

NON-NERNSTIAN PLANAR SENSORS BASED ON YSZ WITH AN Nb₂O₅ ELECTRODE: DISCUSSION ON SENSING MECHANISM

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ABSTRACT

Solid electrolyte based sensors have been widely studied for the detection of CO/HC and NO_x at high temperature. Nevertheless, the discussion about the sensing mechanism of non-nernstian electrochemical gas sensors, with a semiconducting sensing electrode, is still open. In this work, a study of the influence of the metallic electrode under the semiconducting metal oxide Nb₂O₅ on the sensor response was performed. Planar sensors based on tape-cast YSZ layers were fabricated. Two Pt or Au finger electrodes were deposited in a parallel arrangement on a single side of YSZ. One of these electrodes was covered with Nb₂O₅ thick film. In order to better understand the sensing mechanism, the electrical measurements were correlated with catalytic measurements performed on both sensing and reference electrodes.

INTRODUCTION

Non-Nernstian electrochemical gas sensors offer a single, inexpensive way of measuring combustion gas emissions. Several reports on solid electrolyte-based sensors, for the detection of pollutants such as NO_x (1-16) and CO/HCs (13-22), have been proposed over the last two decades. Many prototypes with metal (Pt, Au, etc.) and metal oxides as sensing electrodes have been studied and developed.

The generation of an anomalous non-Nernstian electromotive force (emf) in yttria-stabilized zirconia (YSZ)-based sensors was first observed by Fleming (23), which opened the investigation on sensing mechanism for that type of sensor. According to most of the authors (11, 12, 17-26), the electrode potential is determined by the rates of the electrochemical reactions occurring at the three-phase boundary between the solid electrolyte, the electrode and gas. This is called Mixed Potential. The Mixed Potential Theory can fit well the performance of sensors with different metallic electrodes. The same theory can also explain the sensing response of electrochemical sensors with one Pt electrode exposed to reference air, and one semiconducting oxide electrode exposed to the target gas. Usually, these devices are in tubular or pellet form (11, 12, 17, 19, 23, and 26). On the other hand, when both the metallic and the semiconducting electrodes are exposed to the same atmosphere, without using reference air, the sensing mechanism can be much more complicated because other phenomena may be prevalent. The sign of the

potential difference between two sensor electrodes exposed to a multicomponent test gas is sometimes difficult to interpret. Some of the authors of this work have already observed that in the case of planar sensors, the emf response was negative (positive) for n-type semiconducting electrodes upon exposure to reducing (oxidising) gases and positive (negative) for p-type based sensors upon the same exposure (14, 15). The Mixed Potential Theory cannot explain by itself this change in the emf direction. Thus, the operating temperature, the surface morphology, the adsorption-desorption properties of the oxides, the catalytic and electro-catalytic activity of the electrodes, the sensors design and gas exposure (with or without reference air) have to be considered for the understanding of the processes that govern the response behaviour of these sensors. Moreover, while the equilibrium for the oxidation reaction of CO is easily reached, in the case of NO_x, the situation is even more complicated because many equilibrium reactions (reduction and oxidation) can simultaneously occur depending on the operating temperatures.

Therefore, an alternative explanation has been proposed named “Differential Electrode Equilibria” (15, 27-29). This is a more general term that is meant to be all inclusive, regardless of the source of the difference in equilibria occurring between two different electrodes. Depending on the operating conditions, different mechanisms can occur and explain the potentiometric response of the sensors, either mixed potential theory or the adsorption mechanism of semiconducting oxides. The variation of emf can be compatible with the changes in the Fermi level induced by chemisorption of oxidizing or reducing gas on oxide semiconductors (28, 29). In the case of planar sensors with n-type semiconducting oxides electrodes, it is difficult to distinguish between the mixed potential and semiconducting behaviour. The predictions from both theories are that the emf response is in the same direction: negative for a reducing gas, positive for an oxidizing gas.

