

NO_x gas sensor designed for integration on hot components

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Introduction

In lean-burn engines operating under excess oxygen conditions (air/fuel-ratio $\gg 14.5$), emission control becomes a challenging task to deal solely with conventional after treatment systems. Modern after treatment systems use catalysts and methods that are capable of reducing and controlling NO_x-emission at higher oxygen containing atmospheres. In vehicles, emission control sensors are connected to the OBD-system to record the history of the emission reduction and to track the function of the catalytic converter. This is done mainly by employing single-unit upstream and downstream gas sensors. High efficiency mobile or stationary turbine engines which are predestined to produce larger NO_x-emission do not contain emission after treatment and control system in operation. Instead, emission is defined externally, that means either by measuring emission at periodical testing phases or by calculating the emission characteristics typical to turbine. These do not reflect the emission state ruling under service conditions. Calculation of emission characteristics considers the ideal conditions. Moreover, the emission concentration behind the turbine outlet is influenced by environmental factors. It is needless to say that it is almost impossible to replace a single-unit gas sensor within a gas turbine due to the present harsh environments and turbine's tightly built structure. Turbine geometries can not be easily changed and the aerodynamic and flow conditions should not be disturbed, since these determine the turbine capability and flight conditions.

In the past decade, the efforts into developing powerful single-unit NO_x-sensors were directed to those basing on amperometric and potentiometric measurement principles. Amperometric sensors measure diffusion-limited current by employing metal oxide electrodes to optimize the response. In order to overcome the cross-selectivity towards oxygen, a separate pumping cell is used typically to maintain a constant O₂-concentration at the electrode which requires a complicated device design. The classical potentiometric sensors in turn measure open circuit potential by means of two separate electrodes one of which being in the reference gas. Moreover, the potentiometric sensors suffer under the opposite sign for the EMF-potential of NO and NO₂. Monitoring total NO_x with these sensors becomes difficult [1]. The primary requirement for new generation NO_x-sensors is quantitative detection of total NO_x with high selectivity at elevated operating temperatures. Other requirements are low cross-sensitivity towards other emission gases without the need for a reference gas. A planar design impedance-metric sensor with NiO-SE and EB-PVD manufactured YSZ-electrode may overcome these challenges [2, 3].

Electrochemical solid-state gas sensors employ yttria-stabilized zirconia (YSZ) as electrolyte which is manufactured typically by tape-casting method if planar design is used. This method is cost-effective and easy to handle, but not suitable for integration of the sensors on to the components. Thermal barrier coatings (TBCs) are currently used in the hot gas path of aero-engines and land-based gas turbines on highly loaded turbine blades and vanes to increase turbine efficiency. They typically comprise of a ceramic top coating – partially yttria stabilized zirconia (PYSZ) - of low thermal conductivity that reduces the metal temperature and smoothen the temperature peaks during the transient stage of turbine operation. Utilising the EB-PVD manufactured thermal barrier coatings as electrolytes of gas sensors, the vanes and blades of turbines can be re-functionalized and serve as active systems. This study suggests a novel planar-type NO_x-sensor design which allows the integrated built of the sensors onto the hot parts of engines and turbines.

