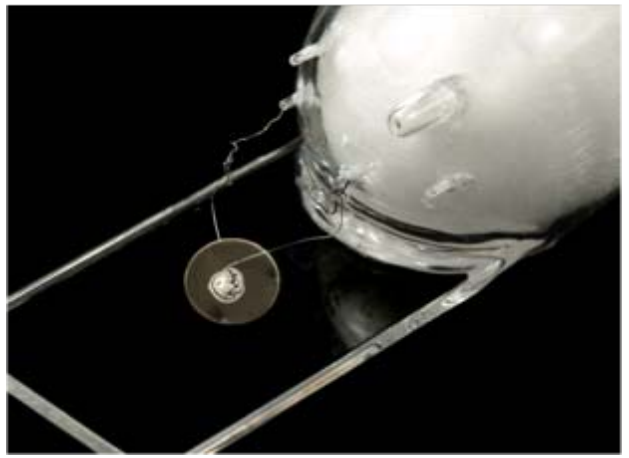
3 Heat-treatment of sensors in air @1000°C/4h

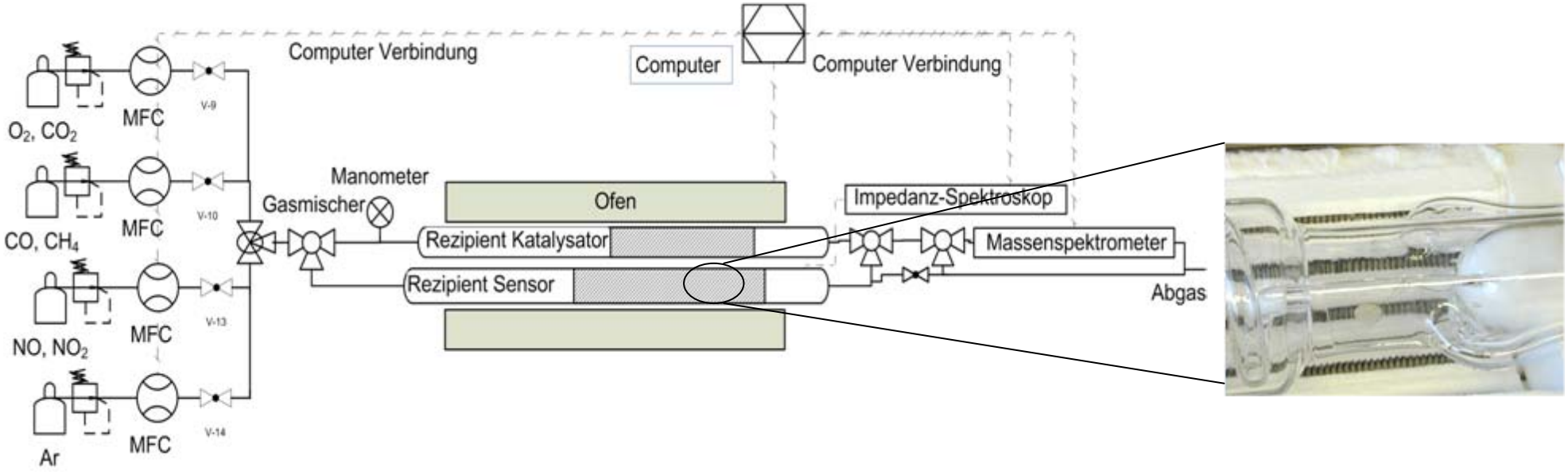
4 Coating of Pt-reference electrode at the bach side of sensors (via DC-Magnetron-Sputter)