This paper is focused on planar YSZ-based sensors with n-type semiconducting Nb₂O₅ as a sensing electrode. The emf was studied in the temperature range between 450 and 650°C in the presence of CO gas. All the sensors were wholly exposed to the same atmosphere without using reference air. To study the influence of the noble metal on the sensing response, different combinations of Pt and Au electrodes with sensing powder were used to prepare various types of sensors. In order to go through the sensing mechanism and to distinguish among different theories, Temperature Programmed Reaction (TPR) analysis was performed to correlate the catalytic properties with the electrical results.

EXPERIMENTAL

Materials preparation

Commercially-available, tape-casted YSZ layers (8 wt % Y₂O₃-doped, 10 x 10 mm, 150 μm thickness) were used as solid electrolyte materials for planar sensors. As metallic electrodes, either Pt or Au paste was deposited on one side of the YSZ surface in parallel fingers and thin gold wires were used as current collectors. The firing temperature of both Pt and Au pastes was 750°C for 10 min.

Nanosized Nb₂O₅ powders were prepared using a sol-gel method as described elsewhere (30). The X-Ray diffraction (XRD) analysis was performed using a Philips X-Pert Pro 500 Diffractometer for phase identification of the synthesized oxide. XRD patterns showed only the peaks of hexagonal phase (JXPDS 28-0317).

For the fabrication of the sensing electrodes, Nb₂O₅ powder was mixed with screen-printing oil. The slurry thus obtained was painted on the area of one Pt (or Au) electrode and fired at 750°C for 3 hours. Four types of sensors have been prepared, changing the combination of the metallic electrodes. The investigated electrochemical cells are as follows:

Pt/YSZ/(Au)Nb₂O₅ (sensor *a*)
 Au/YSZ/(Pt)Nb₂O₅ (sensor *b*)
 Pt/YSZ/(Pt)Nb₂O₅ (sensor *c*)
 Au/YSZ/(Au)Nb₂O₅ (sensor *d*)

An Au/YSZ/Pt sensor was prepared as a reference. The schematic view of these planar sensors is reported elsewhere (15).

Microstructures of the powder and of the electrodes of the different sensors were observed by field emission scanning electron microscopy (FE-SEM Leo Supra 35).

Potentiometric measurements

CO-sensing experiments were carried out in a conventional gas-flow apparatus equipped with a controlled heating facility. The sensors were alternatively exposed to air or CO (200-1000 ppm in air) at the total flow rate of 200mL/min, in the temperature range between 450°C and 650°C. At least three specimens were prepared for each type of sensor and each specimen was tested several times to check the reproducibility. The difference in potential (emf), between the two electrodes of the sensor, was measured with a digital multimeter (Keithley 2000). In all the measurements, the metallic electrode was connected to the negative terminal.

Catalytic analysis

Temperature programmed reaction (TPR) analysis was performed on Pt/YSZ, Au/YSZ, Nb₂O₅(Pt)/YSZ and Nb₂O₅(Au)/YSZ electrodes taken from pieces of the investigated sensors. TPR analysis was carried out with the sample loaded in a thin quartz reactor and the effluent gas was analysed by a Quadrupole Mass Spectrometer. A pre-treatment was performed, consisting in flowing He gas while heating the sample from 70 to 750°C with a heating rate of 30°C/min. The sample was then treated with a gas mixture of 1000 ppm of CO and 4000 ppm of O₂ in the same range of temperatures. A gas mixture of 1000 ppm CO and 4000 ppm O₂, in absence of powders and electrodes, was also measured as the blank reference signal.

RESULTS AND DISCUSSION

Morphology of the thick films

Figures 1 (a) and (b) show the SEM micrographs of the Nb_2O_5 electrode before and after the emf measurements, respectively. The grain size is smaller than 100 nm. After several weeks of measurements at high temperatures, as high as 650°C , no appreciable modifications in grain size and morphology were observed.

