YSZ-Cells for Potentiometric Nitric Oxide Sensors

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Abstract. Potentiometric sensors based on zirconia can be used for determining gaseous NO at temperatures between 400 and 480 °C. For such mixed potential sensors, NO sensitive electrode materials such as $CdMn_2O_4$ and V_2O_5 have been described. In order to improve the cell voltage response, composite electrode materials based on V_2O_5-γ-Al_2O_3 were investigated. Sensors employing these materials show a better voltage response and an improved adhesion to the solid electrolyte compared with pure V_2O_5. The optimal temperature was found to be 440 °C. The NO sensitivity is nearly independent on the oxygen partial pressure in the gas.

1. Introduction

The development of NO sensors is strongly driven by the increasing interest to measure and control this gas in order to prevent its formation and to reduce its concentration by exhaust treatment.

The exhaust gas of lean burn and diesel engines cannot be cleaned by the well known three-way catalyst. Concepts using chemical reducing agents are promising to remove the NO [1]. It seems to be that the addition of urea, its thermal decomposition and the subsequent reaction of NH_3 and NO in a special catalyst is a suitable method to meet governments requirements. For that purpose, there is a need of two types of NO sensors: firstly, a sensor for high concentrations (up to 2000 vol.-ppm) before and a second sensor for the low NO concentrations behind the conversion catalyst, see Fig. 1.

For mixed potential sensors based on zirconia solid electrolytes, electrode materials are necessary that exhibit a high NO and a low oxygen activity. For that purpose several materials were described, e.g. $CdMn_2O_4$ [2] and V_2O_5 [3]. However, electrodes consisting of those materials show a low voltage response versus an air reference and poor adhesion on zirconia. Therefore, the long term stability is poor.

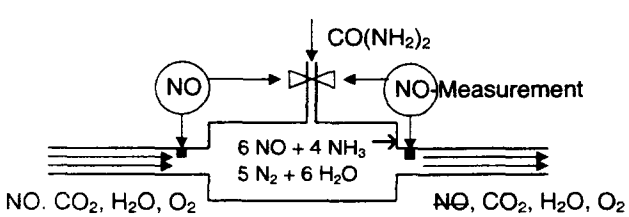

Fig. 1. Schematic view of Selective Catalytic Reduction of NO with urea.

To improve the cell voltage of such mixed potential sensors, NO-sensitive electrode composite materials based on V_2O_5 were investigated. The basic idea was to increase the electrode surface by means of small particles of insulating materials. γ-Al_2O_3 was found to be an effective material for catalysts. Moreover, admixtures of γ-Al_2O_3 can improve the mechanical stability and the conductivity of the ionic conductors by so called heterogeneous doping [4].

2. Theoretical Background

The oxidation of NO to NO_2 takes place in dependence on the oxygen partial pressure at temperatures lower than 600 °C. The conversion rate $\alpha = 1-\frac{\varphi_{NO_2}}{\varphi_{NO}+\varphi_{NO_2}}$ is shown in Fig. 2. The equilibrium shifts with decreasing temperature and increasing oxygen partial pressure in the sample gas toward the side of NO_2. The oxidation of NO is a suitable reaction for mixed potential electrodes on YSZ because oxygen is involved and the reaction takes place in a temperature

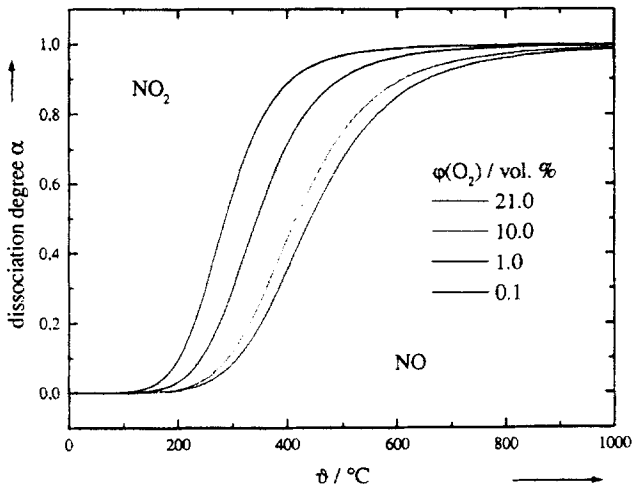

Fig. 2. NO-NO_2-equlibrium in dependence of temperature and oxygen partial pressure [3].

