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Electronic Noses, a Different Approach to the Sensitivity and Selectivity Issues

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Abstract

Many approaches have been made during the past years to the gas sensing task. It may be addressed using one sensor or a set of arranged sensors. Solid state chemical sensing has been systematically used for the development of gas sensor devices, based on semi conducting metal oxides. There are three major issues related to chemical sensing: sensitivity, selectivity and stability. Selectivity may be improved by the use of sensor arrays (also referred as electronic noses), while the use of additives may improve sensitivity (pure doped materials or porosity control). In this paper we describe our current work about the sensitivity and selectivity issues. A tentative explanation of the observed resistance and impedance changes by porosity control is given. © 1999 Elsevier Science Limited. All rights reserved

Keywords: porosity, electrical conductivity, sensors.

1 Introduction

The sense of smell is perhaps the least appreciated of the five senses. While many animals rely heavily on their acute sense of smell, it is becoming decreasingly important to man. As Doty notes:[1] 'The field of olfaction science only recently began to enjoy the bouquet of respectability it now has. An instrument that could perform simple odour discrimination and provide measurement of odour intensity, would be most useful'. Such an instrument, an Electronic nose, has received much attention in recent years both from the academic and industrial world. The first use of the term Electronic nose has been ascribed to Gardner who uses the following definition:[2] 'An Electronic nose is an instrument, which comprises an array of electronic chemical sensors and an appropriate pattern-recognition system, capable of recognising simple or complex odours'.

2 Chemical Sensing

The use of ceramic oxides in gas detection devices involves different issues. The most important characteristics in gas detection sensors are sensitivity, selectivity and stability of the sensing devices. Sensitivity is the capacity that a device has of detecting the presence of a certain type of gas, in different concentrations. Selectivity is the capacity that a sensing device has to detect different types of gases. Stability refers to the capacity that a device has to give the same information under certain conditions, independently of the number of times this device has already been used. In this paper we deal with the sensitivity and selectivity issues.

3 Towards an Integrated Sensing System

3.1 Selectivity issue

A sensor array is a system involving a suitable data analysis procedure, constituted by a number of sensors, which are generally based on different chemical and physical working principles. It is well known that the use of sensor arrays is advantageous for the identification of gases because of the poor selectivity of many gas sensors, when only one sensor alone is applied.[3–5] The first use of a sensor array was reported with semiconductor gas sensors.[6] As to the shape of our electronic nose, we are trying a different type of design, as seen in Fig. 1. We chose this shape due to a unique reason. Some of our research partners are working on an injection moulding project with ceramics. Based on their knowledge on that subject we designed a ceramic substrate where we will implant the sensors with this conical shape (in opposition with the traditional planar sensor disposition), similar to a real human nostril. It will have 16 sensor elements

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disposed uniformly around the inside of the surface. This form has been designed in such a way that all the sensors have the same exposure area to the gas, which may have different flow along the inside of the nose due to its conical shape.

3.2 Sensitivity issue

Sensors are devices that pick up physical, chemical and dimensional variables and translate them into a signal with appropriate fidelity to give feedback to control units. Sensors become most important as engineering performance is optimised by electronic controls. Ceramic materials derive much of their importance from the fact that they are generally more stable than non-oxide ceramics such as the nitrides, carbides or sulphides at elevated temperatures and under corrosive conditions.

The preparation of ceramics is based on the use of powder, which are compacted and subsequently densified by sintering. It is obvious that characteristics of the powders will influence, first, the usability of the powders for the ceramic process, second, the settling of the processing parameters, and, third, the resulting properties of the materials. The pore size in the green body directly determines the sintering behaviour of the material, the sintering rate typically being inversely proportional to the cube of the pore diameter. The aim of any fabrication process is, therefore, to achieve bodies with a small average pore size and with a narrow pore size distribution.