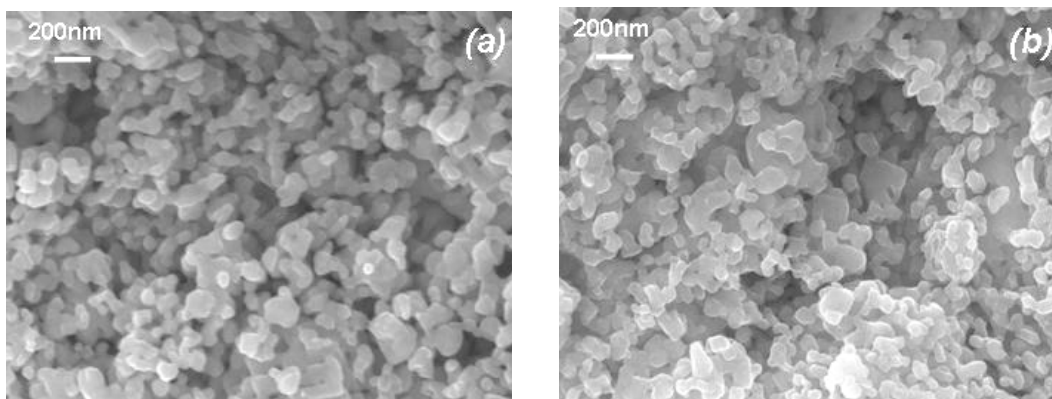
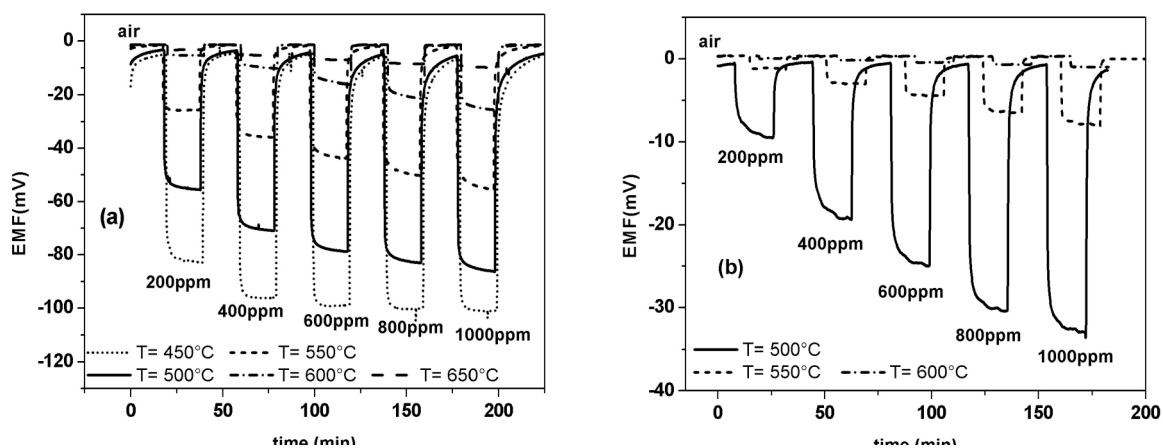


Figure 1. SEM micrographs the Nb_2O_5 sensing electrode before (a) and after (b) the emf measurements at high temperatures.

EMF sensing performance of the sensors

Figures 2 (a), (b), (c) and (d) show the emf response under different concentrations of CO in air at different temperatures of sensor (a), sensor (b), sensor (c), and sensor (d), respectively. With the exception of sensor (c), for all the sensors, the measured emf signal was in the negative direction at all the investigated temperatures. By increasing the temperature, the response upon switching from air to gas became more stable and faster, but the amplitude of the emf decreased. An inversion of the emf signal was observed for sensor (c) starting from 550°C . By comparing the emf responses of the four sensors, it can be noticed that the largest and more stable signal was obtained for sensors (a) and (d), which have $\text{Nb}_2\text{O}_5(\text{Au})$ as the sensing electrode.