5 Contacting with Pt-wires and Pt-Paste

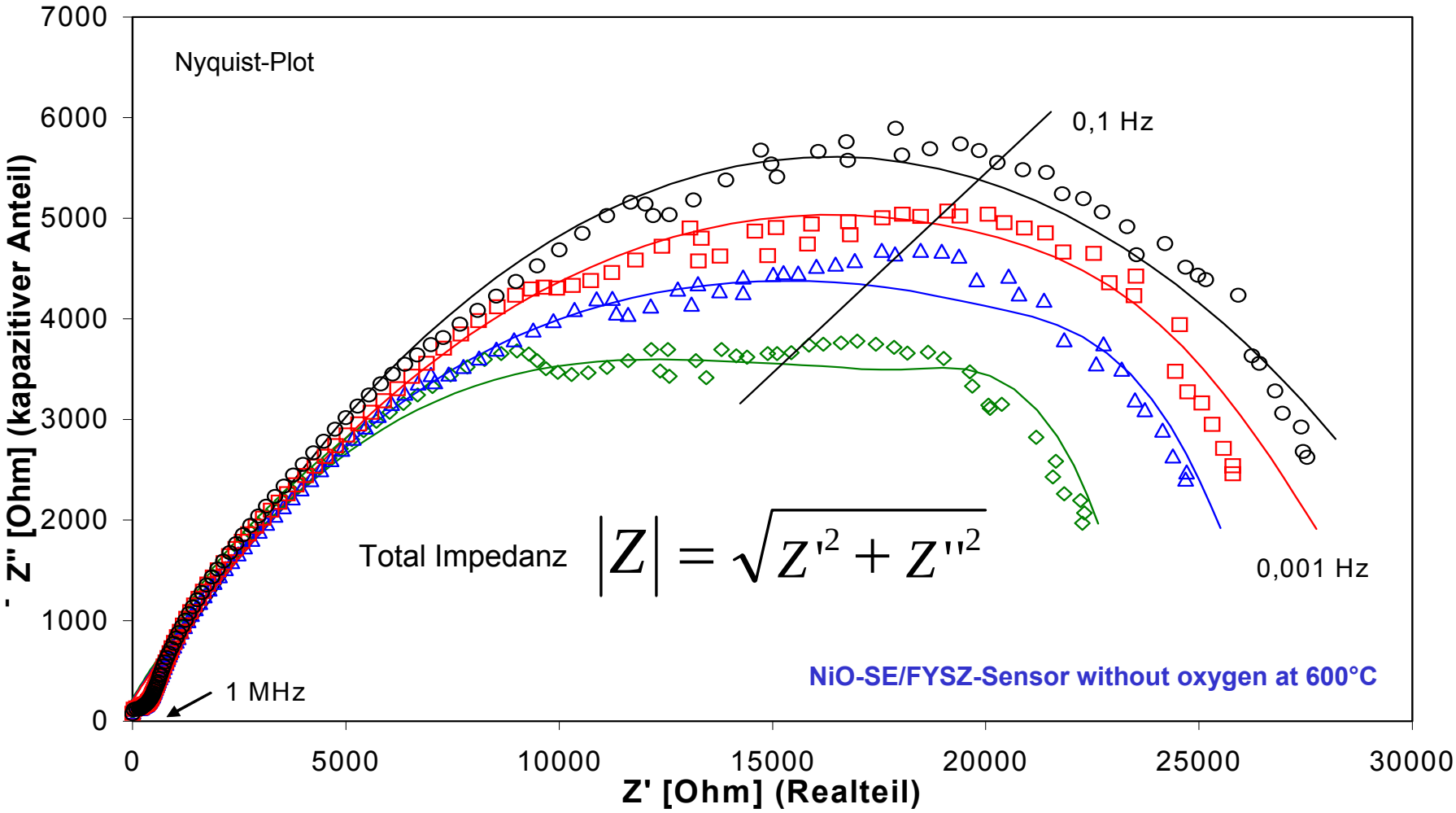
Experimental Set-up

- 5-Channel Gas mixture (NO, NO_2, O_2, CO, CO_2, CH_4, carrier gas Argon)
- Liquid fuel injection (high chained HC)
- Water vapor source (humidity)
- Furnace up to 1200 °C
- Gas temperature up to 1100 °C (pre-heating over 3 m long spiral)
- Quartz Recipient
- Impedance Spectroscopy (Frequency area: 1 MHz – 0,001 Hz)
- Mass Spectroscopy
- NO/NO_2-Analysis
- max. Operation pressure ~ 3 bar