Materials and Experimental Methods

The sensor configuration contains of an electrolyte that is constructed of quasi-single crystalline columns of 7 wt. % yttria stabilised zirconia manufactured by EB-PVD technique. EB-PVD deposition was performed in a 150 kW dual source coater used in single source evaporation mode. The substrates for deposition of electrolytes were FeCoCrAlY disks of 12.7 mm diameter. To ease the characterisation process, the EB-PVD zirconia deposited substrates are etched out to obtain free-standing layers having a diameter of 12.7 mm and thickness of 500 μm . XRD analysis revealed tetragonal phase for electrolytes. Since the as-coated morphology of EB-PVD-coatings shows changes with temperature, to achieve a stable morphology at the electrolytes, the free-standing layers are heat-treated at 1100°C for one hour. The electrolytes maintained their quasi single crystalline and preferentially oriented columnar structure after ageing. The pre-aged electrolytes were reactive-sputtered with a 3 μm thick NiO on their SE-side. XRD and EDX measurements showed that the as-sputtered sensor electrode layers are amorphous and non-stoichiometric. After heat-treatment at 1000°C for 4 hours, a porous and polycrystalline layer with an average grain size of approximately 0.5 μm and cubic NiO-phase was obtained. Figure 1 shows the morphology at the electrode/electrolyte-interface. On the RE-side of the electrolyte, a thin and porous Pt layer was sputtered as the conductive layer. The schematic presentation in Figure 2 demonstrates how this planar design sensor can be integrated on the hot parts of turbines such as vanes and blades.

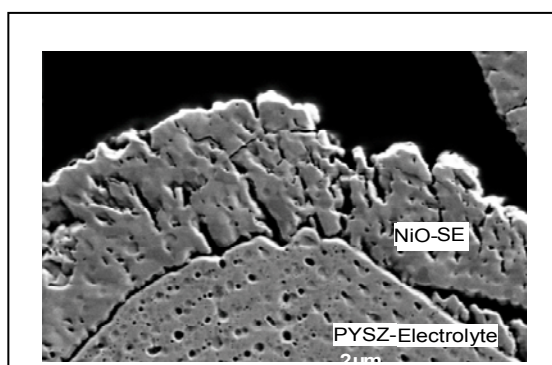


Figure 1: SEM micrograph of the sensor element with NiO-SE and PYSZ-electrolyte showing the morphology at the polished cross-section of electrode/electrolyte interface

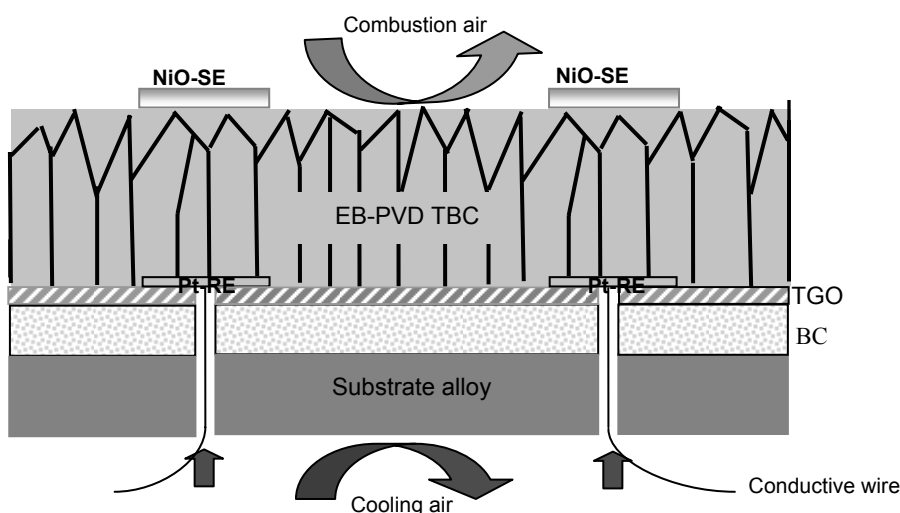


Figure 2: Schematic presentation of sensor integration into hot parts of turbines

The sensor elements were then tested for their sensitivity towards NO at various temperatures up to 700°C. Gas sensing characterisation was carried out in a specially constructed apparatus consisting of a tube furnace with cascade control, a custom-built quartz glass reactor providing a thermocouple directed at the specimen and an impedance spectroscope at the tail. The gas flow rate was adjusted to 200 sccm/min and the NO-concentration was varied between 0 and 1000 ppm. Cross-sensitivity of the sensors were determined towards oxygen (5 vol. %) and other emission gases (CO, CH₄). Argon was used as balance gas in all cases and no humidity was added to the gas mixture. For the impedance analysis a Solartron

1255b combined with a Solartron 1286 was applied. Impedance spectra were recorded from 0.001 up to 1 MHz with no bias and limited voltage (200 mV) and current (20 mA).