The principles of chemical sensors are schematically illustrated in Fig. 2. Solid state sensors are

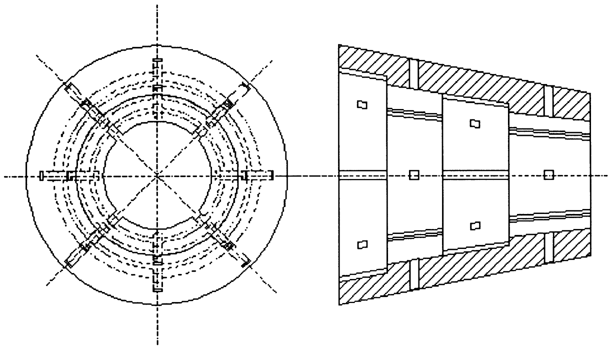

Fig. 1. Electronic nose design.

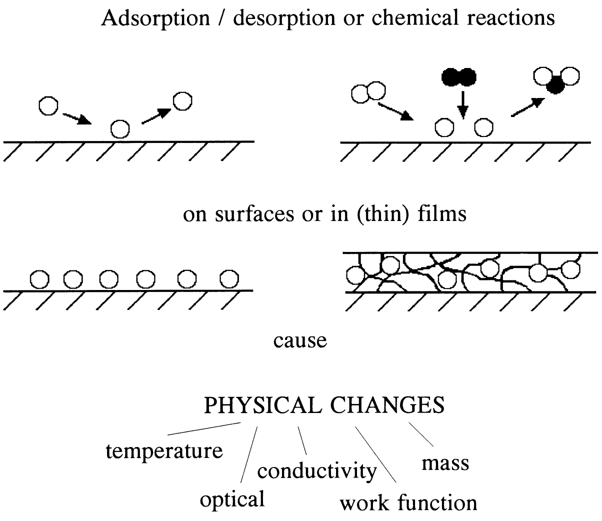

Fig. 2. General principles for solid state based sensing.

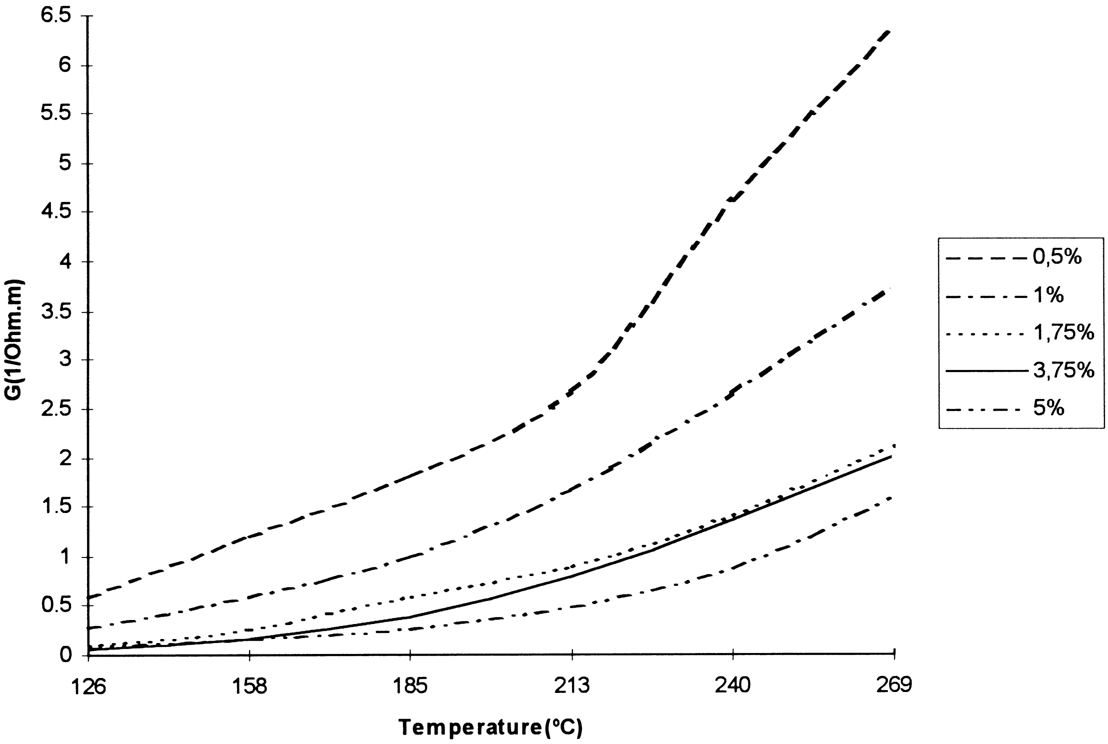

Fig. 3. Conductivity variation for several wt% mixture of additive in Fe_2O_3 samples.