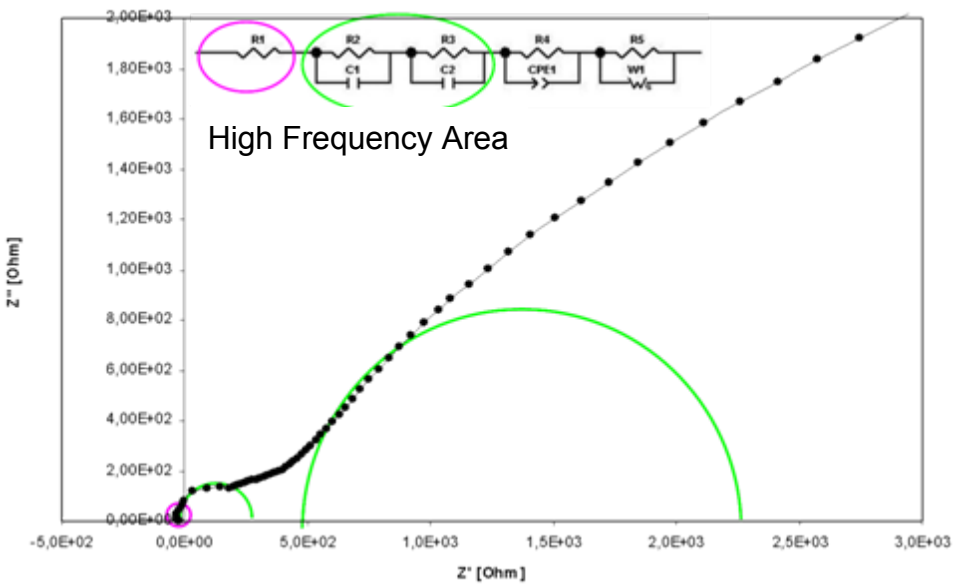


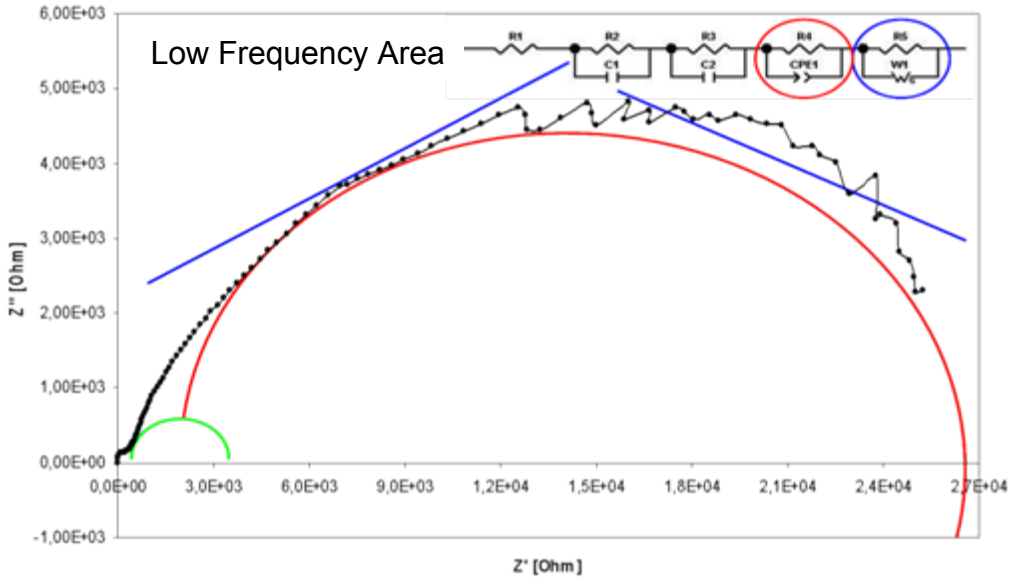
Impedance Analysis of Sensor Behavior



Measured Impedance Spectrum (Symbols) under various NO-concentrations (○: Argon, □: 100 ppm NO, Δ: 500 ppm NO, ◊: 1000 ppm NO) and the fitting results using the equivalent circuit design (Lines)

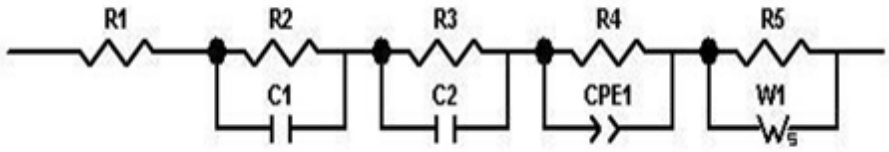
Impedance Analysis of Sensor Behavior with Equivalent Circuit