Results

The sensor devices were characterized by means of impedance spectroscopy in a temperature range of 100° to 700°C. Due to the thermodynamic equilibrium at the test temperatures only NO was used as test gas. Lower frequency range of the Nyquist-plots yielded a decrease in impedance values with NO-concentration increasing from 0 to 1000 ppm (Figure 3). The maximum working temperature for the tested sensors was 650°C. The high frequency range of the impedance plot showed no change with the variation of NO-concentration. For characterisation of sensitivity and response time, the frequency was fixed at 0.1 Hz and $|Z|$ -signals were recorded. This application is proved to be practical yielding a good compromise. The $|Z|$ -signal of the sensor elements decreased almost linearly with NO-concentration with and without oxygen (5 vol. % O₂) indicating a non-Nernst-like behaviour.

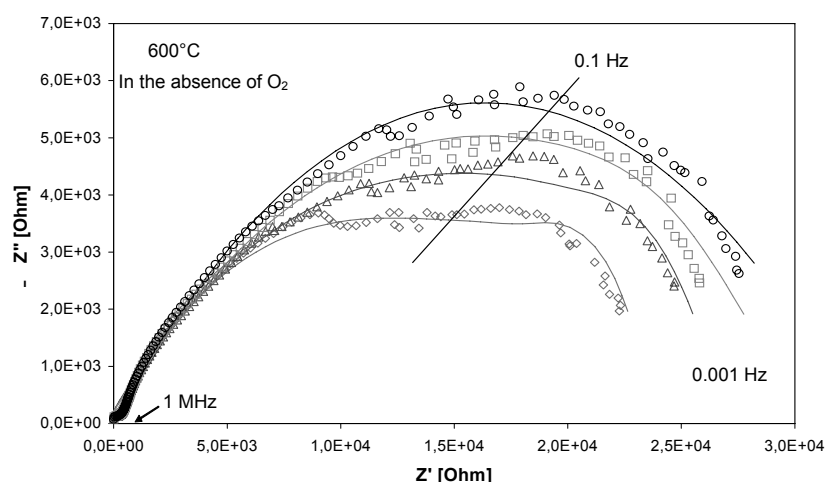


Figure 3: The measured and fitted impedance spectrum of NiO/PYSZ-sensor obtained at 600°C. NO-concentration increases from 100 ppm (circles) to 1000 ppm (triangles).

Sensitivity - The investigated sensor elements show a consistent variation of impedance with the NO-concentration. Total impedance ($|Z|$) values obtained from the Nyquist plots at a fixed frequency of 0.1 Hz decrease linearly as the NO-concentration increases from 0 to 1000 ppm at the test temperature of 650°C (Fig. 4). Experiments confirmed that the optimum compromise between sensitivity and sampling rate was at 0.1 Hz [1, 3]. Miura reports operating temperatures as high as 800°C with a potentiometric sensor having Rh-doped NiO-SE [4]. Moreover, 30 % higher sensitivity is achieved with Rh-doped NiO in comparison with pure NiO. These measurements are carried out in the presence of 5 vol. % H₂O which leads to an O²⁻ ion- exchange with the electrolyte through the formation of hydrolytes driving the occurrence of the catalytic reactions. Since the thermodynamic equilibrium between NO and NO₂ at 600°C is about 90% on the NO-side, the tests are carried out with gas mixtures having only pure NO. The applied temperature profile increases from RT to 600°C with 50°C steps. At each temperature step, impedance values under different NO concentrations are collected.

