

PLANAR, IMPEDANCE- METRIC NO_x SENSOR WITH SPINEL- TYPE SE FOR HIGH TEMPERATURE APPLICATIONS

M. Stranzenbach^{1*}, B. Saruhan¹

¹ German Aerospace Center, Linder Hoehe, D-51147 Cologne

*Corresponding author: M. Stranzenbach, Phone: +49-(0)2203/6012508, Fax: +49-(0)2203-696480, e-mail: Mathias.Stranzenbach@dlr.de

Abstract: This study displays the results obtained with a planar, impedance- metric sensor having a NiCr₂O₄-SE and a specially manufactured FSZ electrolyte. The sensing characteristics to NO and to O₂/NO-gas mixtures were analyzed at temperatures up to 700 °C. The cross-selectivity to other flue-gases was tested. As a new capable type of sensing parameter the total impedance was applied.

Keywords: Mixed Oxide Sensing Electrode, High temperature flue gas sensor, Impedance

Introduction

Recently, an urgent need for high performance gas sensors has arisen. Especially in the automotive sector, where engines are more and more operated in lean burn areas, the flue gas compositions have changed to net oxidizing conditions. Therefore, new catalysts for the reduction of NO_x are necessary, which makes a permanent sensor control ineluctable. The requirements for these new generation sensors are high temperature stability and a long lifetime. Temperatures for closed coupled catalysts can rise temporarily up to 900°C to which the sensor needs to withstand. A major expectation from such sensors is to be able to monitor total NO_x in the exhaust gas under the presence of oxygen at working temperatures between 500 and 700°C. Standard potentiometric sensors suffer under the opposite sign for the emf potential of NO and NO₂ which makes it very hard to monitor total NO_x [1]. To overcome these problems different design changes and sensor types have been suggested (e.g. multi chamber amperometric sensors) [2,3]. But the need for cost-efficient and simple sensor systems with high lifetime holds back their commercial use until today. Therefore, we suggest a new planar NO_x-sensor type with an EB-PVD manufactured electrolyte and a magnetron sputtered spinel-type oxide sensing electrode (spinel-SE) for use at high temperature and in harsh environments such as turbo engine vehicles and aircraft turbines [4,5].

Experimental

In this study, an innovative type of sensor configuration is used which consists of an electrolyte constructed of quasi-single crystalline columns, a porous thin layer of sensing electrode (SE), a thin porous Pt- collector layer on top and a conductive Pt reference electrode (RE) deposited on the backside. As electrolyte EB-PVD manufactured discs of FSZ composition were used. The discs were 12.7 mm in diameter and about 500 μm thick. The special columnar microstructure of the electrolyte features a smooth RE side and a high surface area SE side. It's preferentially

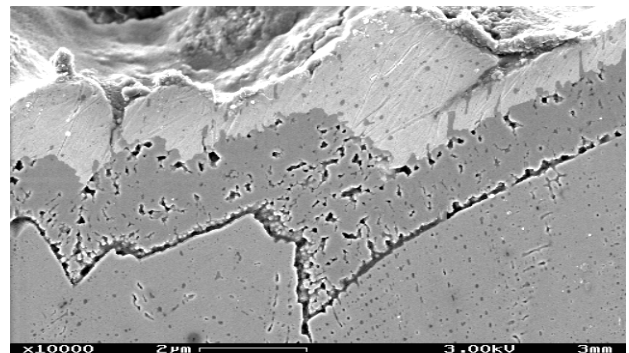


Figure 1: SEM picture of the MMO SE/ Electrolyte-Interface showing a SE average grain size of 0.2 μm. Top layer is the porous Pt- collector.