range in which the thermodynamic equilibrium is not established. So, the measured potential should be very strongly influenced by the temperature and the NO concentration. The oxygen partial pressure in the sample gas should not play a decisive role, because the oxygen reaction is slow at temperatures lower than 600 °C. The two competing reactions taking place on the electrode can be described in detail as

$$1/2\ O_2 + V_{ad} \rightarrow O_{ad}$$
$$O_{ad} + V_{ad} + 2e^-(Me) \rightarrow O_O^\times + V_{ad}$$
$$1/2\ O_2(g) + V_O^{\bullet\bullet} + 2e^-(Me) \rightarrow O_O^\times$$

for the oxygen reaction, and

$$NO + O_{ad} \leftrightarrow NO_2 + V_{ad}$$

for the NO oxidation with adsorbed oxygen, and

$$NO(g) + V_{ad} \rightarrow NO_{ad}$$
$$NO_{ad} + O_O^\times \rightarrow NO_{2,ad} + V_O^{\bullet\bullet} + 2e^-$$
$$NO_{2,ad} \leftrightarrow NO_2(g) + V_{ad}$$
$$NO(g) + O_O^\times \rightarrow NO_2(g) + V_O^{\bullet\bullet} + 2e^-$$

for the NO oxidation with oxygen from the electrolyte.

The fastest reaction has the strongest influence on establishing the mixed potential [5].

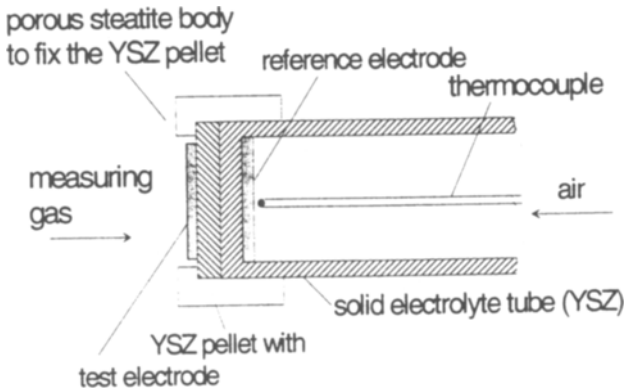

Fig. 3. Schematic cell arrangement [3].

3. Experimental Description

The NO sensitive electrodes were prepared by screen printing of a paste consisting of V_2O_5 and the desired amount of γ-Al_2O_3. The layers were sintered at 620 °C for 20 min. Figure 3 illustrates the cell arrangement for the measurements of the NO characteristics of the samples. The YSZ with the composite electrode to be investigated is pressed onto the closed end of a zirconia tube. The air reference electrode in the inner side of the tube consists of platinum. The cell voltage is measured by a multimeter (Keithley 199). The measuring gases were prepared by mixing different parts of oxygen (2.5 to 20.5 vol.-%) and NO (0 to 1150 vol.-ppm) balanced by nitrogen. The measuring temperature was varied between 420 and 460 °C.

4. Results and Discussion

In Fig. 4, results of the cell voltage measurements of a V_2O_5 electrode are presented. The temperature showing the

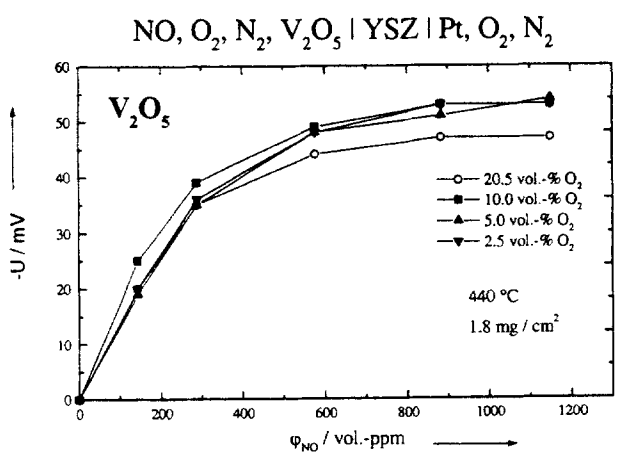

Fig. 4. NO-characteristic of a V_2O_5 electrode in dependence of temperature measured vs. Pt air reference.