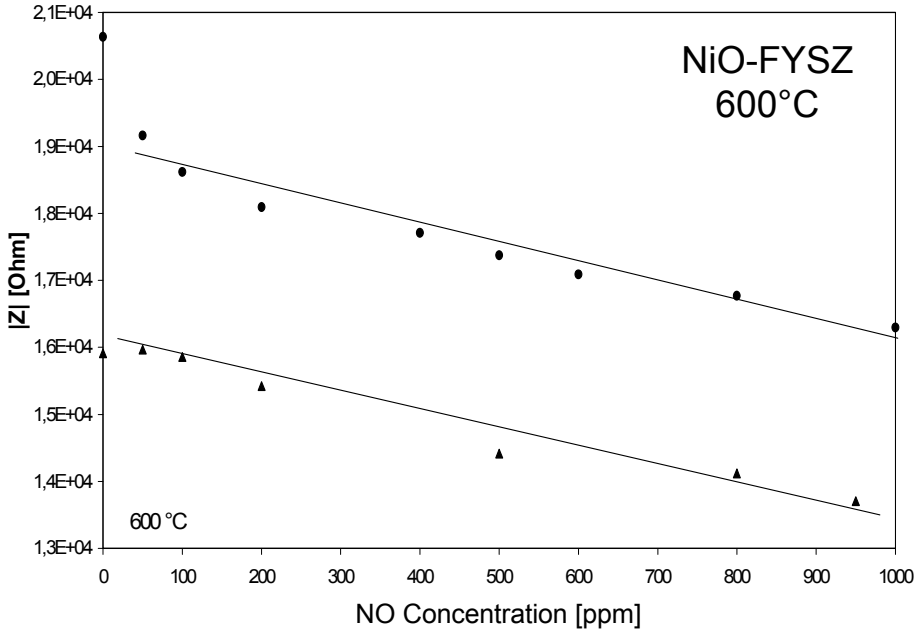
- Impedance spectra of sensors contain three and more connected semi-circles which are shifted at the real axis
- High frequency area consists of two semi-circles which correspond to the electrolyte related effects
- semi-circles consist of linear parts or are non-ideal-semi-circles.
- These squeezed and shifted semi-circles requires the employment of „Distributed-Elements“ in EC

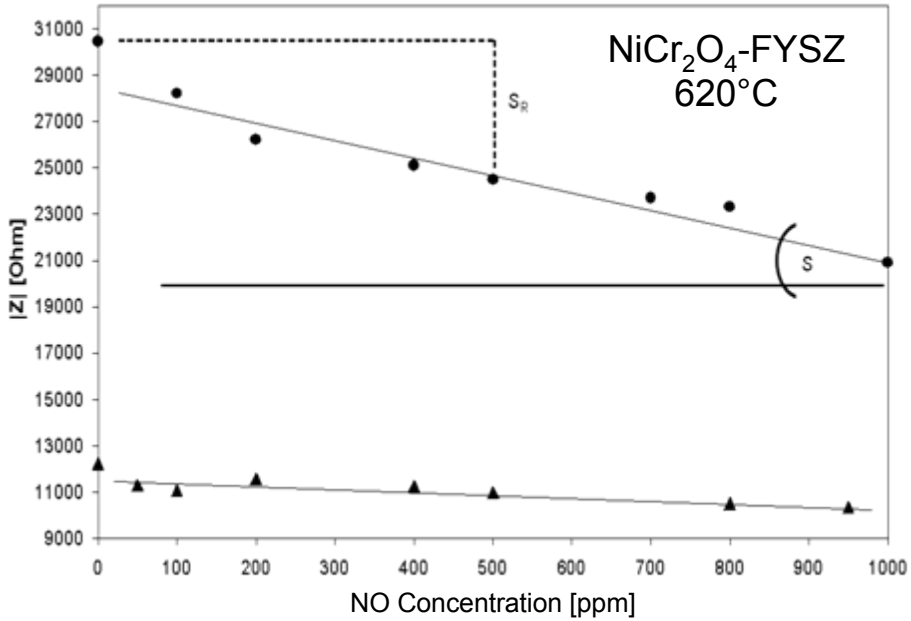
- Gas concentration variation yields shifts with at the imaginary axis in the low frequency area
- presence of two linear areas in lower frequency semi-circles indicate that the use of one Cole- and one Warburg-Element are required in the EC