based on adsorption/desorption or chemical reactions on the surface of and/or in thin films of the sensor material. These reactions lead to physical changes, which are detected by the sensor device. For optimising properties such as strength and thermal conductivity, it is desirable to eliminate as much porosity as possible. For some applications, it may be desirable to improve these properties without decreasing gas permeability.

We are presently studying the influence of additives on porosity of the sensing elements made out of SnO_2 and Fe_2O_3. Our interest is to determine in which way this porosity can influence and improve the sensitivity of the sensor devices. Micro-structural and electrical characterisation of the sensing elements is a very important step for achieving this goal. Our preliminary work on SnO_2 (optimisation of sintering parameters) is not yet finished. Anyway, our initial work on porosity control with Fe_2O_3 showed that it was possible to prepare samples with high strength with a small decrease in conductivity, as seen in Fig. 3, with similar grain dimensions but with higher porosity (which allow us to imagine higher gas permeability) as can be seen in Figs 4 and 5 (the used additive was a polymer with spherical shape which diameters vary from 2 to 70 μm). Figures 6 and 7 show some complex impedance spectroscopy analysis. It can be noticed that as porosity increases, for the same operating temperatures, grain boundary resistance also increases. Figures 4 to 7 reveal the possible existence of a higher contact surface still to confirm with further tests, particularly gas permeability tests.

4 Conclusions and Future Work

We think that porosity control can increase sensitivity. After SnO_2 sintering parameters are fully optimised, the next step in this work will be the introduction of gas (CO_2 and SO_2) at different

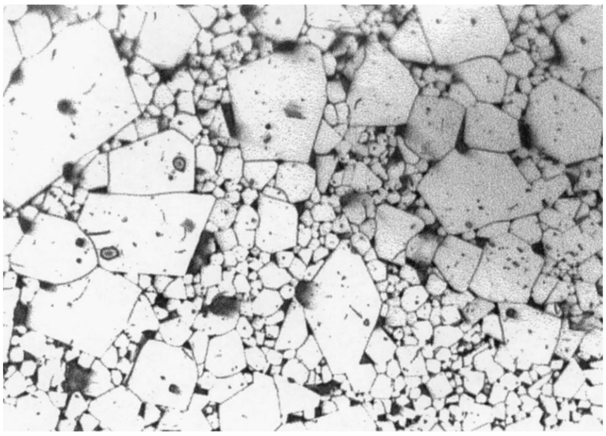

Fig. 4. Microstructure of Fe_2O_3 sample without additives.

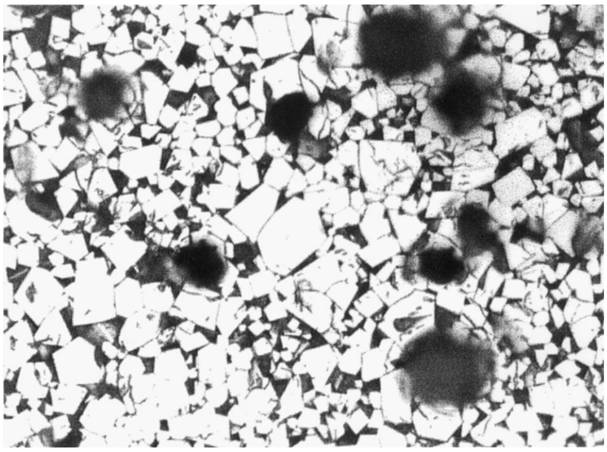

Fig. 5. Microstructure of Fe_2O_3 sample with 5% weight mixture of additive.

