Bull. Mater. Sci., Vol. 25, No. 6, November 2002, pp. 451–453. © Indian Academy of Sciences.

Study of YSZ-based electrochemical sensors with oxide electrodes for high temperature applications

A DUTTA, N KAABBUATHONG, M L GRILLI, E DI BARTOLOMEO* and E TRAVERSA

Department of Chemical Science and Technology, University of Rome, "Tor Vergata", Via della Ricerca Scientifica, 00133 Rome, Italy

Abstract. Potentiometric sensors based on yttria stabilized zirconia (YSZ) with WO_3 as sensing electrode were fabricated using either Pt or Au electrodes. The sensors were studied in the temperature range 550–700°C in the presence of different concentrations (300–1000 ppm) of NO_2 and CO in air. The response to NO_2 was very stable with fast response time (20–40 s). The best sensitivity (18·8 mV/decade) using Pt electrodes was observed at 600°C. At the same temperature a cross-sensitivity (– 15 mV/decade) to CO gas was also noticed. The response to CO was decreased (– 4 mV/decade) using Au electrode. The role played by WO_3 on the sensing electrode was discussed.

Keywords. Gas sensors; YSZ; oxide electrode.

1. Introduction

The environmental concerns have forced the scientists to develop suitable and reliable sensors to detect pollutants such as NO_x, CO, HCs etc. Vehicles industries are among the prominent sources of pollution and are encountering norms for pollution control. Therefore, sensors operating at high temperatures (600–700°C) and in the harsh environment are urgently needed to monitor the level of pollution in the exhaust gases. Solid state electrochemical sensors seem to be the most suitable in such environments. Several reports are available on solid electrolytes based sensors combined with metal (Pt, Au etc) and oxide electrodes for NO_x (Miura and Yamazoe 2000; Grilli *et al* 2001), CO and HCs (Brosha *et al* 2000; Hibino *et al* 2001) detection. Recently, Menil *et al* (2000) have reviewed the actual trends of these kinds of sensors. The major issues concerning the selectivity and the long term stability are yet to be overcome for sensors for high temperature applications. This fact drives scientists to search for new materials, to improve the device fabrication technique and to go through the sensing mechanism.

In this work we report a study on yttria stabilized zirconia (YSZ) based sensors with WO_3 as auxiliary or sensing electrode: (Au)Pt/YSZ/Pt(Au)/WO_3. The sensors were studied in the temperature range between 550 and 700°C in the presence of NO_2 and CO in air (300–1000 ppm). The response was found to be stable, fast and reproducible. Using Au electrodes instead of Pt the sensors showed a better NO_2 selectivity with respect to CO. Amperometric measurements were also performed to better understand their sensing mechanism.

2. Experimental

YSZ (8 mol.% of Y_2O_3) pellets of 10 mm in diameter were used for sensor fabrication. Pt or Au inks were used as electrodes on both sides of the pellets and thin gold wires were connected for current collection. The firing temperatures of Pt and Au were 800°C for 10 min and 850°C for 10 min, respectively. Commercial WO_3 powders (99·995% purity) were mixed with a screen-printing oil and the slurry thus obtained was painted on one electrode and fired at 750°C for 3 h. Sensing experiments were carried out in a conventional gas-flow apparatus equipped with a controlled heating facility. The sensor environment was alternatively exposed to air and NO_2 or CO (300–1000 ppm in air) at the total flow rate of 100 ml/min. Electromotive force (EMF) measurements were performed between the two electrodes of the sensor using a digital electrometer. The electrode with the WO_3 coating was always kept at the positive terminal and both the electrodes were exposed to the same gas environment. Amperometric measurements were performed by applying an increasing d.c. voltage (from – 0·6 V to + 0·4 V) and measuring the current output.

3. Results and discussion

Figure 1 shows the typical NO_2 response of Pt/YSZ/Pt/WO_3 sensor at 600°C. EMF changed quickly upon switching from air to different NO_2 concentrations in air.

*Author for correspondence

At 600°C steady-state values were observed at all measured gas concentrations. The response and recovery times were 20–40 s and 2 min, respectively. Figure 2 shows the linear correlation between the EMF saturation values and the logarithm of gas concentration at different operating temperatures. By increasing the temperature, the EMF response decreased at all different gas concentrations. The largest sensitivity (18·8 mV/decade) was found at 600°C. At temperatures below 550°C, the sensing responses were unstable. For Au/YSZ/Au/WO_3 sensors below 650°C the NO_2 response was very slow though the response magnitude was large. Fast and stable responses were observed at 650°C with a sensitivity of 17·3 mV/decade.