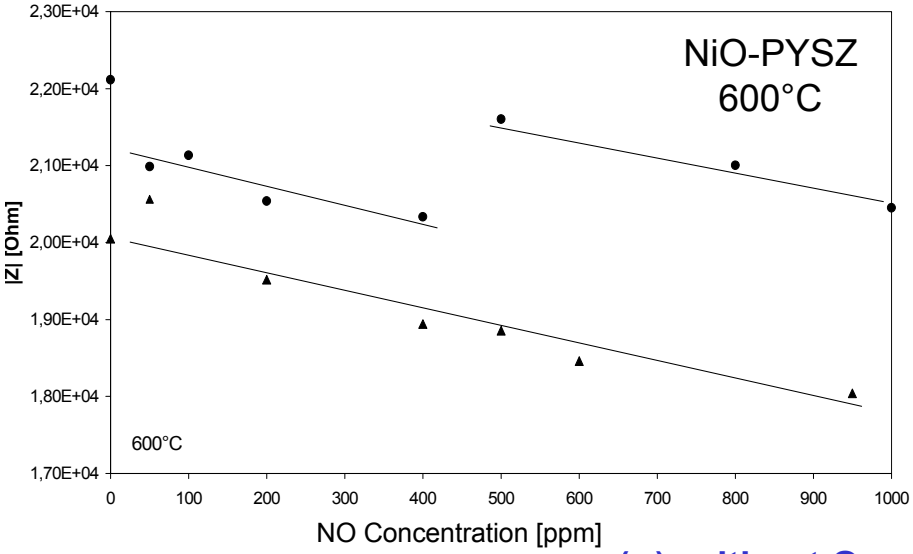


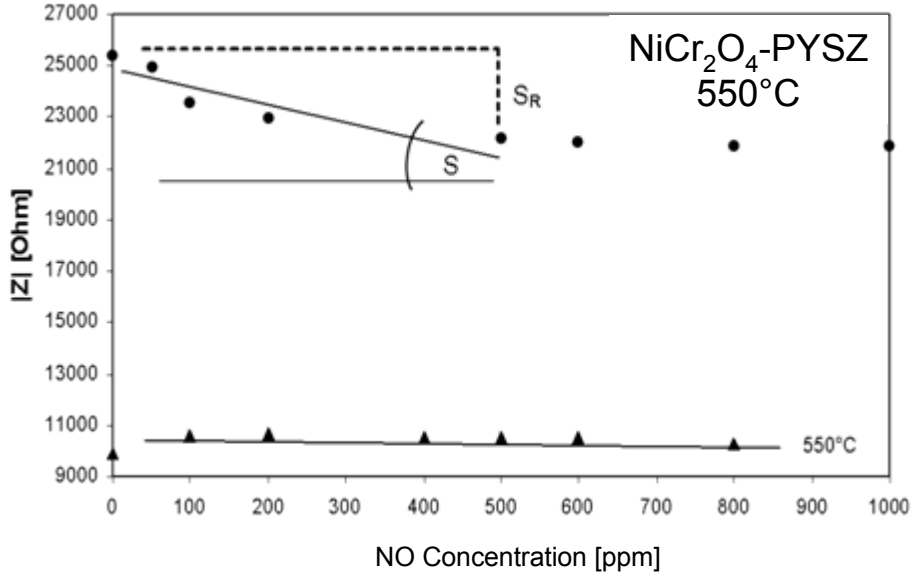
→ ECD consists of minimum 4 parameters

NO-Sensitivity at 0.1 Hz





