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Application of V-doped TiO_2 as a sensor for detection of SO_2

D. Morris and R. G. Egdell*

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.
E-mail: russ.egdell@chem.ox.ac.uk

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Changes in the resistivity of polycrystalline V-doped TiO_2 upon exposure to SO_2 in air allow application of the material as a sensor for detection of this important pollutant. Optimal sensitivity to SO_2 is achieved at low doping levels, where there is also good selectivity relative to CO and CH_4. Concentration of SO_2 as low as 10 ppm† produce a 10% change in the resistance of 0.5% V-doped TiO_2, allowing facile detection of the gas at this level. Analysis of the kinetics of the resistance changes for 1% V-doped TiO_2 as a function of temperature shows that the rate of initial response is only weakly activated.

Introduction

The resistance of polycrystalline n-type oxides is often found to be sensitive to introduction of reducing gases into the ambient atmosphere. The physical basis for the resistance changes lies in the effect of adsorbed oxygen in depleting n-type carriers in the near surface region over a length range determined by the Debye or Thomas–Fermi screening lengths. Reaction between the adsorbed oxygen and a reducing gas releases carriers back into the oxide, thus causing a decrease in resistance.[1–3] The effects are most pronounced in polycrystalline materials where screening lengths may be of the order of the diameter of intergrain contact. Oxide resistivity sensors are available commercially[4] and find application in a wide range of areas. A general problem in the development of new sensor materials lies in optimising selectivity toward particular target gases: at worst an oxide may change its resistance upon exposure to any reducing gas. One strategy for the rational development of selective sensors is to take account of selectivity and turnover in catalytic oxidation reactions involving the target gas: a catalyst that can bring about catalytic oxidation of the target should be regarded as a reasonable candidate for sensor applications. Based on this approach we explore the use of V_2O_5 and V-doped TiO_2 as sensors for detection of SO_2. These materials were selected for investigation by virtue of the well-established use of V_2O_5 as a catalyst for oxidation of SO_2 in the contact process.[5]

V-doped TiO_2 prepared by high temperature solid state reaction between V_2O_5 and TiO_2 in air is essentially $Ti_{1-x}V_xO_2$, with V(IV) substitutionally incorporated on Ti(IV) sites within the rutile lattice.[6–10] XPS indicates that the vanadium at the surface of air fired material is oxidised to V(V), but overall the unpaired electron spin density is typically around 80% of the V-doping level. The V(IV) centres give rise to an occupied donor level whose adiabatic and vertical energies are respectively 0.8 and 2.1 eV below the conduction band minimum. The donor states introduced by oxygen deficiency in TiO_{2-x} are much closer to the conduction band minimum.[11]

Experimental

V-Doped TiO_2 was prepared by a solid state reaction between intimately mixed V_2O_5 and TiO_2 in air at 1200 °C in a recrystallised alumina boat that had been preconditioned by previous reactions between the two oxides. The reaction mixture was subject to several intermediate re-grindings in an agate mortar and pestle over a period of several days. The resulting material gave X-ray powder diffraction measurements characteristic of a well-crystallised rutile phase. After the final regrind, the V-doped TiO_2 was pressed into 13 mm diameter pellets between tungsten carbide dies under a loading of 10 tonnes and subject to a final firing at 1200 °C. The resulting robust ceramic disc was sliced into bars of length 1 cm and square cross section 1.5 mm. For comparison bars of undoped SnO_2, TiO_2 and V_2O_5 were also prepared. We also prepared a mass of single crystal V_2O_5 needles by slow cooling (1 °C min^{-1}) molten V_2O_5 held in a pointed quartz tube. From the conglomerate it was possible to select needles of single crystal V_2O_5 suitable for sensor measurements. Finally Nb-doped TiO_2 with doping levels up to 2% Nb was prepared by the solid state reaction between Nb_2O_5 and TiO_2. In contrast to brown-black V-doped TiO_2 which supports an unpaired spin concentration that may be up to 80% of the nominal V-doping level, Nb-doped TiO_2 is strongly compensated by cation vacancies and essentially all of the Nb is incorporated as Nb(V) after firing in air. The material is thus an off white colour.

