A study of tin-dioxide gas-sensor thermochemistry under conditions of varying oxygen partial pressure

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Abstract

Changes in sensor resistance and temperature observed upon exposure to reducing-gas mixtures have been monitored simultaneously for prototype devices comprising a platinum wire coil surrounded by a sintered tin-dioxide bead. Studies performed in a dry air ambient show that decreases in SnO_2 resistance in the presence of either H_2 or CO are matched by small increases in temperature, which are measured by using the Pt coil resistance. Investigations into the effect of operating temperature on sensor characteristics show that the maximum resistance and temperature changes do not always occur at the same point. Decreasing the oxygen partial pressure of the test environment to a level where the reducing-gas concentration exceeds that of oxygen causes a marked increase in resistance response and this is accompanied by a significant decrease in coil temperature. These findings support the notion that a change in the detection mechanism of tin-dioxide sensors occurs under non-equilibrium conditions, probably as a result of direct reduction of the semiconductor lattice by the reducing gas.

Keywords: Gas sensors; Thermochemistry; Tin dioxide

1. Introduction

Tin-dioxide-based gas sensors exploit resistance changes experienced by the material when flammable gases such as hydrogen, carbon monoxide or methane react with adsorbed oxygen at elevated temperatures on the semiconductor surface. Therefore, the tin dioxide effectively acts as a catalyst for combustion reactions that give rise to the evolution of heat, and hence it is possible to detect reducing gases in an oxygen-containing environment by measuring small changes in the temperature of the sensor. SnO_2-based devices can therefore be used as miniature calorimeters in the same manner as pellistors or catalytic gas sensors. These consist of small-diameter Pt spirals surrounded by a porous refractory bead, typically alumina impregnated with precious-metal catalysts [1]. A constant voltage applied across the coil maintains the pellistor at temperatures of approximately 500 °C. When flammable gases are oxidized at the bead surface, small rises in the sensor temperature can be detected via an increase in the Pt coil resistance, typically by incorporating the sensing element in a Wheatstone bridge circuit.

Recent reports in the literature have shown that this detection method can be used successfully when sintered tin dioxide is substituted for the catalyst-containing refractory bead. Calcium-oxide-doped SnO_2 sensors display high sensitivity to gaseous organic and inorganic species associated with odour [2]. Orlik et al. [3] have studied the gas response of monoelectrode sensors produced by depositing stabilized stannic acid sols onto Pt wire coils. These devices respond to a wide range of reducing gases, including hydrogen, carbon monoxide, methane, formaldehyde and ethanol vapours and ammonia. This gas-detection method is also employed by commercially available devices such as the Cosmos CH sensor (produced by the New Cosmos Electric Company), which consists of a small Pt wire coil surrounded by a sintered bead of SnO_2.

Sensors based on this type of configuration have been fabricated using several SnO_2-containing formulations with a view to investigating the effect of oxygen partial pressure on resistance response to reducing gases. The devices were modified to accommodate an additional electrode attached to the surface of the semiconductor bead to enable simultaneous measurement of both conductance and temperature changes.

2. Experimental

Pt coils (approximately 20 turns) were wound from 0.025 mm diameter wire supplied by Goodfellow Metals

Ltd. These were coated in a polycrystalline tin-dioxide-based bead by repeatedly dipping the coils in a paste of the material prepared using ethyl cellulose stabilized α-terpineol and evaporating the organic vehicle over a hotplate until a bead of sufficient diameter was formed. The sensors were then fired at 800 °C for 2 h with additional 2 h heating and cooling ramps. After mounting the sensors on TO100 circuit headers, additional contacts were made to the bead surface via a conductive Pt paste, which was cured at 600 °C by applying a heater voltage of 6 V to the coil. Schematic diagrams showing the sensor structure and the Wheatstone bridge type control circuit used are shown in Fig. 1(a) and (b), respectively.

$R(1)$ and $R(2)$ are standard resistors of 0.5 kΩ, $R(c)$ is a 10 Ω thin-film resistor while $R(s)$ refers to the sensor's Pt coil resistance, which varies as combustible gases react on the tin-dioxide surface. $V(out)$ is the bridge output measured in millivolts and this can be zeroed by adjusting the variable resistor. The magnitude of $V(out)$ is directly related to the temperature change experienced by the sensor coil and can be used as a measure of the combustible gas concentration present in the immediate vicinity of the sensor. $V(in)$ refers to the d.c. voltage applied (typically between 2 and 6 V)

in order to heat the sensor to the desired operating temperature. The tin-dioxide resistance was measured by monitoring $i(s)$, the current flowing through the semiconductor when applying a d.c. voltage. The reducing-gas sensitivity of the tin-dioxide element is given by the ratio i_{gas}/i_0 where i_0 is the sensor current in dry air and i_{gas} is the measured current in a contaminant gas/air mixture.