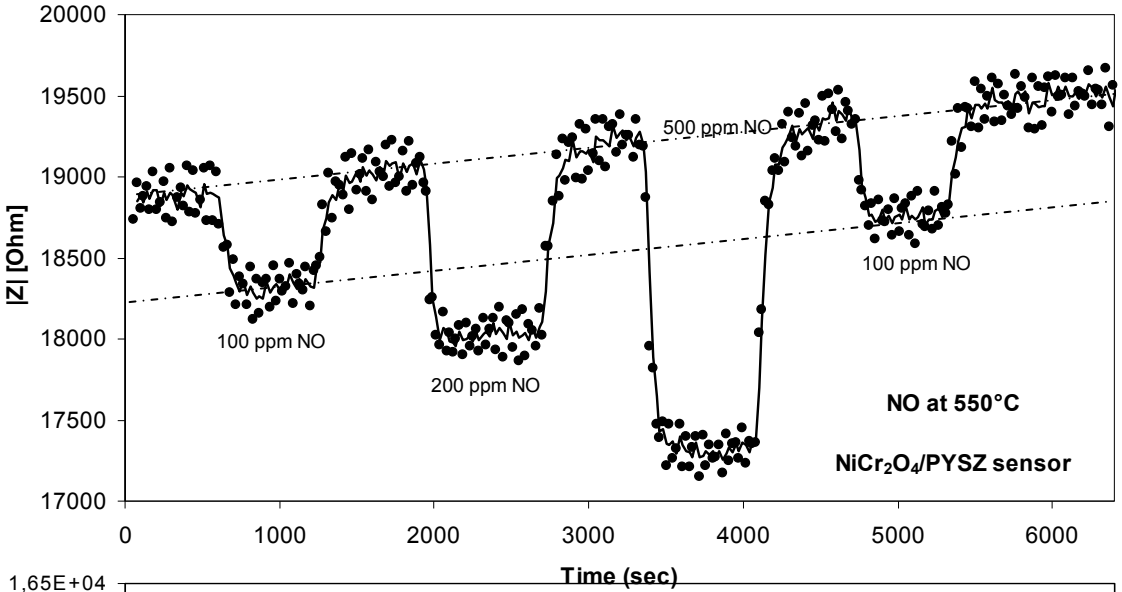




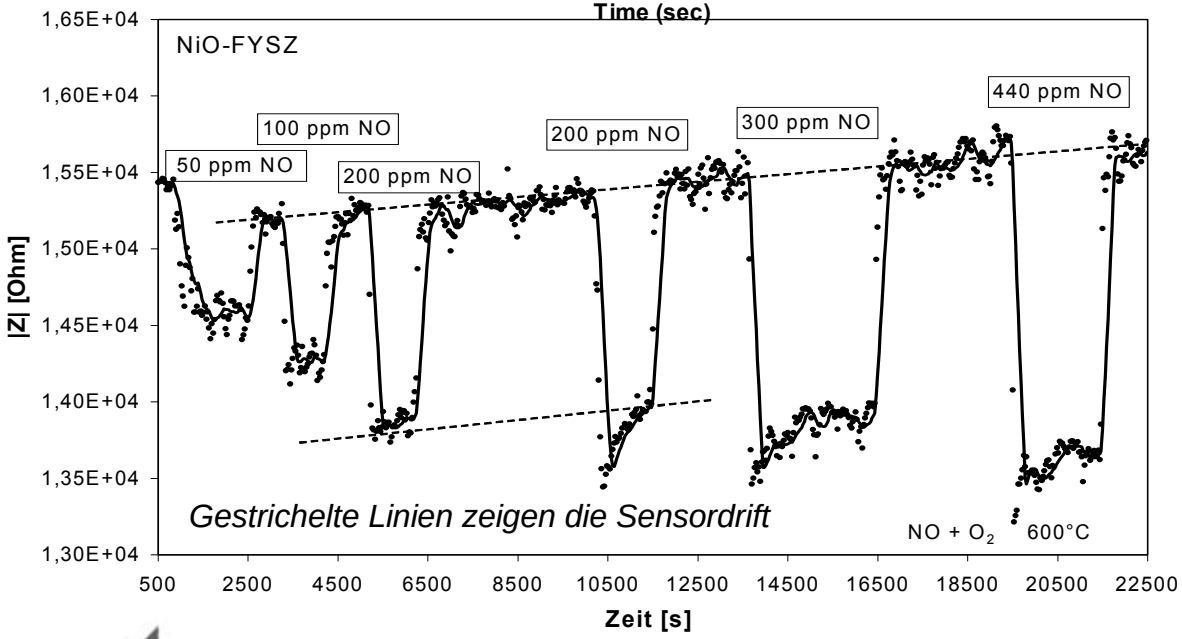
(●) without O_2

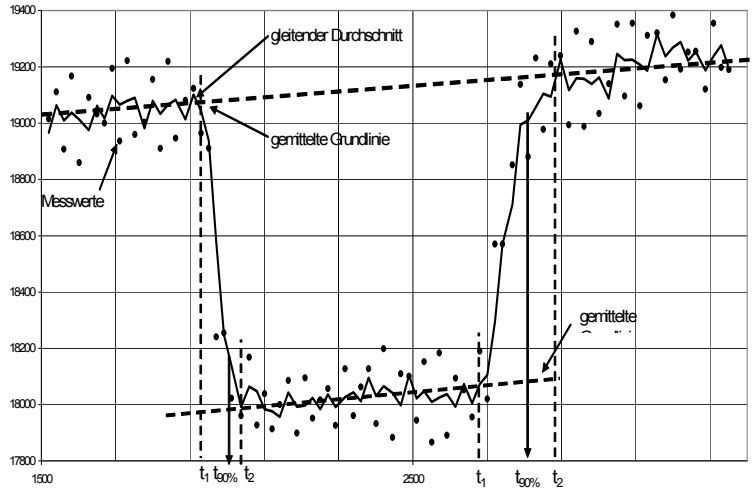
(▲) with 5 vol.% O_2 „non-Nernst-like behavior“