oriented crystal direction lies vertically to the electrodes. For the EB-PVD fabrication of the electrolytes it was necessary to coat the FYSZ on a stable metallic, high temperature substrate, which was afterwards removed by a wet etching process. After a cleaning step, a short aging procedure of the electrolytes has been done, which was necessary to extend the sensor lifetime to optimise its performance. After this an approximately 3 μm thick Ni-based spinel-SE electrode was reactive-sputtered on the SE side of the substrate using O₂ as reactive gas. Annealing up to 1000°C in air led to a porous SE with an average grain size of approximately 0.2 μm (Fig. 1). Following this, thin and porous Pt layers were sputtered on the RE and SE side serving as ultra thin electrodes or electron collector. Finally the sensor was electrically connected using a commercial Pt paste (LPA 88/11S, Hereaus) and 0.15 mm Pt wires which were hardened at 1000°C. Gas sensing characterizations

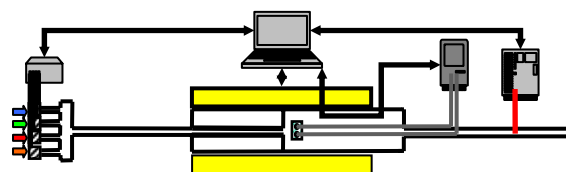


Figure 2: Schematic drawing of the experimental setup. The sensor is connected to the impedance spectroscopy at the rear part of the furnace.

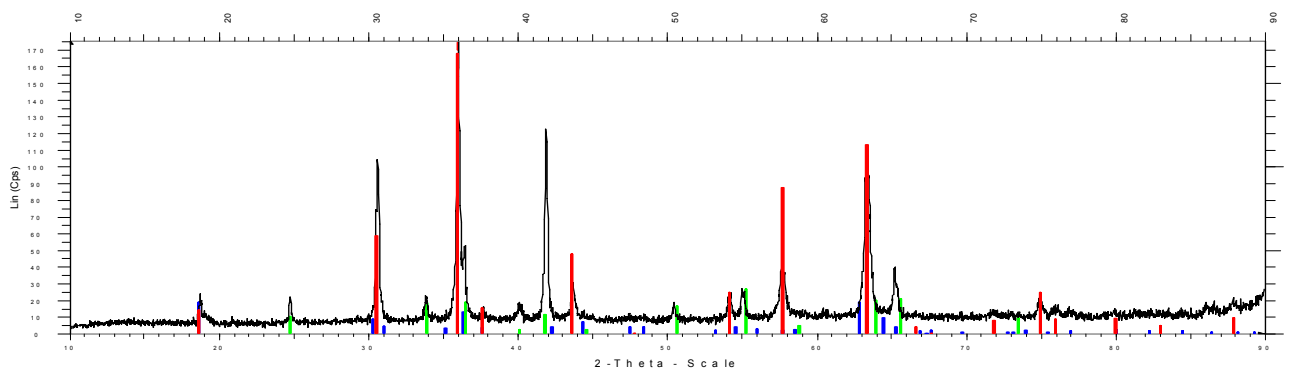


Figure 3: XRD analysis of the sensing electrode after annealing at 1000°C for 4h. The cubic NiCr₂O₄ phase is the dominating crystal phase. — NiCr₂O₄ cubic — NiCr₂O₄ tetragonal — NiCrO₃ rhombohedral

were carried out in a specially constructed apparatus consisting of a tube furnace and a custom-built quartz glass reactor (Fig.2). The gas mixtures were controlled by MFCs and adjusted at a total flow of 200 sccm/min. NO_x concentrations varied between 0 and 1000 ppm. Cross-selectivity was analyzed towards O₂ (0–20 vol.%), CH₄ (0-500 ppm), CO (0-100 ppm) and CO₂ (0-500 ppm). Ar was used as balance gas in all cases. Impedance and potential analysis were carried out by a Solartron 1255b and a Solartron 1286. Impedance spectroscopy was done at a frequency range of 100 kHz to 0.001 Hz and maximum AC amplitude of 200 mV. No DC Bias was applied. Morphological analysis in terms of porosity, grain size and surface condition was done by means of SEM (LEO 982). XRD-analysis was carried out by means of a Siemens D5000 x-ray diffractometer (Cu K α radiation) to determine the phase sequence and crystal structure. Figure 3 shows that the main crystalline phase in the annealed NiCr- Oxide sensing electrode layer is a cubic NiCr₂O₄ spinell phase, aside this phase there are two other crystalline phases (one spinell type and one perovskite type). All other peaks in the spectrum are from the substrate spectrum which is not indicated in the figure.

