Journal of the European Ceramic Society **19** (1999) 887–891

PII: S0955-2219(98)00338-0
0955-2219/99/$ - see front matter

Detection Mechanism of TiO_2-based Ceramic H_2 Sensors

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Abstract

This work reports an H_2-sensing mechanism of TiO_2 thick-films, deposited on alumina substrates by screen-printing. The role of the catalytic activity of the electrode material on the sensor response was tested with platinum and gold electrodes. An impedance analyser (20 Hz–1 MHz) was used to monitor the film impedance before and after exposure to H_2. Continuous monitoring of the film resistance was performed with a simple dc measurement. The film resistance was measured as a function of temperature (500–650°C), time, and gas phase composition (air and 0–10% H_2 in a N_2-based gas stream). The equilibrium gas phase Po_2 (monitored with a zirconia-based oxygen sensor) was also used to identify the hydrogen detection mechanism of the films. © 1999 Elsevier Science Limited. All rights reserved

Keywords: electrical properties, TiO_2, sensors.

1 Introduction

Semiconducting ceramic oxide gas sensors have been used to warn of explosive gases since the 1960s, but more recently other applications in which ceramics may be employed as sensor materials have been considered, including detection of air pollutants and improving fuel efficiency in industrial combustion processes. The reducing gas depletes the coverage of adsorbed oxygen ions on the sensor surface and supplies electrons to the conduction band, leading to a fall in resistance.[1] A current goal in sensor research is to improve the sensor selectivity by eliminating similar responses from interfering gases.

It has been found that the sensor selectivity and sensitivity may be altered by the addition of second oxide phases or elemental metals.[2] One such study has shown the effects of a second insulating phase on the sensing properties of anatase (TiO_2). Although TiO_2 is a well-known oxygen sensor,[3,4] it has more recently been used to detect and measure both CO and H_2.[5,6] These gases are the main constituents of producer gas, a reactant gas in a number of industrial processes, and are also by-products of inefficient hydrocarbon combustion; their detection is, therefore, important both in order to warn of potentially explosive gas leaks and to indicate the efficiency of combustion.

It has been reported that the response time to H_2 exposure is much slower than to CO exposure, and a bulk-controlled mechanism for H_2 compared with a surface-controlled CO detection was proposed to explain this. However, the mechanism of H_2 detection has never been elucidated, despite the fact that many phases show changed electrical responses in the presence of H_2 due to its reactivity. One theory assumes dissociation of H_2 on the surface of TiO_2, yielding H atoms which diffuse into the bulk.

In this case, the H atom could then be ionised producing an interstitial proton and a conduction electron.[2] The oxygen partial pressure also affects the resistance of the sensor materials, but this factor is often overlooked in the sensing of reducing gases. TiO_2 is very sensitive to oxygen, and this effect cannot be ignored, especially when catalytically active metals like platinum are used as electrode materials.

Here, we present a detailed study of the effects of H_2 exposure on the electrical behaviour of screen-printed thick films of TiO_2 (anatase), paying special attention to monitor the oxygen partial pressure close to the film surface. Isothermal experiments (in the range 500–650°C) were used to investigate the a.c. and d.c. responses of the films as a function of H_2 concentration and oxygen partial pressure.

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2 Sensor Fabrication

Thick film sensors of the anatase polymorph of TiO_2 with a diameter of 14 mm were prepared on Al_2O_3 substrates. Pastes suitable for thick film screen printing were made by blending analar-grade powders of the test materials with 'polikim' solution. For substrate fabrication, pellets of a fine mixture of Al_2O_3 and a small percentage of TiO_2 were fired at 1400°C for 1 h (TiO_2 was added to Al_2O_3 as a sintering additive). The wet films were dried, fired at 800°C for 1 h then cooled to room temperature at $5°C\,min^{-1}$. Two strips of conductive Pt paste separated by approximately 4 mm were painted on the sensor surface in order to provide electrical contacts. Conductive gold paint was also used as an alternative to Pt electrode contacts. The sensors were then fired for a short time at 800°C to remove the organic matter from the paste. The anatase modification of TiO_2 in the sensor surface was confirmed by powder X-ray diffraction.