In order to compare the sensing behavior between the sensor elements, the relative sensitivity (S_R) at 500 ppm NO_x is applied and additionally the average sensitivity (S) is introduced to provide an extended comparison base. Table I displays the measured and calculated average and relative sensitivity (S and S_R) values for the tested sensor elements towards NO in the presence and absence of oxygen. The slope of the best-fit-line defines the relative sensitivity (S_R) that can be taken solely for comparison purposes since it varies largely with each NO-concentration. Average sensitivity (S) is the distance between the sensing curve and the base line and allows the obtainment of the signal changes over a broader concentration range without considering the $|Z|$ -value of the carrier gas. Therefore it may provide a better interpretation of the results. Although, the measured relative sensitivity of a sensor consisting NiO-SE/PYSZ-electrolyte is very small, its average sensitivity is higher (Table I).

All characterized sensor elements show a linear non-Nernst-like behavior with similar sensor reactions towards NO and NO₂, which is in good agreement with other studies [3, 5]. Sensor signal of the NiO-SE/PYSZ-electrolyte displays a jump at 500 ppm NO in the absence of oxygen leading to the implication that the O²⁻-ions of the PYSZ-electrolyte contribute to the reaction at higher concentration (Fig. 4). This

may be due to a mechanism change in the reaction sequences in the absence of oxygen. NiO-SE sensors maintain their sensitivity well in the presence of oxygen.

Table I. Relative and average sensitivity of the investigated sensor elements towards NO with and without oxygen.

Material	Electrolyte	S_R	S	NO-Conc. range [ppm]
NiO	PYSZ	0,02	2,4	50 – 1000
NiO	PYSZ	0,06	2,1	200 – 950

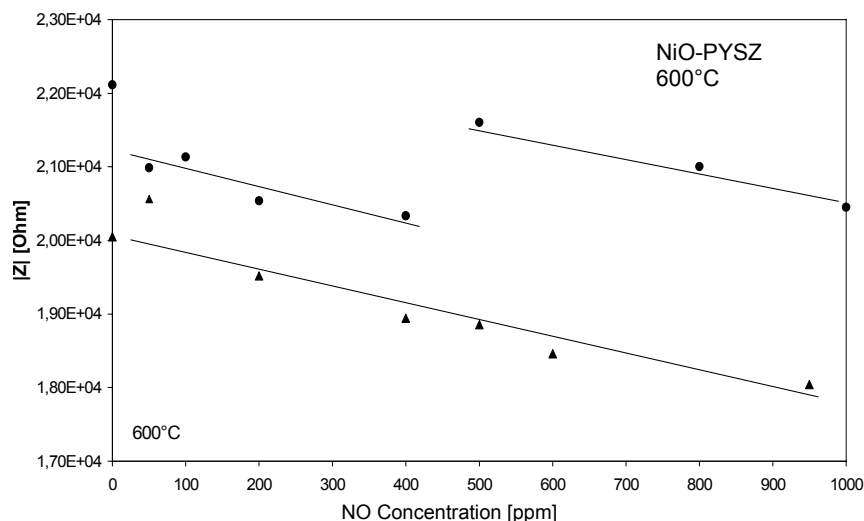


Figure 4: Total impedance change of NiO/PYSZ-sensor with NO-concentration at 600°C with oxygen (triangles) and without oxygen (circles)

Cross-sensitivity –The sensitivity of NiO-SE/PYSZ-sensors were tested under gas mixtures including NO and other individual emission gases such as O_2 , CO, CO_2 and NO_2 . In the presence of oxygen, the absolute impedance values of the investigated sensors decrease, indicating a slight weakening of the sensitivity towards NO. Very little impedance changes was observed in the presence of oxygen. An average sensitivity (S_R) that corresponds half of that towards NO is calculated indicating a low degree of selectivity towards oxygen. This behavior can be attributed to the enhancement of the oxygen atoms in the electrolytes through the increase of the oxygen partial pressure. Cross-sensitivity tests with gas mixtures containing NO and oxygen varying from 2 - 20 vol. % showed a slight cross-sensitivity towards oxygen (Figure 5). Table II lists the relative sensitivity values towards other emission gases. The relative sensitivity towards CO and CO_2 are negligibly low. The cross-sensitivity measurements towards CO and CO_2 confirm these values.