Results

The experiments were carried out between 500 and 700°C. Since the thermodynamic equilibrium of NO_x between NO and NO₂ at 600°C is of about 90% on the NO side, we used a pure NO gas-mixture. The impedance spectroscopy was done with 126 measuring points over the frequency interval with two measuring cycles for each point. For the first NO sensing behaviour characterisation a virgin sensor was used. The Nyquist-plots of the complex impedance showed distinct variations by NO-concentration in the lower frequency range, which many presumably belong to the electrode-electrolyte phase of the spectrum. The high frequency range, belonging to the bulk resistance of the electrolyte shows no change with the variation of the NO-concentration (Fig.4). The maximum operating temperature for the investigated sensor-system was about 650°C.

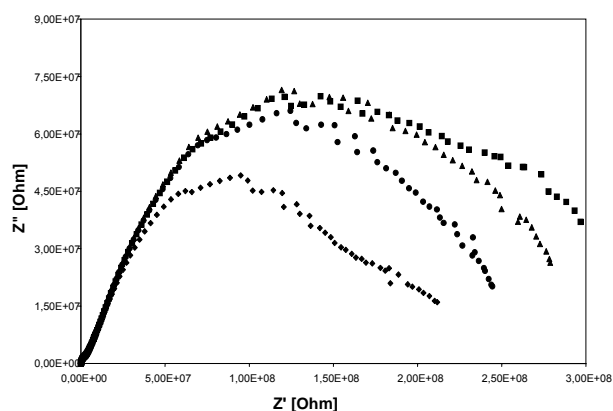


Figure 4: Impedance spectra of various NO concentrations [ppm] (■ = 0; ▲ = 100; ● = 500; ◆ = 1000)

Above this temperature the sensitivity towards NO starts fading away so much, that the detection area of the sensor is limited tremendously. Below 650°C the sensitivity and the detection area is large enough. Therefore we fixed the temperature at 620°C for all following tests.

As shown in Figure 4, the real part of the complex resistance decreases with the applied NO-concentration between 0 and 1000 ppm at 620°C. In order to identify the effect of the electrolyte and the Pt-electrode/Pt-current-collector in the spectra, the systems: Pt/FSZ/Pt and Pt+spinel-SE/Al₂O₃/Pt were analysed by means of impedance spectroscopy. NO was varied from 0 to 1000 ppm. The concentration change results in a different behaviour at these two systems, compared to that observed at the Pt + Spinell-SE/FYZ/Pt –system. Mobile applications require simple and low cost sensor systems. Moreover it is undesirable to measure the complex resistance over the whole frequency range in such systems. So we have chosen to measure the total Impedance $|Z|$ ($|Z| = \sqrt{(z')^2 + (z'')^2}$) at a fixed frequency. As a good compromise of reaction time and sensitivity of the sensor, we fixed it at 0.1 Hz and plotted the total impedance versus various concentrations of NO [6]. The monitored values of the total impedance $|Z|$ at the fixed frequency are given in figure 5. The sensor shows very good total resistance changes over the complete concentration interval, with an almost linear behaviour. Only two slight slope

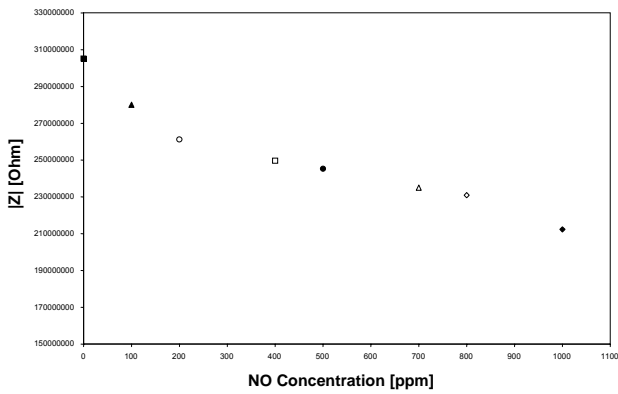


Figure 5: Changes of the total impedance $|Z|$ with NO concentration [ppm] at 0.1 Hz. (■ = 0, ▲ = 100, ○ = 200; □ = 400, ● = 500, △ = 700, ◇ = 800, ◆ = 1000)

changes in the sensor line are observable, which may be due to thermal dynamic changes of the sensing behaviour at the SE- electrode. Most likely the kinetics of the SE- reactions change with NO concentration.

