Improvements to Zirconia Thick-Film Oxygen Sensors

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Abstract

Thick-film zirconia gas sensors are normally screen-printed onto a planar substrate. A sandwich of electrode-electrolyte-electrode is fired at a temperature sufficient to instigate sintering of the zirconia electrolyte. The resulting porous zirconia film acts as both the electrolyte and as the diffusion barrier through which oxygen diffuses. The high sintering temperature results in de-activation of the electrodes due to grain growth of the platinum metal particles in the electrodes. Deactivated electrodes, combined with insufficiently low through-porosity, necessitate high sensor operating temperatures in order to support sufficient currents to drive the sensor into the diffusion-limited region. Power input rises with increasing operating temperature but also operating life is expected to be reduced. It is shown that the use of cobalt oxide as a sintering aid allows reduction of the sensor operating temperature by 100-200 °C with clear benefits. Furthermore, an interesting and new technique is presented for the investigation of the influence of dopants and of the through-porosity of ionically-conducting materials.

1. Introduction

Oxygen gas sensors have many applications including, and in particular, the monitoring and control of combustion processes. The incorporation of oxygen sensors in the latter systems can enable the air-to-fuel ratio to be maintained at an optimum value with respect to both efficiency and emissions. Domestic systems are cost-sensitive and require low-cost sensors. Screen-printed thick-film sensors [1] do offer the prospect of low cost as they can be produced in substantial numbers per substrate [2]. The high temperature necessary for sintering the zirconia results in deactivation of the electrodes due to grain growth of the platinum metal particles in the electrodes. Deactivated electrodes, combined with insufficiently low through-porosity, necessitate high sensor operating temperatures in order to support sufficient currents to drive the sensor into the diffusion-limited region. Power input rises with increasing operating temperature but also operating life is expected to be reduced. It is shown that the use of cobalt oxide as a sintering promoter reduces the through-porosity of the zirconia for given firing conditions; this allows substantial decrease of the sensor operating temperature without adversely affecting electrochemical performance.
Various studies have shown the importance of matching of thermal expansion coefficient (CTE) of thick-film and substrate. Alumina substrates, which are widely used in the electronics industry, have a CTE of $\sim 7 \times 10^{-6} \, ^\circ \text{C}^{-1}$ while zirconia displays a value of 10-11 $\times 10^{-6} \, ^\circ \text{C}^{-1}$. Hence, upon cooling from the sintering temperature of 1300-1400 °C the zirconia film is prone to crack [1-3]. In this work a substrate was used consisting of a mix of magnesia (MgO) and the spinel, MgAl$_2$O$_4$. By choosing an appropriate mix proportion the CTE can be selected between 9-14 $\times 10^{-6} \, ^\circ \text{C}^{-1}$.

2. Experimental

2.1 General

All preparative work was done under clean conditions in a Class 100 enclosure. Substrates of MgO-MgAl$_2$O$_4$ with a CTE to match zirconia, manufactured and supplied by Advanced Ceramics of Stafford, UK, were used throughout.

2.2 Printing, Doping and Firing of Films

A DEK 1202 screen printer was used for all printing operations. Three types of samples were prepared:

1. A platinum electrode was printed and dried then over-printed with a zirconia electrolyte film and dried.

2. As above then overprinted with a second electrode and dried.

3. A zirconia electrolyte film only was printed and dried with no platinum electrodes.

These samples were then either

A. fired without doping or

B. doped with cobalt (nitrate) and then fired (the cobalt nitrate decomposed to the oxide during the firing process).

In order to dope the films a solution of cobalt nitrate hexahydrate in ethanol (50:50 by weight) was prepared (reagents from Sigma- Aldrich, Analytical Reagent grade) which was then applied to the printed layer with a brush and dried prior to firing to provide a level of cobalt doping in the zirconia of approximately 5 cation %. Films were fired in air using a muffle furnace with a maximum operating temperature of 1600 °C.

2.3 Characterisation of Films

Electrodes of the Type 2 films were electrically connected to a voltage supply and the current flowing in the circuit measured. The sensor was operated in a furnace in a mixture of air and nitrogen, using the experimental arrangement described previously [4], gas flow rates being controlled by mass-flow valves. Substrates were scribed on the reverse side to the film, snapped and the fracture edges of Types 1 and 3 films examined using a scanning electron microscope (Cambridge Instruments 240 Stereoscan operated at 30kV).