Table II. Relative sensitivity values obtained towards various emission gases @ 0.1 Hz frequency

SE-Material	Electrolyte	S_R CO (at [ppm])	S_R O_2 (at [vol.%])	S_R CO_2 (at [ppm])	S_R CH_4 (at [ppm])	S_R NO_2 (at [ppm])
NiO-SE	PYSZ	0,003 (400)	0,1 (5)	0,006 (500)	-	0,02 (100)

As shown in Figure 5d, the NiO-SE/PYSZ sensor displays a sensor reaction indicating a cross-sensitivity towards NO_2 . This can be attributed to the dissociation of NO_2 to NO at the test temperature (600°C). In general, NO_2 diffusion rate is slower and the achievement of the thermodynamic equilibrium takes longer. Moreover, it is likely that in the selected test conditions NO_2 will be completely transformed to NO. This contributes to the NO-sensitivity.

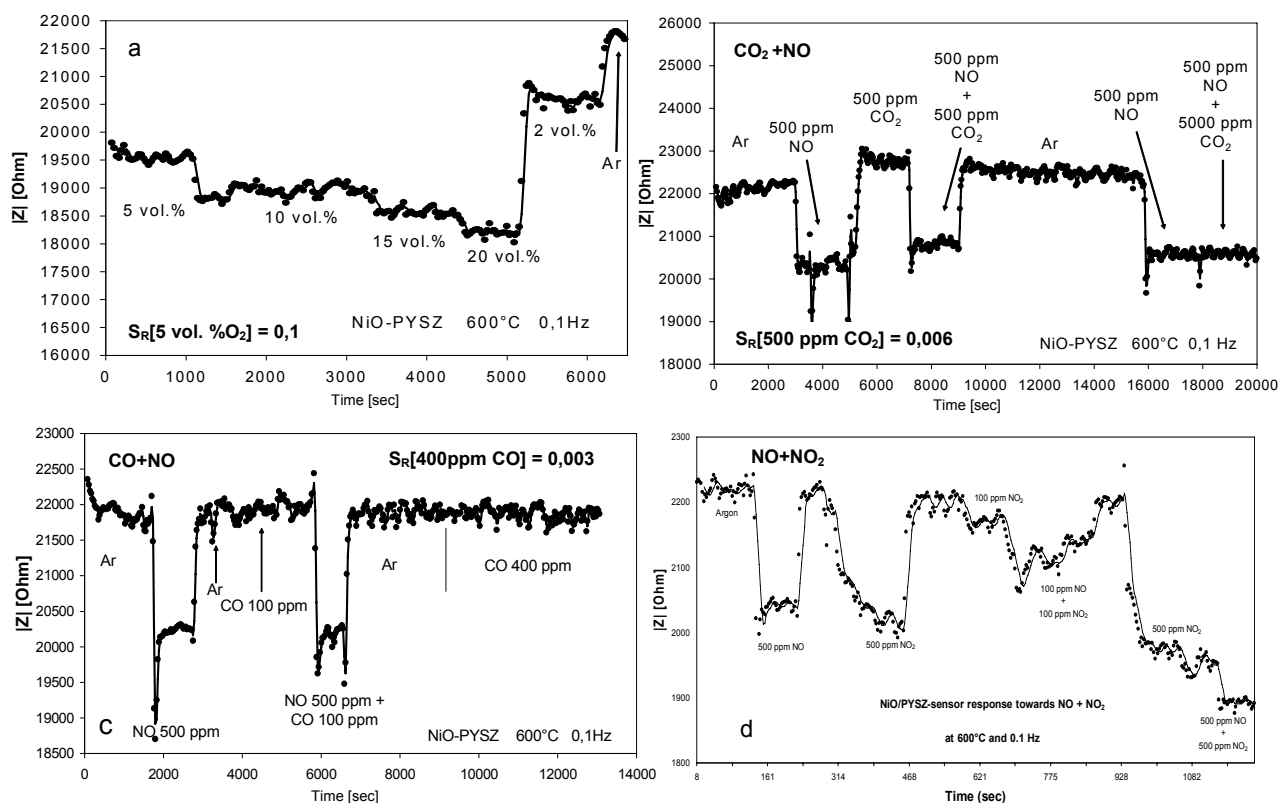


Figure 5: Response of NiO-PYSZ sensor towards gas mixtures containing NO and another emission gas (a-O₂, b- CO₂, c-CO and d-NO₂) at 600 °C and 0.1 Hz indicating cross-sensitivity. The peaks at the outer parts of the curves are the artefacts occurring by switching of the MFC-valves on and off.

Response time and drift- The response times (t_{90}) measurements were carried out with various NO-concentration in argon at 550°C under a gas flow rate of 500 sccm. The sensor drift is determined by the slope of the impedance increase over the time. This is given with the broken lines in Figure 6. It is seen that the drift is constant over the measurement time. A sensor drift of around 1.Ω/min is measured For a sensor having NiO-SE and FYSZ electrolyte This corresponds to a relative drift of $D_R = 9.7 \cdot 10^{-5} \text{ min}^{-1}$. Response time measurements showed a stable signal at 550°C. Response time increases with NO concentration. The response time with this sensor element varies between 60 and 90 seconds for NO concentration varying from 100 to 500 ppm (Fig. 6 and Table III). The measured response times are relatively long and may be related to the longer diffusion times at TPB as well as due to the applied low frequency (0.1 Hz) which requires longer measurement times for a sound signal. The investigated sensor electrode