After the first characterisations and the analysis of the maximum working temperature the same sensor was used to determine the applicability of the sensor in mixed gas medias, by means of the cross-selectivity measurements towards other typical combustible gases like O_2 , CO, CO_2 and CH_4 . The most important requirement at lean-burn processes is to monitor NO during the presence of O_2 . Most commonly in automobile industry about 5 vol.% O_2 is present in flue gases. Therefore tests were performed in a mixed base-gas (5 vol.% O_2 and Ar) and various concentrations of NO. The sensor showed a slightly improved linear characteristic for concentration range between 0 and 950 ppm NO (Fig. 6).

This confirms the potential of our sensor system to function as a NO_x - sensor in net oxidizing atmospheres for exhaust gas applications. The behaviour of the sensor at various concentrations of O_2 between 0 and 20 vol.% was also analysed. The sensor showed a reaction towards major changes in the O_2 concentration (± 2 vol.%), so that the O_2 -concentration at the sensor should be kept constant in an interval of about $\pm 0,2$ vol.% during service. For reductive gases CO and CH_4 an increase in both ohmic and complex resistance could be observed, which is most probably due to the reduction of the FYSZ electrolyte leading to the missing charge carriers, But the sensor showed hardly any changes in the impedance spectra under various concentrations of these two gases. This indicates that there is a principal dependence of net reducing atmospheres to the ion conductivity of FSZ but no cross-selectivity to CO or CH_4 . Regarding the conditions of the aimed applications applying net oxidizing atmospheres this should not restrict the applicability of the system. A cross selectivity towards CO_2 could not be observed. In order to better understand the sensing

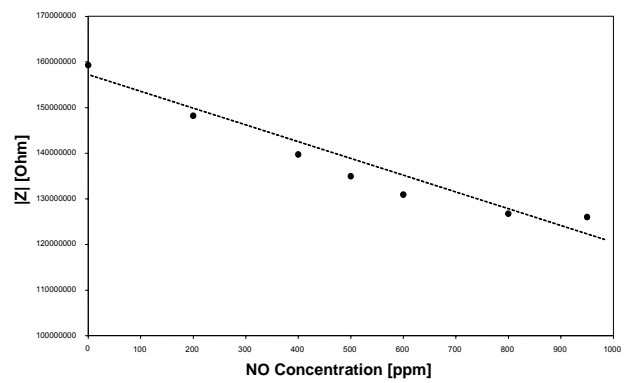


Figure 6: Total impedance changes with NO concentration (0-950ppm) in a 5 vol.% O_2 base-gas mixture. Signal behaviour is linear (dashed line).

behaviour we tried to fit the spectra by applied an equivalent circuit with five elements (Fig.7). It consists of an ohmic resistor and two R-C elements in serial, representing the bulk FSZ part, which is in the high frequency region of the spectra [8]. To fit the sensing relevant parts of the spectra, which are found in the low frequency part of the spectra, we propose an ohmic resistor in parallel connection with a constant phase element and in serial with a Warburg impedance in parallel connection with an ohmic resistor to fit the curves. Changes due to concentration changes of NO mainly occur at the three-phase boundary electrolyte/spinel-SE/gas [7].