In the presence of various CO concentrations the EMF response of Pt/YSZ/Pt/WO_3 sensors increased in the negative direction, unlike NO_2 response (always keeping WO_3 side at the positive terminal). At 600°C the EMF values at any given concentration were much smaller than those measured in the presence of NO_2. However, the sensitivity at 600°C was – 15 mV/decade, comparable to NO_2 sensitivity at the same temperature. An attempt to decrease the CO cross sensitivity was successful when Pt electrodes were replaced with Au. At 650°C the CO sensitivity of Au/YSZ/Au/WO_3 sensors dropped from – 7 to – 4·0 mV/decade, while at the same temperature the NO_2 sensitivity was 17·3 mV/decade. Figure 3 shows the CO sensitivity curves of Pt/YSZ/Pt/WO_3 and Au/YSZ/Au/WO_3 sensors at 600 and 650°C.

Figure 4 shows the amperometric measurements of Au/YSZ/Au/WO_3 sensors upon exposure to air and 1000 ppm of NO_2 and CO in air. A typical non-linear current–voltage characteristic was observed at all different atmospheres. At a given voltage, the current decreased in the presence of NO_2 and increased in the presence of CO.

The electrochemical reactions for NO_2 and CO occurring at the three-phase boundary between solid electrolyte, electrode and gas, can be expressed as follows (Miura and Yamazoe 2000):

$$NO_2 + 2e \Leftrightarrow O^{2-} + NO \ (WO_3 \text{ side})$$
$$O^{2-} \Leftrightarrow \tfrac{1}{2} O_2 + 2e \ (\text{metal electrode side}), \quad (1)$$

$$CO + O^{2-} \Leftrightarrow CO_2 + 2e \ (WO_3 \text{ side})$$
$$\tfrac{1}{2} O_2 + 2e \Leftrightarrow 2O^{2-} \ (\text{metal electrode side}). \quad (2)$$

The number of oxygen ions accumulated at the WO_3 (Pt, Au)/YSZ and YSZ/Pt(Au) interfaces is different and can be strongly influenced by the electrode material, its surface morphology and electrocatalytic activity. The porous layer of WO_3 enhances the adsorption of gas molecules and hence highly promotes reactions (1) and

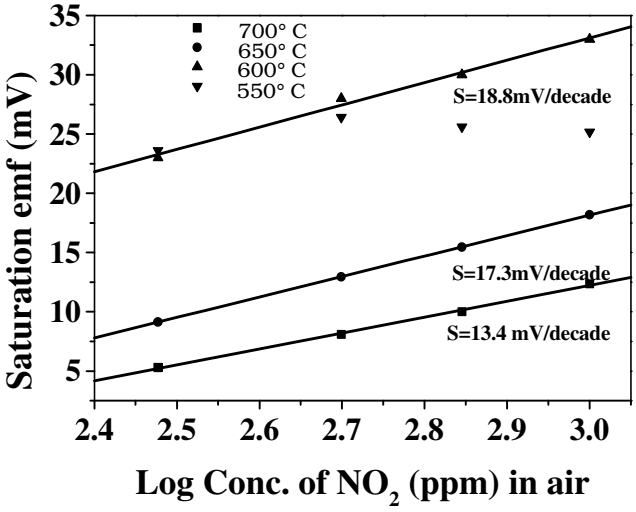

Figure 2. EMF of Pt/YSZ/Pt/WO_3 sensor vs log of NO_2 concentration at different temperatures.

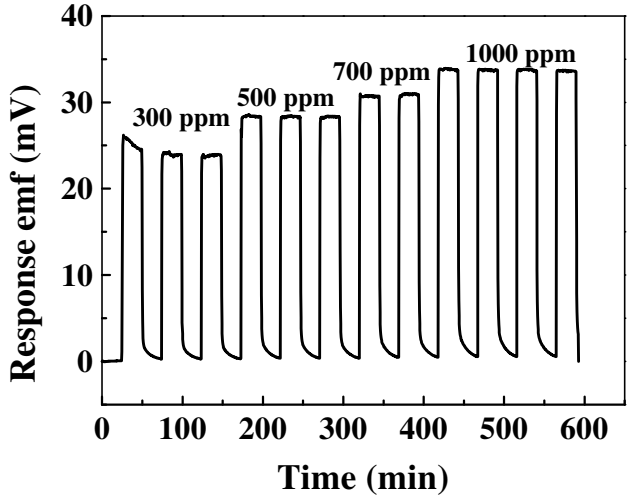

Figure 1. EMF response of Pt/YSZ/Pt/WO_3 sensor at 600°C in cycling air and 100 ppm of NO_2 in air.