The surface concentration of V in the doped oxides was studied by XPS measured in an ESCALAB 5 electron spectrometer (VG Scientific). Scans across the V 2p and Ti 2p core level region revealed pronounced surface segregation of V, as illustrated in the spectra of Fig. 1. Thus for 0.5, 1 and 2% V-doped TiO_2, the surface V concentrations (expressed as a percentage of the total cation concentration) are respectively 7, 15 and 18% *i.e.* there is a 14-fold enrichment in V at the lowest doping level. There was little variation in the V 2p/Ti 2p intensity ratio with angle of electron offtake, suggesting that the surface enrichment in V is over a length range large compared with the electron inelastic mean free path.

Sensor response measurements were carried out in a quartz tube mounted inside a tube furnace. Gas flow was controlled by a series of mass flow controllers (Brooks Mass Flowmeter, Rosemount Ltd., UK) that allowed switching between synthetic dry air (certified BTC474 standard dry air; BOC Special Gases Ltd: <300 ppm CO_2, 1.0 ppm CO, <0.1 ppm NO_x, <1.0 ppm THC, <3.0 ppm H_2O) and certified dry air containing 100 ppm or 1000 ppm SO_2, 1000 ppm CH_4 or 1000 ppm CO. Thin (0.05 mm) platinum leads were attached to the samples using gold paste (Hannovia) which was fired to 850 °C (500 °C for V_2O_5 ceramics and single crystals) for 12 h.

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†ppm = Parts per million expressed in terms of the vapour pressure of the SO_2 relative to the total vapour pressure.

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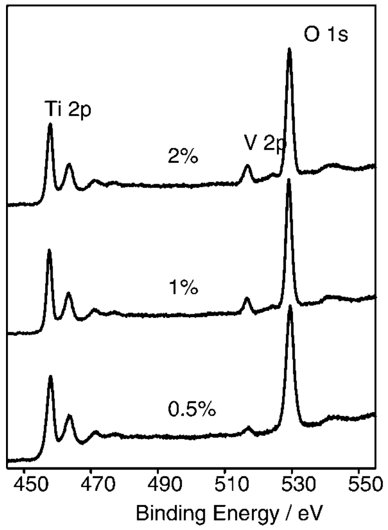

Fig. 1 Al Kα XPS of 0.5, 1 and 2% V-doped TiO_2 in the Ti 2p, V 2p and O 1s region.

Resistance measurements were made using a home built resistance to voltage convertor box interfaced to a personal computer through a digital to analogue convertor. The computer also recorded the output from a thermocouple mounted close to the sample and controlled the gas flows and furnace temperature.

Prior to sensor experiments samples were thermally conditioned by annealing in dry air at 800 °C (500 °C for vanadium pentoxide) to remove any adsorbed water and allow equilibrium to be achieved with oxygen in the air feed.

Results and discussion

Fig. 2 shows a typical resistance *vs.* time plot for 0.5% V-doped TiO_2 subject to switching between gas flows of dry air and 1000 ppm SO_2 in dry air. A pronounced resistance decrease upon exposure to SO_2 is clearly seen, followed by growth in the resistance after switching back to a dry air flow. The rate of recovery was in general slower than the rate of initial response so that after 1000 s the recovery of the resistance is not complete and continued cycling between dry air and SO_2 in dry air leads eventually to an overall fall off in the resistance. However, in general, the resistance recovers back to its initial value after cycling to 800 °C or following an extended recovery period in air at lower temperatures. In our investigations of the temperature and concentration dependence of responses (see below) we always allowed complete recovery of the sensor between successive measurements. From transient plots of the sort shown in Fig. 2 it is possible to define the sensitivity of the response to the first pulse of SO_2 in terms of a dimensionless parameter S:

$$S = \frac{R(1000) - R(2000)}{R(1000)} \tag{1}$$

where $R(t)$ is the resistance at time t.

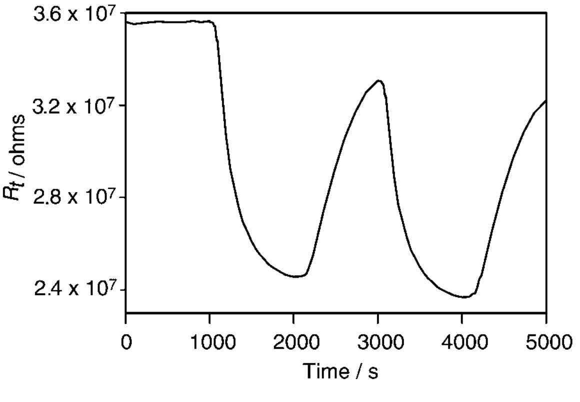

Fig. 2 Resistance of 1% V-doped TiO_2 measured at 440 °C with switching between dry air and 1000 ppm SO_2 in dry air at 1000 and 3000 s and between 1000 ppm SO_2 in dry air and dry air at 2000 and 4000 s.