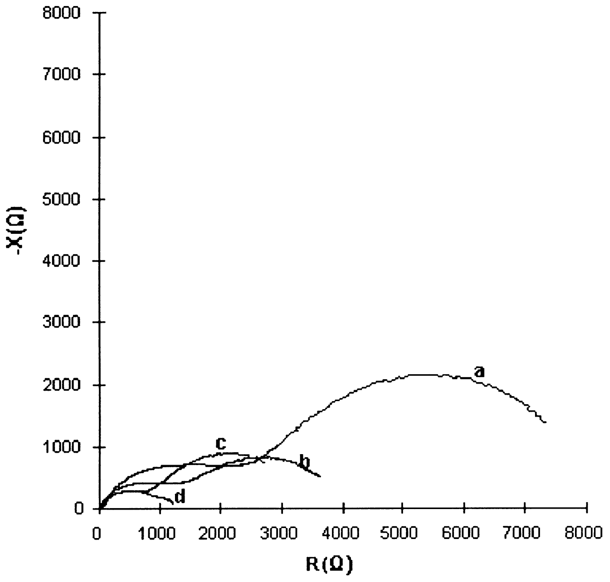

Fig. 6. Complex impedance spectroscopy of Fe_2O_3 samples at 25°C: (a) 5% weight additive; (b) 1·75% weight additive; (c) 1% weight additive; (d) without additive.

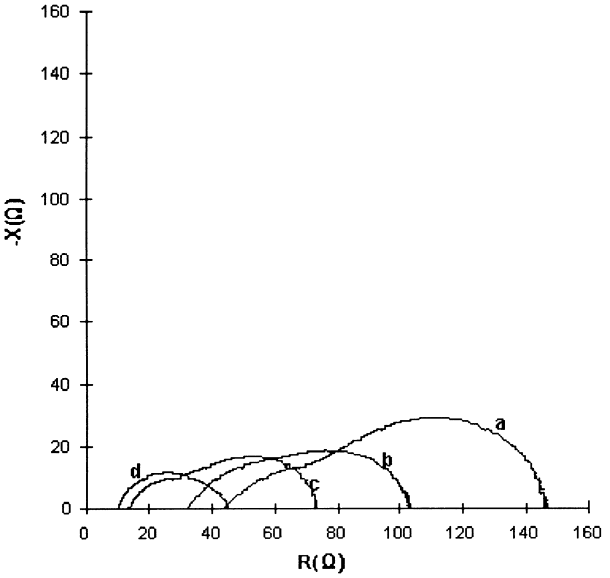

Fig. 7. Complex impedance spectroscopy of Fe_2O_3 samples at 158°C: (a) 5% weight additive. (b) 1·75% weight additive; (c) 1% weight additive; (d) without additive.

levels of concentration in a special designed chamber, allowing up to three different samples, which will be studied at different working temperatures. The working parameters of the sensing elements (sensitivity, response time, repeatability) will be determined this way.

This test chamber will also work as a simulation of a small sensor array. This will allow us to acquire some knowledge in order to improve selectivity for different gases combining information from different elements, before we decide on the definitive shape of the nose.

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References

1. Eisner, R., Olfaction scientist: sniffing out some new applications. *The Scientist*, 1990, **4**, 1,6,11.
2. Gardner, J. and Bartlett, P., A brief history of electronic nose. *Sensors and Actuators*, 1993, **B18**, 211–220.
3. Amamoto, T., Tanaka, K., Takahato, K., Matsuura, S. and Seiyama, T., A fire detection experiment in a wooden house by SnO_2 semiconductor gas sensors. *Sensors and Actuators*, 1990, **B1**, 226–230.
4. Keshavaraja, A., Jayashri, B., Ramaswarmy, A. and Vijayamohanan, K., Effect of surface modification due to superacid species in controlling the sensitivity and selectivity of SnO_2 gas sensors. *Sensors and Actuators*, 1995, **B23**, 75–81.
5. Souteyrand, E., Nicolas, D., Queau, E. and Martin, J., Influence of surface modifications on semiconductor gas sensor behaviour. *Sensors and Actuators*, 1995, **B26–27**, 174–178.
6. Persaud, K. and Dadd, G., Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose. *Nature*, 1982, **299**, 352–355.