displays a relatively fine grain morphology and lower porosity. It is well-known that denser SE-morphologies yield longer response times. NiO sensor electrode manufactured in this study is relatively porous, however, contain very fine grain and pore sizes. Such morphology leads to long diffusion times, and thus, the thermodynamic equilibrium of the mixed gases at TPB requires longer soaking times. Moreover, the thermodynamic equilibrium between NO/NO₂ may limit the response time. NO₂ is converted fully to NO under these conditions which also contributes to the sensitivity towards NO. As the |Z| vs. time curve obtained with NO and NO₂ given Figure 5d exhibits that the sensor has longer response times under NO₂ flow, in other words, longer soaking times are required until a steady signal is achieved with NO₂ than NO. Moreover, the peak size obtained under NO and NO₂ mixed gas flow is approximately at the summed amount for NO alone. These findings imply that the sensor response to NO₂ at the test temperature of 600°C has a pseudo character and NO₂ gradually converts to NO confirming the observation of Elimalai et al. [6] who reported that about 90% of NO₂-dissociation to NO occurs at 600°C. The response times of the aged sensors are longer measured reaching to 150 and 213 sec depending on the NO-concentration.

Conclusions

The operating temperature of the sensor having PYSZ-electrolyte and NiO-SE is determined by impedance analysis and corresponds to 600°C. NiO-SE/PYSZ-electrolyte sensors display a linear sensitivity towards NO at 550-600°C. Cross-selectivity measurements towards other emission gases reveal that the sensors maintain

their NO-sensitivity in oxygen rich atmospheres well with a very low cross-sensitivity towards oxygen. The cross-sensitivity of the investigated sensors with NiO-SE is very low towards CO, CH₄ as well as CO₂, making them good NO-sensors. Sensitivity towards NO₂ counts on to NO at the measurement temperature, since the equilibrium at this temperature is at the NO-side.

Table III. Response and regeneration times obtained with NiO-PYSZ-sensor towards NO at 550°C.