In general S varies with temperature. We therefore investigated the variation in S upon exposure to 1000 ppm SO_2 for a series of different V-doping levels between 0.5 and 10%. Fig. 3 summarises the results of these investigations. The magnitude of the maximum response is greatest at the lowest doping level. Moreover the temperature at which the maximum response is achieved decreases with decreasing doping level. Unfortunately it was not possible to investigate doping levels much below 0.5% because the relatively high value of the absolute resistivity made it difficult to carry out resistance measurements at the lower end of the temperature range where the magnitude of the response is greatest. For *undoped* TiO_2 samples the high resistance precluded resistance measurements below 500 °C: at this temperature a resistance *increase* was observed upon exposure to 1000 ppm SO_2 with $S = -0.185$. By contrast both single crystal and polycrystalline V_2O_5 had low resistances but exhibited only very small responses to 1000 ppm SO_2 with maximum S values below 10^{-3} in the temperature range 500–600 °C.

Fig. 4 shows the variation in the dimensionless sensitivity factor S with temperature for exposure of 0.5% V-doped TiO_2 to 1000 ppm SO_2. The response is seen to maximise with a value in excess of 0.6 at the comparatively low temperature of 375 °C. The excellent selectivity of the 0.5% V-doped toward SO_2 relative to CH_4 and CO is evident from the very small S values upon exposure to CO and CH_4, also shown in Fig. 4. Across the complete temperature range the sensitivity factor is less than 0.05 for response to 1000 ppm CO or CH_4. At 400 °C the ratio of sensitivity factors are as follows: $S(1000\ \text{ppm}\ SO_2)/S(1000\ \text{ppm}\ CO) = 14.2$ and $S(1000\ \text{ppm}\ SO_2)/S(1000\ \text{ppm}\ CH_4) = 64.9$. For Nb-doped TiO_2 a maximum response to

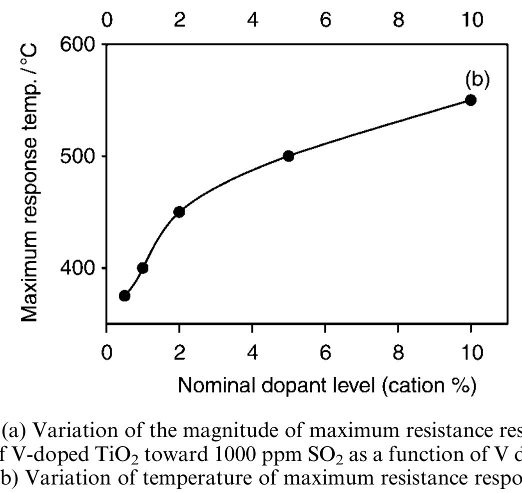

Fig. 3 (a) Variation of the magnitude of maximum resistance response S_{max} of V-doped TiO_2 toward 1000 ppm SO_2 as a function of V doping level. (b) Variation of temperature of maximum resistance response of V-doped TiO_2 toward 1000 ppm SO_2 as a function of V doping level.

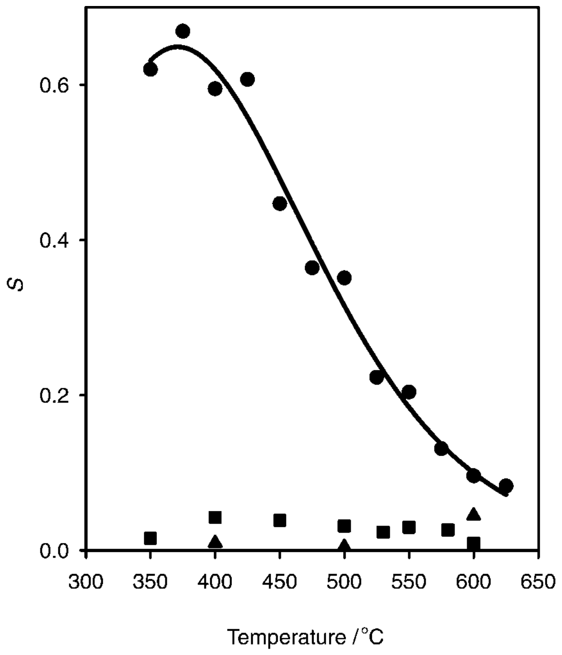

Fig. 4 Solid circles: resistance response S of 0.5% V-doped TiO_2 toward 1000 ppm SO_2 in dry air as a function of temperature. The solid line is a heuristic fit to the data. Solid squares: resistance response S of 0.5% V-doped TiO_2 toward 1000 ppm CH_4 in dry air as a function of temperature. Solid triangles: resistance response S of 0.5% V-doped TiO_2 toward 1000 ppm CO in dry air as a function of temperature.