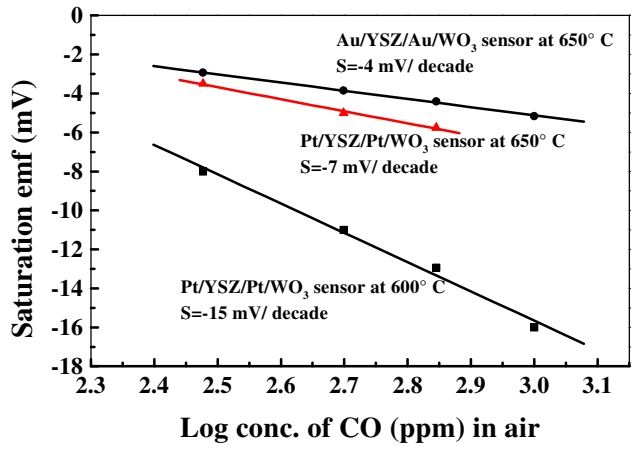

Figure 3. EMF of Pt/YSZ/Pt/WO_3 and Au/YSZ/Au/WO_3 sensors vs log of NO_2 concentration at 600 and 650°C.

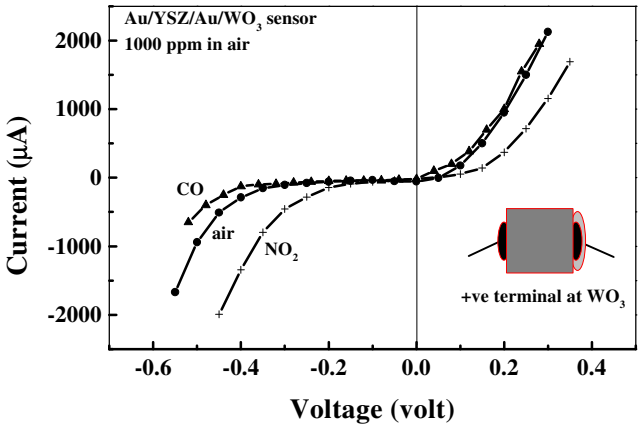

Figure 4. Amperometric measurements characteristics of Au/YSZ/Au/WO_3 sensors upon exposure to air and 1000 ppm of NO_2 and CO in air at 650°C.

(2) upon exposure of NO_2 and CO, respectively. Upon applied potential, the decrease in the current observed upon NO_2 exposure can be related to the increase in the resistance and reactance at the electrolyte/oxide electrode interface due to an increase in the number of oxygen ions accumulated at the WO_3(Pt, Au)/YSZ interface. Under positive bias voltage the current flow is very small. For NO_2 exposure, under negative bias voltage, the oxygen ions move from higher to lower accumulation region (metal electrode side) and hence the current flow increases. The opposite behaviour is observed upon CO exposure. Since the CO sensitivity of sensors with Au electrodes is much lower than the NO_2 sensitivity, a small difference in the current values was observed with respect to the amperometric measurements in air. The amperometric measurements clearly showed that the sensing reaction took place at the WO_3 electrode.

4. Conclusions

YSZ-based electrochemical sensors with a WO_3 auxiliary oxide electrode and Pt or Au electrodes were found to show stable and fast response in the temperature range 600–700°C in the presence of NO_2. The high operating temperatures make these sensors suitable for automotive applications. The use of Au electrodes instead of Pt significantly lowers the response to CO, improving the selectivity of the sensors. The role of WO_3 as auxiliary electrode was established as crucial in the sensing mechanism of gases.

Acknowledgements

One of the authors (AD) gratefully acknowledges the "Programme for Training and Research in Italian Laboratories, ICTP, Trieste", Financial support by the National Research Council (CNR) under the frame of the Project MSTA II and the Ministry of University and Scientific and Technological Research of Italy (MURST).

References

Brosha E L, Mukundan R, Brown D R, Garzon F H, Visser J H, Zanini M, Zhou Z and Logothetis E M 2000 *Sensors and Actuators* **B69** 171

Grilli M L, Di Bartolomeo E and Traversa E 2001 *J. Electrochem. Soc*. **148** H98

Hibino T, Hashimoto A, Kakimoto S and Sano M 2001 *J. Electrochem. Soc*. **148** H1

Ménil F, Coillard V and Lucat C 2000 *Sensors and Actuators* **B67** 1

Miura N and Yamazoe N 2000 in *Sensors update* (eds) H Baltes, W Göpel and J Hesse (Weinheim, Germany: Wiley-VCH) **Vol. 6**, pp. 191–210