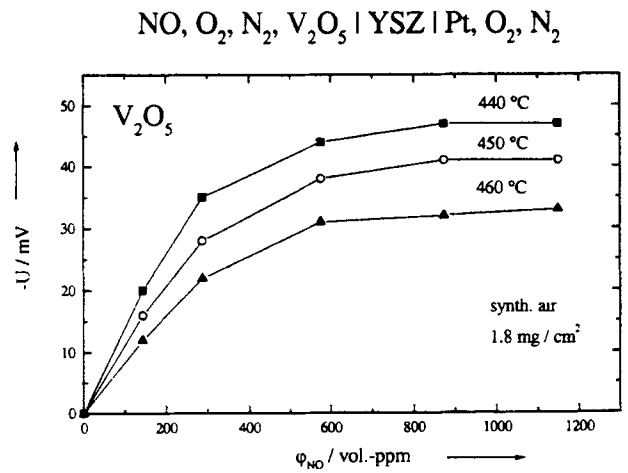

Fig. 5. NO-characteristic of a V_2O_5 electrode in dependence of oxygen part in sample gas measured vs. Pt air reference.

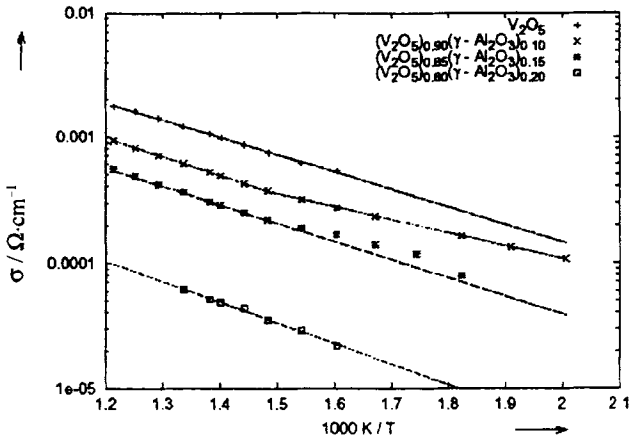

Fig. 7. Conductivity of V_2O_5 and V_2O_5 / γ-Al_2O_3 mixtures.

highest voltage response was 440 °C. The cell voltage increases with increasing NO concentration typically in non-Nernstian behaviour. The sensitivity $S = \left(\frac{\partial U}{\partial \varphi_{NO}}\right)_{\varphi_{NO} \to 0}$ for small NO concentrations is 0.14 mV/ppm NO at 440 °C.

Figure 5 shows the cell voltage in dependence of the NO concentration for different oxygen concentrations. This influence is small at least for oxygen concentrations < 10 vol.-%. The cell voltage increases up to twice the value by using electrodes consisting of V_2O_5-γ-Al_2O_3 composites (Fig. 6). The sensitivity also increases up to 0.28 mV/ppm NO.

It is suggested that the reason for this effect is the dispersion of V_2O_5 by γ-Al_2O_3 and an increase of the electrode surface. Electronic phenomena do not play an important role as can be shown by conductivity measurements in the system V_2O_5-γ-Al_2O_3. The conductivity decreases with the increasing amount of γ-alumina. A composite effect could not be observed (Fig. 7).

Gold and silver electrodes were investigated in addition to the V_2O_5 containing electrodes.

Gold electrodes show a larger NO sensitivity than the pure V_2O_5 electrode (see Fig. 8). The gas sensing behaviour of pure gold electrodes depends very strongly on the treatment of the electrode. Pure gold electrodes show a so-called "memory effect" – which means that the sensitivity of gold electrodes changes with time [3].

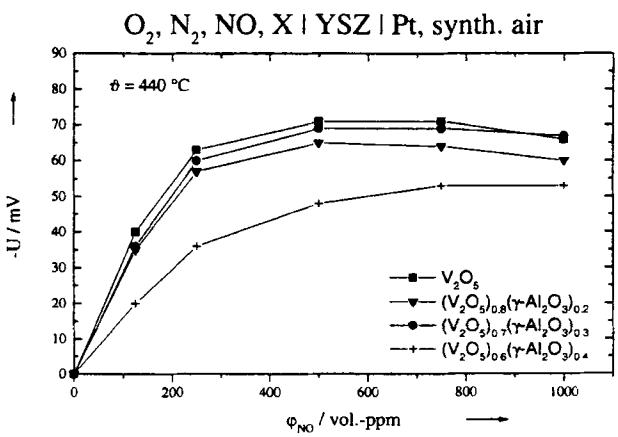

Fig. 6. Overview about the NO-characteristics of different V_2O_5 / γ-Al_2O_3 mixtures measured vs. Pt air reference.