1000 ppm SO_2 was found in the 2% doped material; this gave maximum response at 550 °C with $S = 0.39$. This value is not much lower than for the V-doped material. However the selectivity toward SO_2 relative to CH_4 and CO was very much poorer than for the best V-doped TiO_2 sensor: thus at 550 °C we found that for 2% Nb-doped TiO_2 S(1000 ppm SO_2)/S(1000 ppm CH_4) = 2.8 and S(1000 ppm SO_2)/S(1000 ppm CO) = 0.99. Further work is needed to establish the response of the V-doped TiO_2 sensors toward H_2O and the effects of water vapour on the SO_2 response.

The variation of the response with variation in concentration of SO_2 was investigated by switching between air flows and blended flows of dry air and 1000 ppm or 100 ppm SO_2 in dry air as set by the mass flow controllers. All these measurements were performed at the appropriate temperature of maximum response to 1000 ppm SO_2 with sufficient time under a pure dry air flow between measurements at different concentrations to allow recovery of the sensor. The variations are shown in Fig. 5. The responses are non-linear except at very low SO_2 concentrations below about 100 ppm and tend toward saturation values in the response at 1000 ppm. The sensitivity toward SO_2 in 0.5% V-doped TiO_2 is just above 0.1 for 10 ppm SO_2 in air allowing facile detection of the gas even at this very low concentration.

In the hope of developing some understanding of the mechanism of the response we made detailed kinetic studies of the response and recovery of V-doped sensors. The decay in resistance after switching from a dry air flow to a flow of 1000 ppm SO_2 in dry air was fitted to a relationship of the sort:

$$R(t) = R(\infty) + \Delta R e^{-kt} \tag{2}$$

where $R(t)$ is the resistance at time t, $R(\infty)$ is the limiting resistance (which may not actually be reached in the 1000 s of SO_2 flow, but which can be derived from the fits), $R(\infty) + \Delta R$ is the resistance at $t = 0$ and k is first order rate constant for the response. Fig. 6 shows a typical fit for 1% V-doped TiO_2 at 440 °C. Because of the first order nature of the response $t = 0$ can be chosen arbitrarily.

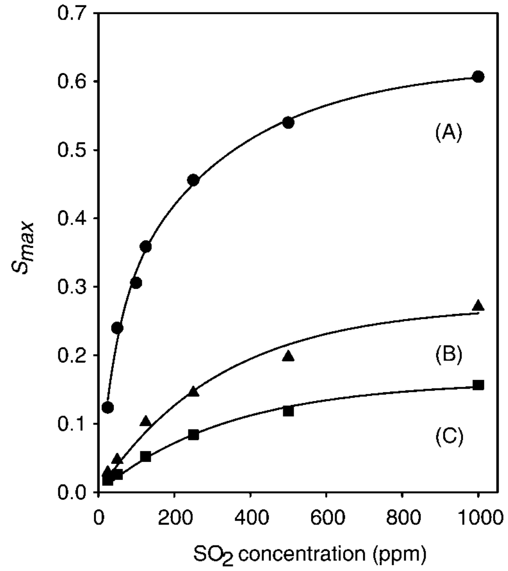

Fig. 5 Variation of resistance responses S_{max} of V-doped TiO_2 as a function of SO_2 concentration (ppm). The data all relate to the temperature of maximum response. (A) 0.5% V-doped TiO_2 at 375 °C, (B) 1% V-doped TiO_2 at 400 °C, (C) 2% V-doped TiO_2 at 450 °C.