Initial experiments were carried out to determine the sensor response to mixtures of CO, CH_4 and H_2 in dry air (1% v/v unless otherwise specified) over a wide range of sensor operating temperatures. After establishing the optimum operating conditions for each gas, the effect of varying the oxygen partial pressure in the test atmosphere upon both coil and semiconductor resistance response was investigated. Three basic sensor formulations were studied during the course of this work: (a) undoped SnO_2; (b) $SnO_2 + Pd$ (1% w/w); (c) SnO_2/Bi_2O_3 (15% w/w) + Sb_2O_3 (1% w/w). The last forms a gas-sensitive element that responds selectively to carbon monoxide and hydrogen in the presence of lower hydrocarbons [4]. The Sb(III) additive acts as an electron donor and is incorporated in order to reduce the resistivity of the SnO_2/Bi_2O_3 formulation.
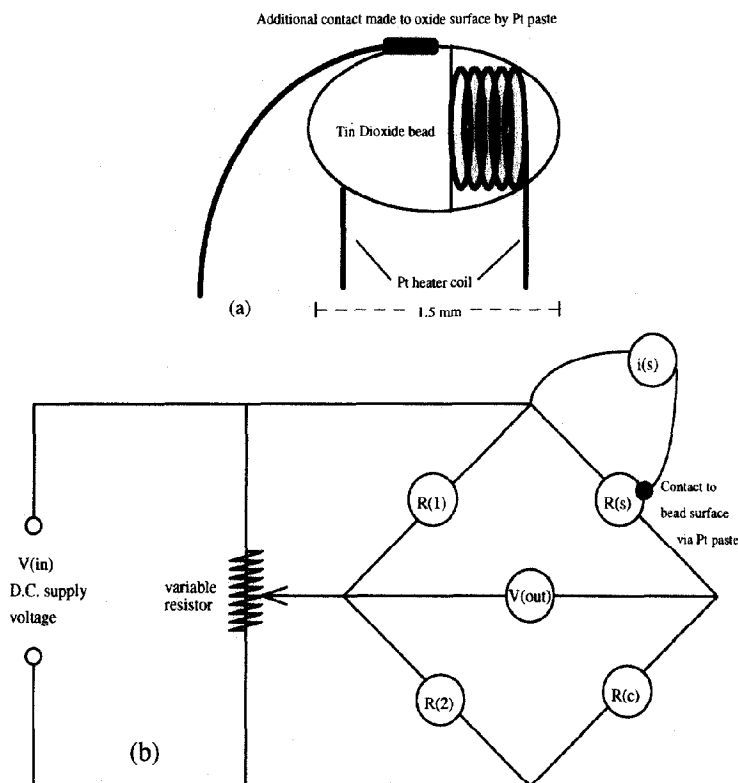

Fig. 1. (a) Configuration of a modified hot-wire SnO_2-based sensor; (b) interrogating circuit for hot-wire-type sensor.

3. Results and discussion

3.1. Preliminary studies carried out in dry air

In general, results obtained in dry air environments showed that the highest sensitivities and Pt coil temperature changes are displayed when hydrogen is used as the test gas. Sensitivities to CO and especially CH_4 are small in comparison, though significant bridge deflections are observed in the presence of CO at low operating powers. The characteristics of the SnO_2/Pd formulation that shows typical sensor behaviour are plotted in Fig. 2. In this case, both reducing-gas sensitivity and bridge output reach a maximum at approximately the same temperature (≈ 300 °C). However,

it was noted that for both of the other formulations tested, the optimum power requirement for maximum bridge output in H_2 was significantly higher than that needed for maximum sensitivity. For example, in the case of the Bi- and Sb-doped SnO_2 sensor whose characteristics are shown in Fig. 3, maximum bridge output occurs at 500 °C while the greatest semiconductor resistance response is obtained at 380 °C.