NO Concentration [ppm]	Response Time [sec]	Regeneration Time [sec]
100	61	61
200	60	60
300	62	92
500	89	63

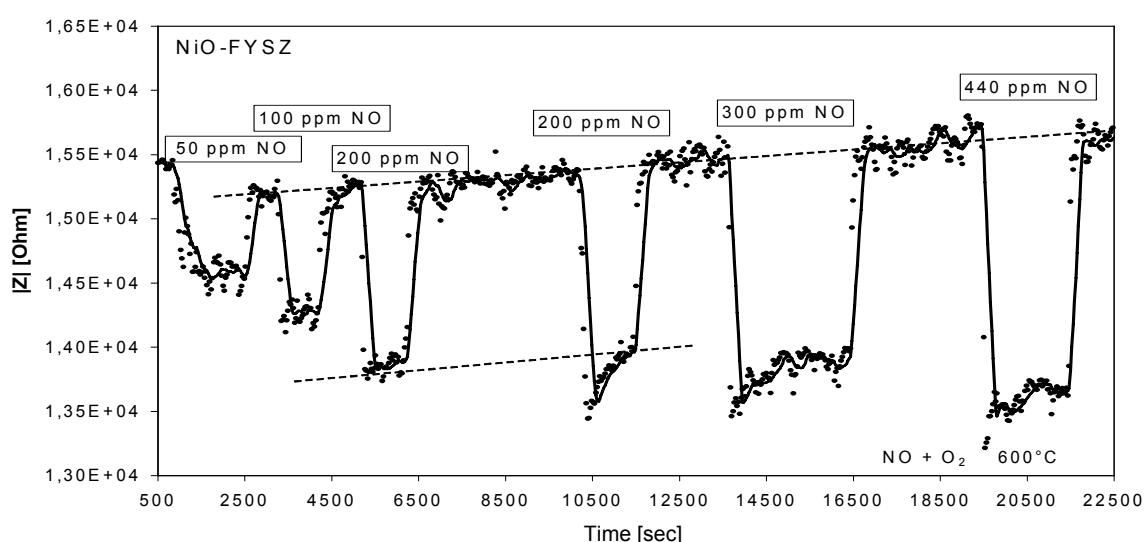


Figure 6: Response behaviour of NiO-FYSZ-sensor under various NO-concentrations at 600 °C.

References

- [1] F. M  nil, V. Coillard, C. Lucat, Critical review of nitrogen monoxide sensors for exhaust gases of lean-burn engines, *Sensors and Actuators B: Chemical*, 67, 1-23 (2000).
- [2] M. Stranzenbach, E. Gramckow, and B. Saruhan, "Planar, impedance-metric NO_x-sensor with spinel-type SE for high temperature applications," *Sensors and Actuators B: Chemical*, 127, 224-230 (2007).
- [3] J. W. Fergus, "Materials for high temperature electrochemical NO_x gas sensors," *Sensors and Actuators B: Chemical*, 121, 652-663 (2007).
- [4] N. Miura, M. Nakatou, and S. Zhuikov, "Impedancemetric gas sensor based on zirconia solid electrolyte and oxide sensing electrode for detecting total NO_x at high temperature," *SnAs B: Chemical*, vol. 93, pp. 221-228, 2003.
- [5] L. Y. Woo, L. P. Martin, R. S. Glass, and R. J. Gorte, "Impedance Characterization of a Model Au/Yttria-Stabilized Zirconia/Au Electrochemical Cell in Varying Oxygen and NO_x Concentrations," *J. of The Electrochemical Society*, vol. 154, pp. J129-J135, 2007.
- [6] P. Elumalai, J. Wang, S. Zhuikov, D. Terada, M. Hasei and N. Miura, Sensing characteristics of YSZ-based mixed-potential-type planar NO_x-sensors using NiO sensing electrodes sintered at different temperatures, *J. of Electrochemical Society*, 152[7] (2005) H95-H101.