3 Measuring System

A schematic diagram of the test system used for measuring the resistance of the sensor and oxygen partial pressure near the sensor surface is shown in Fig. 1. The sensor was attached to a pressure mount in a sealed vertical tube furnace, such that the sensor surface faced away from the direction of the gas stream. The gas atmosphere was supplied to the furnace with a Bronkhurst (Hi-tec) gas flow meter set to supply a constant gas flow rate of $50\,ml\,min^{-1}$ from N_2 and 10% H_2 in N_2 gas lines. The H_2 concentration in an N_2 flow could be varied between 0 and 10%, and a line of compressed air could, thus, be supplied to the furnace. The gas lines were attached through the top metal endcap of the furnace and an outlet to a bubbler was provided at the bottom; the bubbler acted as a lock to the outside atmosphere, preventing oxygen diffusion into the furnace chamber. An yttria stabilised zirconia (YSZ) oxygen sensor was inserted through the bottom endcap of the furnace tube so that its tip was in close proximity to the surface of the sensor. The YSZ sensor electrodes were also made of platinum paste.

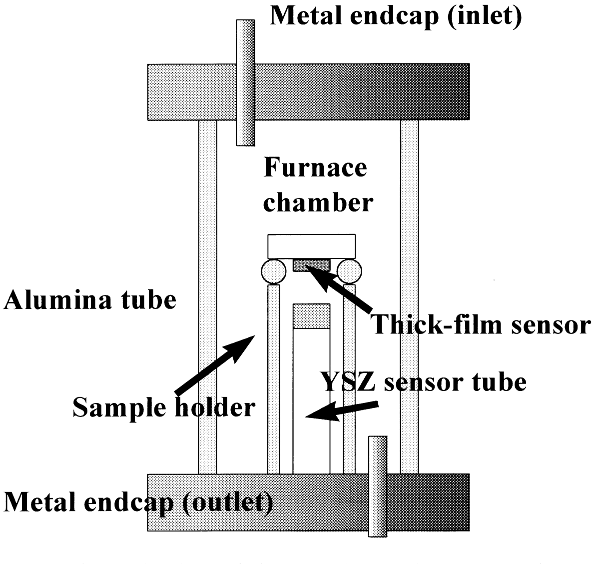

Fig. 1. Schematic view of the experimental set-up used to test the anatase thick-film sensors.

For electrical characterisation, the a.c. response of the test sensor was measured with a Hewlett Packard 4284A a.c. impedance analyser working in the frequency range 20 Hz–1 MHz. d.c. resistance and the oxygen sensor electromotive force (emf) were measured with two separate Fluke 45 multimeters. Both multimeters were computer controlled so that the oxygen partial pressure (Po_2) and thick-film resistance (R) responses were measured simultaneously. The electrical apparatus was connected to the sensor by Pt wires attached to the Pt or Au electrode contacts on the sensor surface by a pressure contact.

4 Results and Discussion

Particular attention was paid to ensuring that the same conditions were met before, during and between test runs in order to repeat results. Before the introduction of hydrogen, the furnace was flushed first with air, to regenerate the sample bulk and surface, then nitrogen for approximately 1 h to ensure that the furnace chamber was as oxygen-free as possible. Impedance spectra were recorded before and after each cycle, i.e. in air and then in 10% H_2 + 90% N_2. Figure 2(a) and (b) show typical impedance responses in air and hydrogen, respectively. In the first case (air), the cell impedance was close to the upper limit of the impedance analyser operating range. In the second case (10% H_2 + 90% N_2), the cell impedance was much smaller. However, in neither case was there evidence for the possible deconvolution of the impedance spectra into different contributions. Since little information was garnered by a.c. methods, other than the sample resistance, the complete cycle was monitored by simultaneous d.c. resistance and Po_2 measurements so that variations in Po_2 on changing gas atmosphere could be correlated directly with the sensor resistance.