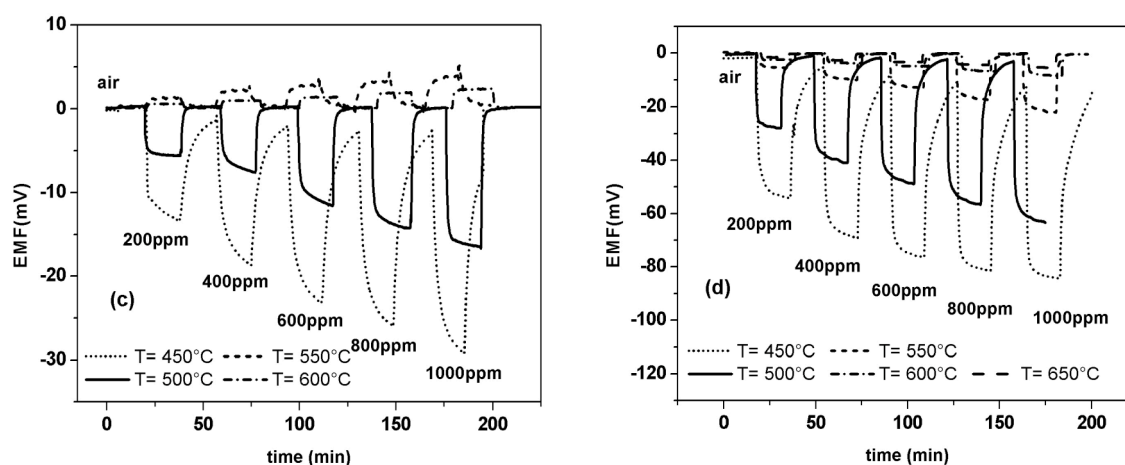


Figure 2. Emf response of (a) Pt/YSZ/(Au)Nb₂O₅ (sensor (a)), (b) Au/YSZ/(Pt)Nb₂O₅ (sensor (b)), (c) Pt/YSZ/(Pt)Nb₂O₅ (sensor (c)) and (d) Au/YSZ/(Au)Nb₂O₅ (sensor (d)) to different CO concentrations in air at different temperatures.

The emf response of the Pt/YSZ/Au reference sensor (with Pt connected on the negative pole) is shown in figure 3. It is important to stress that all the measurements on similar samples, reported in the literature, have been performed on pellet or tubular sensors using an air reference electrode (30, 31). For the first time in this work, emf results on planar Pt/YSZ/Au sensor, with both electrodes wholly exposed to the same atmosphere, are shown. At all the investigated temperatures, the emf signal was in the positive direction.

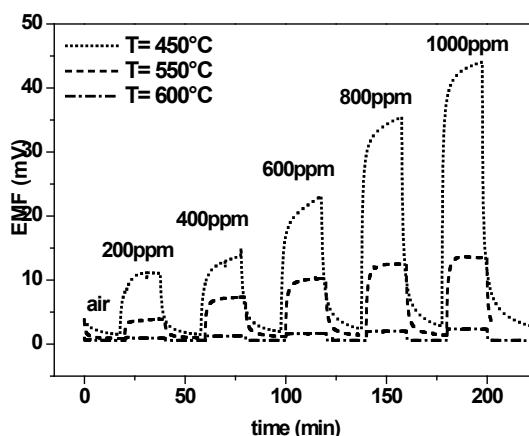
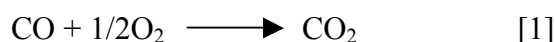


Figure 3. Emf response of the sensor (-)Pt/YSZ/Au(+) to different CO concentrations in air at different temperatures.