Similarly the recovery profiles were fitted to a function of the sort:

$$R(t) = R(0) + \Delta R'(1 - e^{-k't}) \tag{3}$$

Values for the rate constants k and k' as a function of temperature are shown in Fig. 7 for 1% V-doped TiO_2. The initial response to SO_2 as defined by the decay parameters k of eqn. (3) is a very weakly activated process, with an apparent activation energy of only 6.7 kJ mol^{-1}. Alternatively the weak temperature dependence may be interpreted in terms of the $T^{1/2}$ dependence expected for a diffusive process, for example intergrain diffusion within the ceramic material. The scatter of the experimental data points is too large to distinguish between a $T^{1/2}$ dependence and an $\exp(-E/RT)$ dependence of the rate constant. The rate constants are of the order $4 \times 10^{-3}\ s^{-1}$, giving half-lives for the response of about 160 s. Using the same apparatus and the same gas flow rate we have measured rate constants as high as $2 \times 10^{-2}\ s^{-1}$[12] for the response of thin film Sb-doped SnO_2 sensors[3,13] to CH_4, so we can rule out the possibility that the response rate is limited by the rate of gas flow through the sensor tube. The rates of recovery of the SO_2-exposed sensors were also essentially independent of

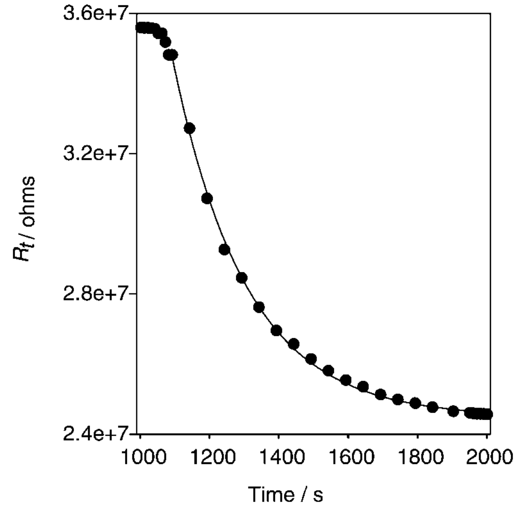

Fig. 6 A fit of the resistance of 1% V-doped TiO_2 after exposure to 1000 ppm SO_2 at 440 °C to a first order decay curve as given in eqn. (2).

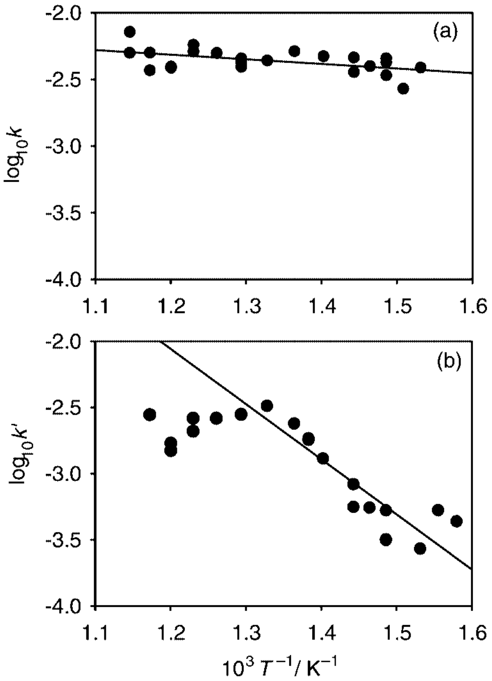

Fig. 7 (a) Logarithmic variation of first order rate constant k [eqn. (2)] for decrease in resistance of 1% V-doped TiO_2 upon exposure to 1000 ppm SO_2 in dry air as a function of inverse temperature. The response is seen to be very weakly activated. The solid line is a least squares fit to the experimental data points. For visual appraisal of the weak temperature variation, the rate constants are plotted on the same scale as in (b) where the temperature variation is stronger. (b) Logarithmic variation of first order rate constant k' [eqn. (3)] for increase of resistance of 1% V-doped TiO_2 upon switching from a gas flow of 1000 ppm SO_2 in dry air to pure dry air as a function of inverse temperature. The solid line is a least squares fit to experimental data points at temperatures below 485 °C.

temperature at high temperature, but at low temperature the recovery became activated with an activation energy of about 80 kJ mol^{-1}. This activation energy may be interpreted simply as desorption of the product of SO_2 oxidation *i.e.* SO_3 or SO_4^{2-}. At high temperatures we presume that the loss of the oxidation product is diffusion limited with an essentially negligible temperature dependence.