Sensor response



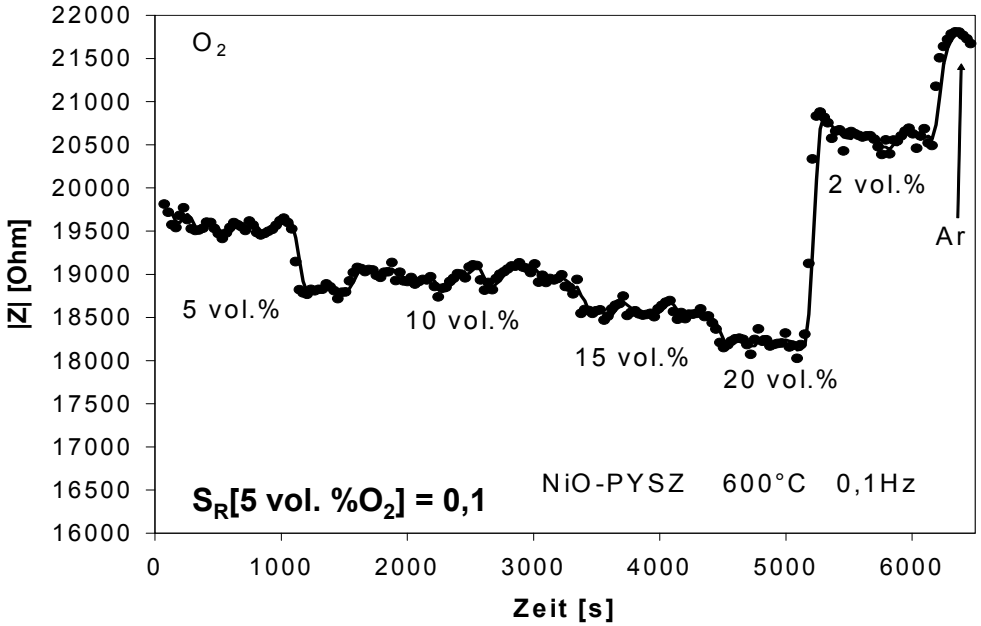
SE-Material	Ansprech-Zeit t_{90} [sec]	Reaktions-Zeit R_{90} [sec]	Drift Rate D_R [min^{-1}]
$NiCr_2O_4$	95	93	$3{,}06 \cdot 10^{-4}$
NiO	67	74	$9{,}74 \cdot 10^{-5}$