TPR analysis

Figure 4 (a) and (b) show the TPR results under a constant CO + O₂ flow of the different samples of our electrodes. These figures report only the CO concentration; the results about CO₂ and O₂ were neglected. However, it was checked that the production of CO₂ and the consumption of O₂ were proportional to the decreasing in CO concentration according to the reaction:



From figure 4 (a), it can be seen that no catalytic reactions occurred in the presence of Au-based electrodes. In fact, in the case of both Nb₂O₅(Au)/YSZ or Au/YSZ pieces, no oxidation of CO in CO₂ was observed. As shown in figure 4 (b), in the presence of Pt-based electrodes, a high catalytic activity was observed above 200°C. The two TPR curves showed different trends; above 500°C, the Pt/YSZ electrode became more catalytic for CO oxidation than the Nb₂O₅(Pt)/YSZ electrode, while at lower temperatures the opposite was observed.

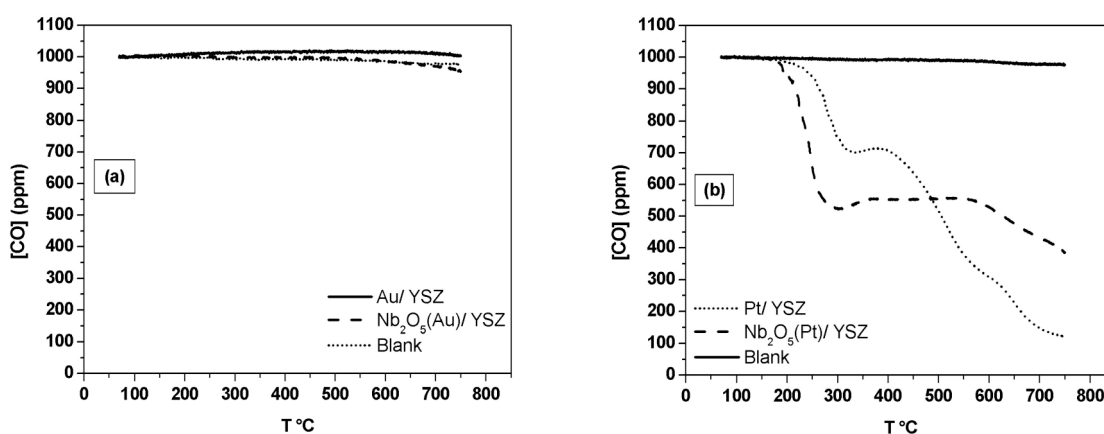


Figure 4. TPR analysis of (a) Au-based electrodes and (b) Pt-based electrodes in the temperature range 70-750°C.

Because of the different concentrations used, these measurements can be correlated with the emf response only in a qualitative way. In fact, the oxygen concentration used for the TPR analysis was 0.4 vol.%, while the oxygen concentration used for the electrochemical measurements was about 21 vol. %, similar to the O₂ percentage in the atmosphere.

Sensing mechanisms

The authors of this paper have already claimed that the Mixed Potential Theory cannot explain by itself the complex behavior of the electrochemical sensors with a semiconducting oxide electrode (8, 9, 13-15, 27-29). As mentioned before, in the case of planar sensors with n-type semiconducting oxides electrodes, it is difficult to distinguish between the Mixed Potential and the semiconducting behaviour. Thus, the use of Au and Pt metallic electrodes, with different catalytic properties, and the study of TPR measurements on different electrodes helped us in the explanation of the emf results. By correlating the catalytic measurements of the electrodes to the electrical response of the sensors, some findings on the sensing mechanism can be deduced.

With the exception of the sensor (*c*) at high temperatures (above 550°C), the response of all the investigated sensors was always in the negative direction, meaning that the CO oxidation reaction takes place at the Nb₂O₅ based electrode. Moreover, the emf response of the sensors with Nb₂O₅(Au) sensing electrode (i.e., sensors (*a*) and (*d*)) showed better performance in terms of signal amplitude and stability than that of sensors with Nb₂O₅(Pt) sensing electrode, such as sensor (*b*) and (*c*). Thus, the higher catalytic activity of Nb₂O₅(Pt) electrode decreases the electrical gas response of the sensors.