Discussion

0.5% V-doped TiO_2 proves to be a useful material for detection of SO_2 at concentrations down to at least 10 ppm. The system offers much better selectivity toward SO_2 than the SnO_2 sensors examined by us, as well as optimal response at lower temperature. It should however be noted that SnO_2 may be preconditioned in SO_2 at elevated temperature to give a modified material whose peak response to SO_2 is at 200 °C.[14] However the magnitude of the response was not quantified in this earlier work. The temperature of maximum response in the present work is lower than for WO_3 or Ag-loaded WO_3 conductivity sensors which have recently been proposed[15] for detection of SO_2. The detection limit in the present work is comparable to that achieved using galvanic cells incorporating solid sulfate electrodes.[16–21] These cells give a Nernstian response in which the generated e.m.f. is proportional to the logarithm of the SO_2 concentration. In most cases these cells must operate at temperatures in excess of 500 °C in order to achieve sufficient ionic conductivity in the solid electrolyte incorporated within the cell. However a new cell design incorporating a thin film solid electrolyte has recently been described which allows detection of ppm levels of SO_2 at temperatures as low as 250 °C.[22] Nonetheless the conductivity sensor described here is much simpler to construct than the thin film galvanic cell of ref. 22 and achieves comparable lower detection limits for SO_2. It should however be realised that neither of the two types of sensor are sufficiently sensitive for application in general environmental monitoring where concentrations of SO_2 in the parts per billion range must be identified.[23]

References

1 M. J. Madou and S. R. Morrison, *Chemical Sensing with Solid State Devices*, Academic Press, London, 1989.
2 D. E. Williams and P. T. Mosely, *J. Mater. Chem.*, 1991, **1**, 809.
3 C. S. Rastomjee, R. S. Dale, R. J. Schaffer, F. H. Jones, R. G. Egdell, M. J. Lee, T. J. Tate and L. L. Cao, *Thin Solid Films*, 1996, **279**, 98.
4 For example Capteur Sensors & Analysers Ltd., Didcot, Oxfordshire market a conductivity sensor based on doped Cr_2O_3 which displays a p-type response to SO_2.
5 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1989.
6 A. E. Taverner, C. Rayden, S. Warren, A. Gulino and R. G. Egdell, *Phys. Rev. B*, 1995, **51**, 6833.
7 R. G. Egdell, A. Gulino, C. Rayden, G. Peacock and P. A. Cox, *J. Mater. Chem.*, 1995, **5**, 499.
8 R. Dixon, R. G. Egdell and G. Beamson, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3495.
9 D. Morris, R. Dixon, F. H. Jones, R. G. Egdell, S. W. Downes and G. Beamson, *Phys. Rev. B*, 1997, **55**, 16083.
10 R. G. Egdell, in *The Science of Ceramic Interfaces II: Impact on Properties and Applications*, ed. K. Uematsu, Trans Tech Publications, Zurich, 1995, pp. 11–37.
11 *Semiconductors. Physics of Non-Tetrahedrally Bonded Binary Compounds III*, ed. O. Madelung, Landolt-Bornstein New Series, Group III, vol. 17, Pt. g, (Springer Verlag, Berlin, 1984).
12 I. York, Chemistry Part II Thesis, Oxford, 1994.
13 R. S. Dale, C. S. Rastomjee, F. H. Potter, R. G. Egdell and T. J. Tate, *Appl. Surf. Sci.*, 1993, **71**(72), 359.
14 D. Girardin, F. Berger, A. Chambaudet and R. Planade, *Sens. Actuators B*, 1997, **43**, 147.
15 Y. Shimizu, N. Matsunaga, T. Hyodo and M. Egashira, *Electrochemistry*, 2001, **69**, 109.
16 M. Gauthier and A. Chamberland, *J. Electrochem. Soc.*, 1977, **124**, 1579.
17 G. Rog, A. Kozlowskarog, K. Zakula, W. Bogusz and W. Pycior, *J. Appl. Electrochem.*, 1991, **21**, 308.
18 Y. Yan, Y. Shimizu, N. Miura and N. Yamazoe, *Chem. Lett.*, 1992, 635.
19 Y. T. Yan, Y. Shimizu, N. Miura and N. Yamazoe, *Sens. Actuators B*, 1993, **12**, 77.
20 H. Nakamura, Y. Ogawa, A. Kasahara, Y. Isida and K. Matsuda, *Mater. Trans. JIM*, 1998, **39**, 281.
21 S. Suganuma, M. Watanabe, T. Kobayashi and S. Wakabayashi, *Solid State Ionics*, 1999, **126**, 175.
22 J. F. Currie, A. Essalik and J. C. Marusic, *Sens. Actuators B*, 1999, **59**, 235.
23 A. W. E. Hodgson, P. Jacquinot and P. C. Hauser, *Anal. Chem.*, 1999, **71**, 2831.