3. Results and Discussion

3.1 Micrographs

Types 3A, 3B 1A and 1B zirconia films fired at 1000°C showed no significant differences as this was below the temperature at which significant sintering occurred. The zirconia thick-
film (Fig. 1) shows individual particles which remain essentially separate (unsintered) after firing at 1000°C.

Fig. 1 Cross-section of thick-film (∆1) on a substrate (∆2). The thick-film is zirconia doped with cobalt and the sample was fired at 1000 °C for 10 minutes. A similar micrograph (not shown) without cobalt-doping, fired at the same temperature, indicated no significant difference to this.

Figures 2 and 3 show the structure of the zirconia thick films fired at 1300°C without and with cobalt doping respectively. It can be seen that sintering (joining together at the contact points of the particles, shrinking of small particles, grain growth of larger particles and reduction of porosity) had taken place in both cases but that this had occurred to a greater extent where cobalt was present. The zirconia films in Type 2 and 3 samples showed no difference in appearance indicating that the interposition of a platinum thick-film between the substrate and the zirconia did not modify the sintering behaviour of the ceramic film. The micrographs confirm, as has been reported elsewhere [5], though not with respect to thick films, that cobalt acts as a sintering promoter for zirconia.

3.2 Current-voltage characteristics

As the voltage applied to an amperometric oxygen sensor (positive to front electrode, negative to electrode in contact with the substrate) in an oxygen-containing gas is increased from zero, the current rises and then reaches a plateau when the current becomes controlled and limited by the rate of diffusion of oxygen through the diffusion barrier. In the case of the sensors under discussion here, the diffusion barrier is the porous electrolyte. Where diffusion in the pores is normal bulk diffusion, the limiting current in an amperometric sensor is essentially proportional to the oxygen concentration up to about 10%, showing progressive
Fig. 2 Cross-section of thick-film (◇1) on a substrate (◇2) with no intervening layer of platinum. The interface between the thick-film and the substrate is shown by the broken line. The thick-film is zirconia, there was no doping with cobalt and the sample had been fired at 1300 °C for 1 hour.

Fig. 3 Cross-section of thick-film (◇1) on a substrate (◇2) with no intervening layer of platinum. The interface between the thick-film and the substrate is shown by the broken line. The thick-film is zirconia, doped with cobalt and fired at 1300 °C for 1 hour.
deviation from linearity towards 21% (the concentration in air) and above. This arises because the differential equation describing transport through the film contains a diffusion term and a flow term. The latter term becomes progressively more important as the oxygen concentration is raised [6]. Where diffusion in the pores is governed by Knudsen diffusion it is less clear whether the flow term should be included; this requires further consideration.

It was found that sensors made without cobalt addition required an operating temperature of 800 °C in order to achieve diffusion limitation in the percentage range of oxygen. Where doping with cobalt was used, this was reduced to 700 °C in air and even to 600 °C in a gas containing 5% oxygen. The marked effect of cobalt addition on the electrochemical (current-voltage) characteristics is shown in Fig. 4 and 5. Substantial reductions in limiting currents are shown to result as a consequence of cobalt addition. So the reduction in operating temperature by use of the dopant was 100-200 °C which is remarkable and provides the important benefits of reduced operating power and expected increase in the operational life of the sensor.

![Graph](image)

**Fig. 4** Current-voltage curves for sensor fired at 1400°C for 2 hours without cobalt addition. Sensor operated at 800°C in (□) 21% oxygen, (△) 5% oxygen.

3.3 Other aspects

The device (sensor) structure and associated techniques provide interesting and new tools for the preparation and characterisation of porous ionic-conducting materials.

4. Conclusion

The addition of cobalt oxide (formed from the decomposition of the nitrate) to zirconia thick films promoted sintering of the zirconia reducing the through-porosity for given firing conditions or permitted reduced sintering temperature for similar final film structure. The
sensors produced using cobalt oxide as dopant operated in the percentage oxygen range at temperatures 100-200 °C lower than those produced in the absence of the cobalt sintering promoter. This has positive benefits in terms of operating power and expected increase in sensor operating life. Furthermore, a new technique for investigating the through-porosity of zirconia and related materials and the influence of sintering aids is proposed and demonstrated.

![Graph](image-url)

**Fig. 5** Current-voltage curves for sensor fired at 1400°C for 2 hours with cobalt addition. Sensor operated at 700°C in (□) 21% oxygen, (☺) 5% oxygen.

5. Acknowledgements

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6. References

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