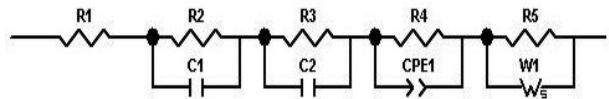


Figure 7: Equivalent circuit for the planar spinel-SE sensor

To identify the spinel-SE relevant parts in the impedance plot, some experiments with NO and O_2 were carried out on the systems Pt/FSZ/Pt and Pt+spinel-SE/ Al_2O_3 /Pt, confirming that the changes in the spectra are mainly caused by concentration changes and the SE- electrode and obviously occur in the low frequency part. All fits and spectra analysis were done with ZView 2.8 from Scribner Associates. A more detailed analysis of the fits showed the main changes with concentration in the ohmic resistors R_4 , R_5 and the constant phase element, which is for instance shown in figure 9.

As shown in Fig. 5, the catalytic reaction over the SE- electrode seems to change with concentration. Therefore the changes in the Spectra can be most likely attributed to electrical phase change in the double layer charge between electrode and electrolyte which may be caused by the catalytic reaction of NO over the spinel-SE. The Warburg impedance shows also changes with NO-concentration. In general this element represents

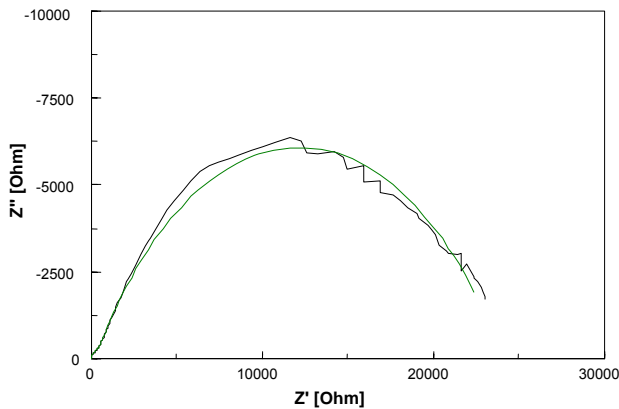


Figure 9: Equivalent circuit fit for an impedance spectrum of the sensor at 620°C and 800ppm NO (— Sensor signal, - - fit)

diffusion processes. In this case it most likely represents the motion of the charge carrier (O^{2-}) through the electrolyte. Therefore it may be related to the diffusion of oxygen ions from the three-phase boundary into the bulk FSZ, which would explain the concentration dependence. But further analysis needs to be done and will be presented later.

Conclusion

This study shows the potential of Ni-based spinel-SE impedance-metric sensors as high temperature NO_x sensors for use in exhaust gas applications and harsh environments and the applicability of the total impedance as a reliable sensor signal. As shown the sensor works over a wide range of NO concentrations at high temperatures up to 650°C. The $NiCr_2O_4$ -SE is able to monitor NO under the presence of O_2 , but oxygen concentration should be kept constant at the sensing electrode over a certain interval. A cross-sensitivity towards reducing gases was also observed. Regarding the aimed service conditions of the sensor, this should not influence the sensing behaviour, under net oxidizing atmospheres. Regarding these results, it can be postulated that Ni based spinel-SEs could be good candidates for SEs in planar flue-gas sensors at high temperatures.

REFERENCES

1. F. Ménil, V. Coillard, C. Lucat; *Sensor and Actuators B*, 67 (2000), pp 1-23.
2. J. Schalwig, S. Ahlers, P. Kreisl, C. Bosch-v. Braunmühl, G. Müller; *Sensor and Actuators B*, 101 (2004), pp 63-71.
3. W. Göpel, G. Reinhardt, M. Rösch; *Solid State Ionics*, 136-137 (2000), pp. 519-531.
4. S. Zhuiykov, T. Nakano, A. Kunimoto, N. Yamazoe, N. Miura; *Electrochemistry Communications*, 3 (2001), pp. 97-101.
5. N. Wu, Z. Chen, J. Xu, M. Chyu, S. Mao; *Sensors and Actuators B*, 110 (2005), pp. 49-53.
6. P. Elumalai, N. Miura; *Solid State Ionics*, 176 (2005), pp. 2517-2522

7. A. Cheikh, A. Madani, A. Touati, H. Borsetta, C. Monty; *Journal of the European Ceramic Society*, 21 (2001), pp.1837-1841