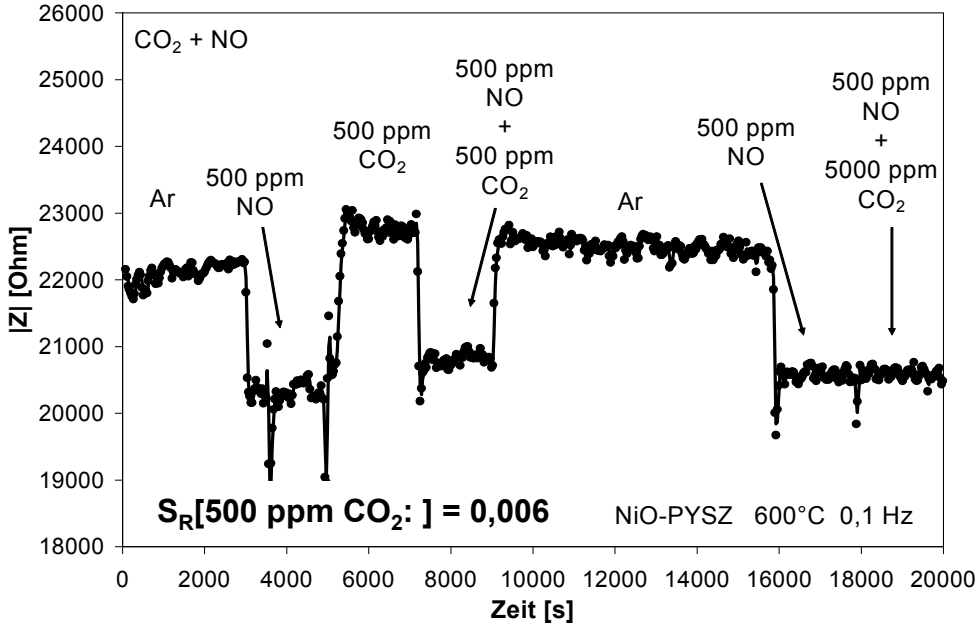


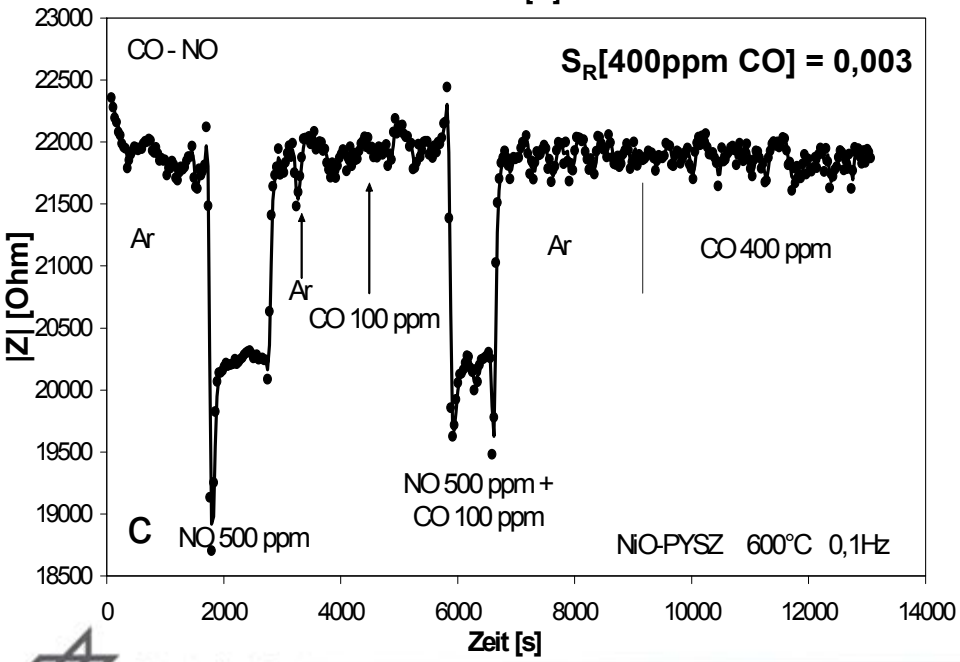


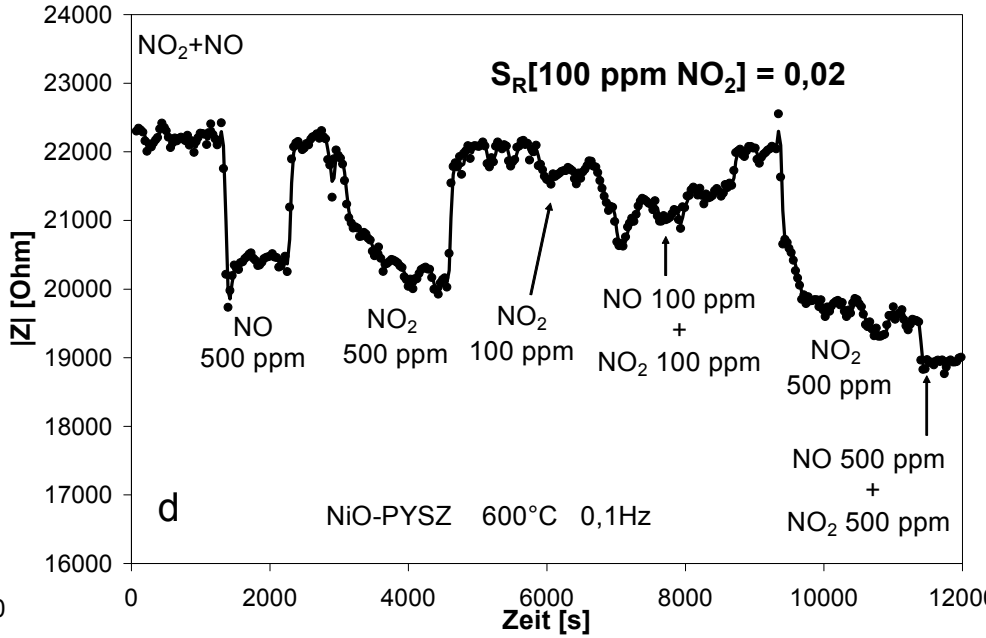
Peaks at the Sensor response curves are due to on/off -switching of the MFC-valves

Cross sensitivity of sensors









Further research on gas sensors

- Development of doped nano-scale SnO_2 und TiO_2 sensor electrodes for NO_2-detection
- Signal integration
- Unification of sensor und catalyst systems
- Thermal barrier embedded sensors
- Development of humidity-, HC- and CO-Sensors