The (*a*), (*b*), and (*c*) sensors and the Au/YSZ/Pt reference sensor have at least one Pt/YSZ or Nb₂O₅(Pt)/YSZ interface and thus they have at least one catalytic electrode for the CO oxidation reaction. In the case of Au/YSZ/Pt sensor, in the absence of any semiconducting powder, the sensing response can be clearly explained by the Mixed Potential Theory. By comparing the results of this reference sensor to the (*a*), (*b*), (*c*) sensor responses, some remarks can be emphasized.

The emf of the sensor (*a*) (Pt/YSZ/(Au)Nb₂O₅) and of the reference sensor (connecting Pt electrode to the negative pole) went in opposite directions. The response of sensor (*a*) was always in the negative direction in accordance with YSZ based sensors with different n-type semiconducting oxide electrodes under CO exposure (15-17, 28). Therefore, it can be concluded that the semiconducting mechanism is prevailing for this sensor. CO gas reacts with the adsorbed oxygen ions at the oxide surface releasing CO₂.

For the sensor (*b*) (Au/YSZ/(Pt)Nb₂O₅), it was difficult to distinguish between the two proposed mechanisms. The negative emf signals are in accordance both with the semiconducting mechanism and with the Mixed Potential Theory. In fact, comparing the responses of sensor (*b*) with the Au/YSZ/Pt reference sensor (connecting Au to the negative pole in both sensors), they were in the same direction. In both cases, the electrochemical oxidation reaction of CO prevailed at the more catalytic electrode.

For the sensor (*c*), up to 550 °C, the oxidation reaction occurred on the Nb₂O₅(Pt) electrode which has the highest catalytic activity, according to TPR results. Above 550°C, the inversion in the direction of the emf response can be correlated to the crossing of the TPR curves. At highest temperatures, the Pt/YSZ interface seems to become more catalytic than the Nb₂O₅(Pt)/YSZ electrode, and thus this became the sensing electrode at which the CO oxidation reaction takes place. This inversion in the emf signal cannot be explained with both the Mixed Potential and semiconducting behaviors. In this case, the catalytic activities of the electrodes seem to be the most important parameters to take into account.

Finally, the sensor (*d*), with two Au-based electrodes, showed a high emf response to CO, in spite of the very low catalytic activity of both electrodes. The negative emf values are consistent with the reaction of a reducing gas with the oxygen ions adsorbed on the

surface of a n-type semiconductor. From TPR analysis, only a slightly decrease in CO concentration occurred at high temperatures. This may be due to the very small amount of Nb₂O₅ powder (few µg) present on the Nb₂O₅(Au)/YSZ electrode, introduced in the quartz reactor of the TPR equipment. In that case, the CO gas reacts with the adsorbed oxygen ions on the semiconducting powder releasing very small amount of CO₂. Therefore, the response of this sensor can be explained mainly by the semiconducting mechanism.

CONCLUSIONS

In this paper, it has been shown that planar YSZ-based electrochemical gas sensors, using nanosized Nb₂O₅ semiconducting powder as sensing electrode, are promising for measuring CO gas in combustion emissions.

From the comparison between electrical and catalytic measurements, we confirmed the idea that the Mixed Potential Theory was unable to explain all the phenomena occurring at the electrodes. In fact, in the case of an n-type semiconducting oxide based sensors, because the emf response is in the same direction according to both theories, it has been possible to distinguish between the mixed potential and the semiconducting behaviour by using the TPR analysis. The different metallic paste (Pt or Au) used for sensor fabrication affected the catalytic properties of the electrodes, and thus the response and the sensing mechanism of the sensors. In the presence of an Nb₂O₅(Au) electrode, the semiconducting mechanism seemed to prevail on the Mixed Potential Theory. At Nb₂O₅(Pt) electrodes the situation is still unclear. Both mechanisms, semiconducting and Mixed Potential can be possible. Further studies on the electro-catalytic activity of the electrodes are needed to clarify this point.

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