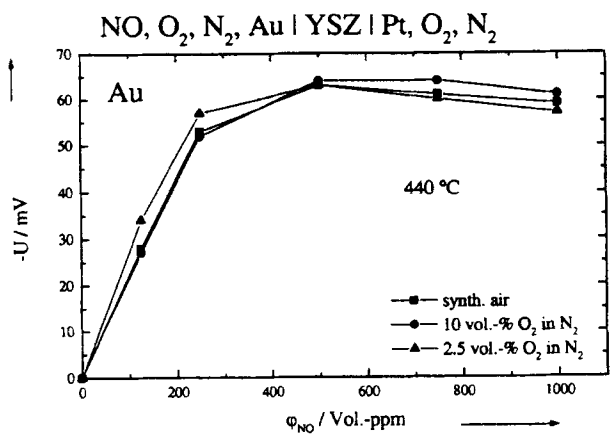

Fig. 8. Cell voltage response of an Au electrode in dependence of oxygen part in sample gas measured vs. Pt air reference.

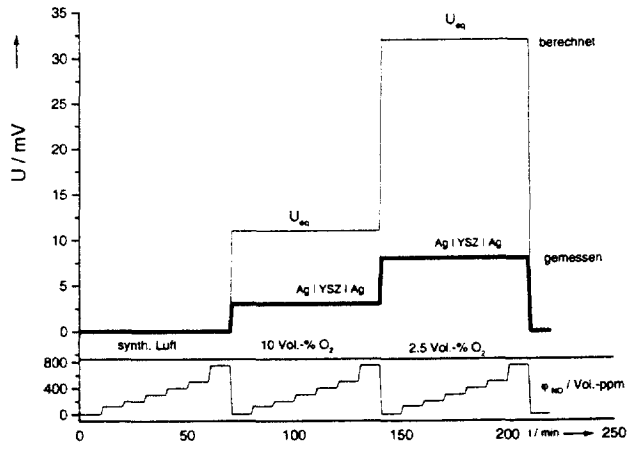

Fig. 9. Behaviour of an Ag electrode at 440 °C at different oxygen and NO-concentrations in the sample gas.

Silver electrodes do not show a NO sensitivity in the temperature range between 420 and 460 °C under these conditions. The influence of the oxygen partial pressure is lower than calculated from the Nernstian equation. Figure 9 shows the cell voltage response of an Ag electrode sintered at 700 °C. A change of the oxygen partial pressure from 20.5 to 2.5 vol.-% induces a cell voltage of 8 mV (calculated value: 32 mV). The reason for this behaviour could be found in the morphology of the electrode layer. The layer is gas-tight and exhibits only closed pores (see Fig. 10). This behaviour and the assumption of low catalytic activity of the Ag is considered to result in more simple constructions and cheaper gas symmetrical cells with Ag reference electrodes.

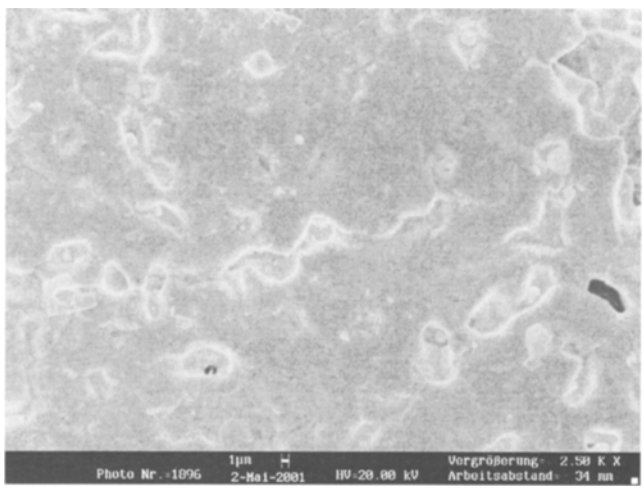

Fig. 10. SEM picture of an Ag electrode sintered at 700 °C.

5. Conclusion

Electrodes with V_2O_5-γ-Al_2O_3 composite show a better voltage response as compared to pure V_2O_5 electrodes and an improved adhesion on the solid electrolyte. The optimum measuring temperature was found to be 440 °C. The NO sensitivity is nearly independent on the oxygen partial pressure in the sample gas.

6. Acknowledgement

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7. References

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