Figure 3 shows the typical resistance of a TiO_2 sensor at 650°C and corresponding YSZ sensor emf response when such a gas-cycle (air$\rightarrow N_2 \rightarrow N_2 + H_2$) is employed: as we would expect, in air the oxygen sensor emf is close to zero and the TiO_2

sensor resistance is very large (~21 MΩ). When the air is cut off, and N_2 is introduced, the responses stabilise after approximately 45 min, reaching ~11 MΩ and 154 mV for the *R* and emf readings, respectively. On introducing 10% H_2 in the N_2 flow, there is a sudden increase in the oxygen-sensor emf to ~1 V, and a rapid decrease in the sensor resistance (reaching ~1·4 kΩ). Both curves change in an almost reciprocal way, thus suggesting a strong correlation between the behaviour of both sensors.

Data shown in Fig. 3 can also be treated in a different manner, in order to show the relationship between the titania-sensor resistance and the gas-phase equilibrium oxygen partial pressure, measured by the YSZ sensor. This can be seen clearly in Fig. 4 where one observes that, overall, the titania sensor resistance changed by about 4 orders of magnitude whereas the oxygen partial pressure changed by 24 orders of magnitude, giving a gradient of about 1/6 in the log(*R*) versus log(Po_2) plot.

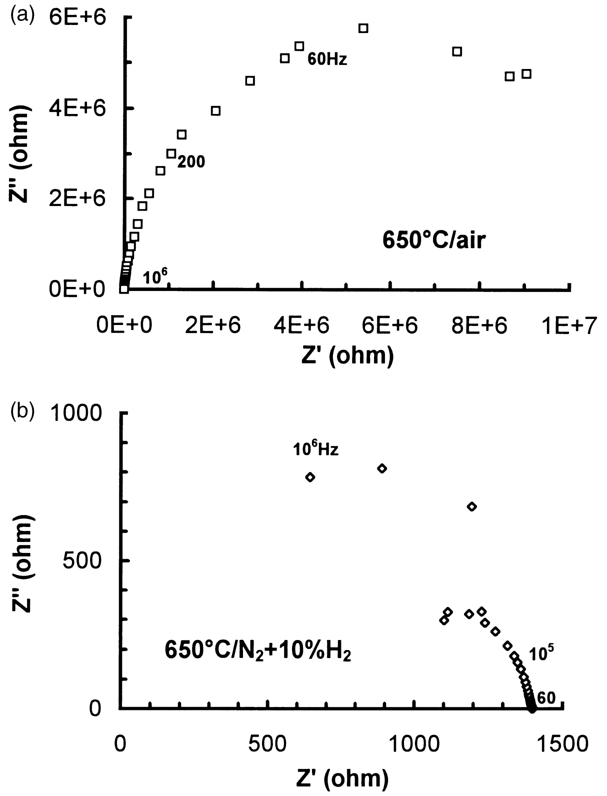

Fig. 2. Impedance spectra of a titania thick-film sensor at 650°C: (a) in air; (b) after long exposure to a 10% H_2 + 90% N_2 gas mixture.

The positive slope of this curve would suggest that n-type conductivity is dominant and is, thus, a reasonable hypothesis to explain the Po_2 dependence of the thick-film sensor resistance. This means that the basic detection mechanism involves the formation of fully ionised oxygen vacancies when the sensor is exposed to reducing conditions, as described by:

$$O_o^x \Longleftrightarrow \frac{1}{2}O_2 + V_0^{\bullet\bullet} + 2e' \qquad (1)$$

with the Kroger–Vink notation. The thermodynamic equilibrium constant

$$K = n^2.Po_2^{1/2}.\left[V_0^{\bullet\bullet}\right] \qquad (2)$$

can be combined with a simplified electroneutrality condition involving dominant defects generated by eqn (1):

$$n = 2.\left[V_0^{\bullet\bullet}\right]; \qquad (3)$$

this gives $n \propto Po_2^{-1/6}$ and $R \propto Po_2^{1/6}$.

The gradient of + 1/6 seen in Fig. 4 can, thus, be simply explained by a classical defect-chemistry model, where bulk equilibrium between the sensor film and the surrounding atmosphere is assumed. This explanation of the performance of the 'hydrogen sensor' is coherent with previous work performed in the early 80s on titania-based lambda sensors to monitor the air/fuel ratio in cars.[7]

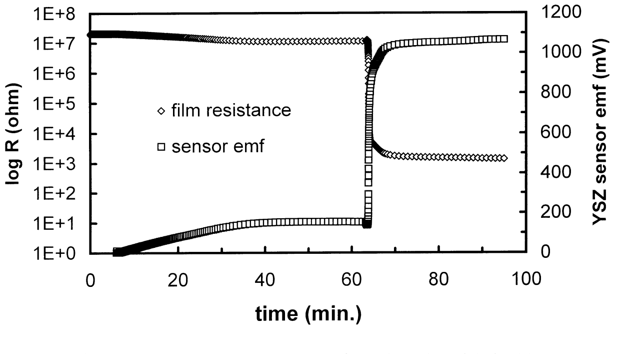

Fig. 3. Time response at 650°C of a titania thick-film sensor (*R*) with Pt electrodes, and a YSZ oxygen sensor (emf) when the furnace atmosphere is flushed with air, then N_2 and lastly 10% H_2 + 90% N_2.

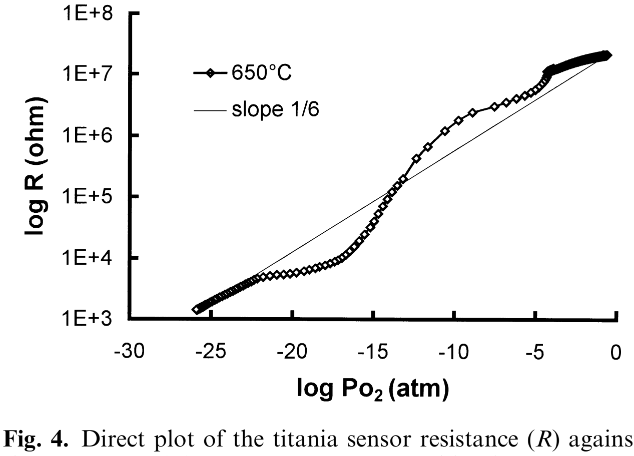

Fig. 4. Direct plot of the titania sensor resistance (*R*) against the oxygen partial pressure (Po_2) measured by the YSZ sensor (data already shown in Fig. 3).

The main deviation from the 1/6 slope shown in Fig. 4 occurs for intermediate values of Po_2, and two factors might explain this deviation. The first is related to the extremely steep change in Po_2 (by several orders of magnitude) when the furnace is flushed with a gas mixture containing hydrogen. This occurs when the hydrogen/oxygen ratio reaches the value needed to produce water vapour and corresponds to an effect similar to a sudden shift in pH during a typical acid-basic chemical titration. The second reason for the deviation from ideal behaviour in Fig. 4 is a similarly documented saturation effect, observed with YSZ sensors in this range of working conditions, where the buffer behaviour of the gas-phase is quite small.[8] The behaviour of the sensor is slightly improved by additions of CO_2 (or CO), H_20 (or H_2), etc.

Logothetis[7] stated that platinum greatly enhances the catalytic activity of titania. However, the role of the catalytic activity of the metallic electrodes on the establishment of equilibrium between the sensor material and gas-phase deserves some attention, and alternative electrodes were thus tested. Figure 5 shows the results obtained with a titania thick-film sensor with gold instead of platinum electrodes. Again, the resistance of the titania sensor and the YSZ sensor emf respond to the gas phase composition in a closely related manner. These experiments thus show that, at temperatures close to 600°C, the equilibration of titania films with the surrounding Po_2 is already fast enough to ensure that bulk effects dominate over surface effects, irrespective of the nature of the electrodes.

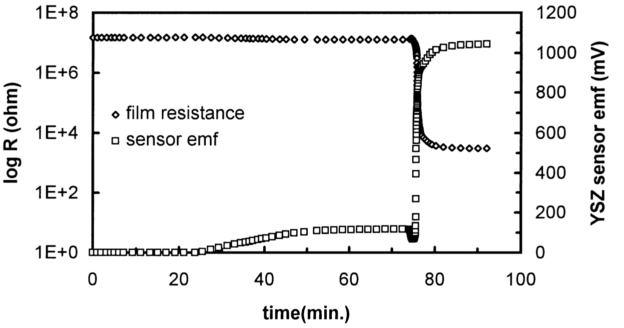

Fig. 5. Time response at 650°C of the titania thick-film sensor (*R*) with Au electrodes, and a YSZ oxygen sensor (emf) when the furnace atmosphere is flushed with air, then N_2 and lastly 10% H_2 + 90% N_2.

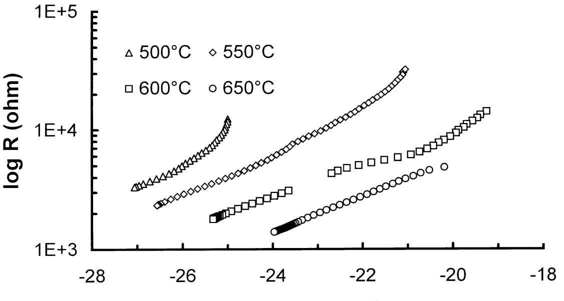

Fig. 6. Effect of temperature on the response of a titania thick-film sensor (*R*) with Pt electrodes. The YSZ oxygen sensor was used to monitor the furnace Po_2.

Figure 6 shows a plot of log *R* versus log Po_2 at four temperatures. Only highly reducing conditions are shown in order to avoid the range where the sensor responses deviate from each other for kinetic reasons. These results were again obtained with the titania film with Pt electrodes, and the YSZ sensor was used to measure the values of Po_2. The curves once more show that the 1/6 gradient is preserved, and no change in detection mechanism is expected.

Recyclability of the sensor response between air and reducing conditions was not fully attainable; this is a phenomenon which will receive further attention in future work.

5 Conclusions

The change in resistance of the TiO_2-based sensor on exposure to hydrogen is highly dependent on the oxygen partial pressure. It is probable that, rather than detecting H_2 directly, the basic detection mechanism involves the formation of fully ionised oxygen vacancies. Evidence for this is provided from simultaneous oxygen partial pressure and sensor resistance measurements: log Po_2 versus log *R* plots have a gradient of 1/6 over isothermal temperatures in the range 500–650°C, consistent with n-type conductivity.

Experiments with both Pt and Au electrodes show that their catalytic activity on the equilibration process is not significant, and that bulk effects dominate over surface effects, irrespective of the nature of the electrodes.

Acknowledgements

Financial support from FCT (Program PRAXIS) is greatly appreciated.

References

1. Windiscmann, H. and Mark, P., A model for the operation of a thin film SnO_2 conductance—modulation of carbon dioxide sensor. *J. Electrochem. Soc.*, 1979, **126**, 627–633.
2. Birkefeld, L. D., Azad, A. M. and Akbar, S. A., Carbon monoxide and hydrogen detection by anatase modification of titanium dioxide. *J. Am. Ceram. Soc.*, 1992, **75**(11), 2964–2968.

3. Tien, T. Y., Stadler, H. L., Gibbons, E. F. and Zacmanadis, P. J., TiO_2 as an air-to-fuel ratio sensor for automobile exhausts. *Am. Ceram. Soc. Bull.*, 1975, **54**(2), 280–285.
4. Logothesis, E. M., Metal oxide sensors for automobile applications. *J. Solid State Chem.*, 1975, **12**, 331.
5. Azad, A. -M., Akbar, S. and Younkman, L., Ceramic sensors for carbon monoxide and hydrogen. *The Electrochemical Society Interface*, 1994, **3**(4) (Winter), 31–34.
6. Akbar, S. A. and Younkman, L. B., Sensing mechanism of a carbon monoxide sensor based on anatase titania. *J. Electrochem. Soc.*, 1997, **144**, 1750–1753.
7. Logothesis, E. M., Resistive-type exhaust gas sensors. *Ceramic Engineering and Science Proceedings*, 1981, **1**, 281–301.
8. Marques, F. M. B. and Wirtz, G. P., Oxygen fugacity control in nonflowing atmospheres: I, experimental observations in CO/CO_2 and O_2/N_2 mixtures. *J. Am. Ceram. Soc.*, 1992, **75**(2), 369–374.