All the formulations tested showed very little response to methane both in terms of bead sensitivity (i_{gas}/i_{air}) and observed temperature changes (V(out)). This appears surprising in the light of results previously obtained for thick-film sensors based on Pd-doped tin dioxide, which display high CH_4 sensitivity with little interference from CO [4]. However, the difference may arise as a consequence of the different sensor geometries involved, i.e., a spherical bead may give contrasting behaviour to that of a thick film. Values of V(out) obtained
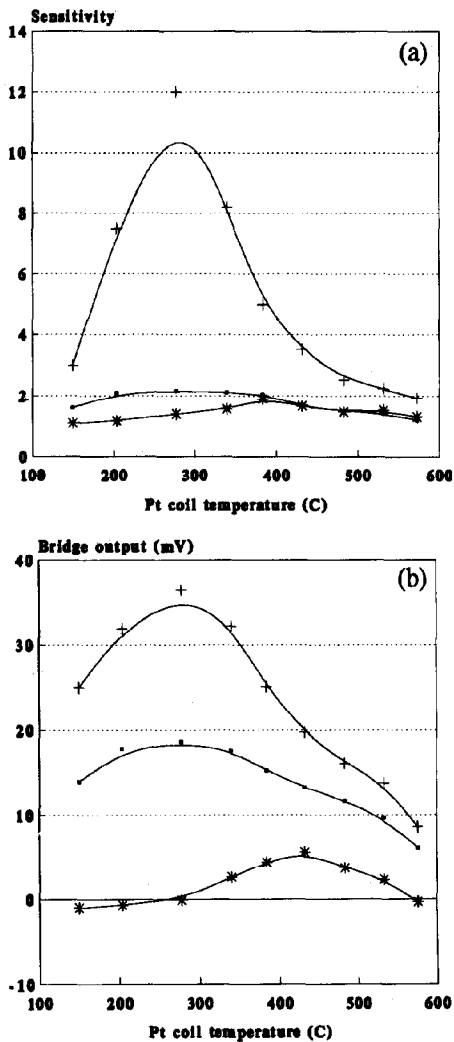
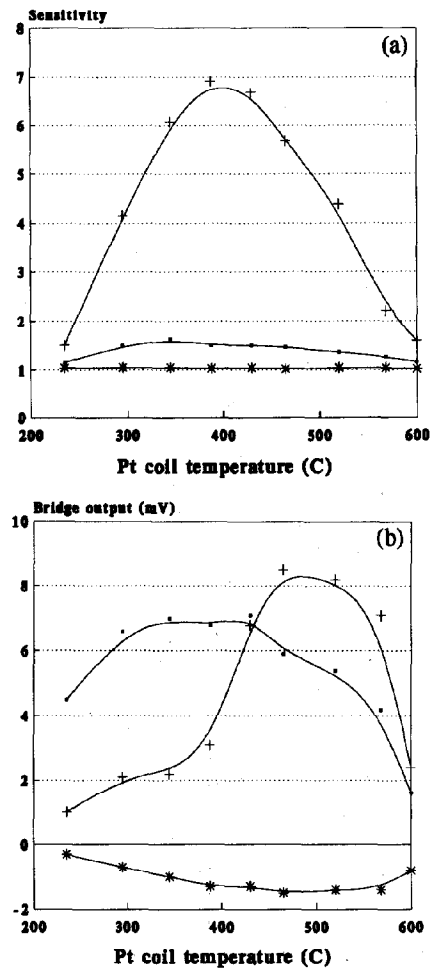Fig. 2. The variation of (a) i_{gas}/i_0 and (b) bridge output with Pt coil temperature for a hot-wire sensor based on an $SnO_2 + PdCl_2$ (1.5% w/w) formulation upon exposure to 1% v/v reducing-gas concentrations in dry air.

Fig. 3. The variation of (a) i_{gas}/i_0 and (b) bridge output with Pt coil temperature for a hot-wire sensor based on an SnO_2/Bi_2O_3 (15% w/w) + Sb_2O_3 (1% w/w) formulation upon exposure to 1% v/v reducing-gas concentrations in dry air.

indicate that the SnO_2 used is a poor catalyst for methane oxidation by atmospheric oxygen. The absence of any significant SnO_2 temperature increase upon exposure to methane is not altogether unexpected in the light of the findings of Dutronc et al. [5]. These authors observed moderate cooling of a screen-printed tin-dioxide sensor upon the introduction of methane even though resistivity changes indicated the occurrence of combustion, which should have led to an increase in temperature. It was concluded that this phenomenon was caused by convection processes that were dominating combustion effects.

It had been envisaged that the results of this study would give some insight into how tin dioxide selectivity is achieved, most notably by the SnO_2–Bi_2O_3–Sb_2O_3 system that responds to CO in the presence of CH_4 over the whole operating temperature range. Results showed that in contrast to Pd-doped tin dioxide, maximum sensitivity and bridge output in H_2 do not occur at the same point, while a change in polarity of $V(out)$ occurs when CH_4 is used as the test gas over the entire applied power range (see Fig. 3). However, since un-doped SnO_2 also behaves in a similar manner upon exposure to CH_4, it is difficult to glean any evidence on how the Bi_2O_3 and Sb_2O_3 additives confer selectivity to CO in preference to CH_4.

3.2. Sensor behaviour under conditions of varying oxygen concentration

Experiments were performed to determine sensor characteristics in reducing-gas-containing environments under conditions of varying oxygen partial pressure. Sensors were maintained at the optimum temperature, determined previously in air, and then exposed to 1% v/v CO, CH_4 or H_2 concentrations in a base gas containing varying oxygen levels ($1 \geq [O_2] \geq 10^{-4}$ atm) in nitrogen. Detailed tests were carried out on an undoped SnO_2 sensor and the results are shown in Fig. 4. When the oxygen concentration is greater than that of the reducing gas, a positive bridge output is observed, indicating that an exothermic process is taking place. As the oxygen partial pressure is decreased from 1 to 0.01 atm, a gradual increase in $V(out)$ is observed while the bead sensitivity remains constant. However, under conditions where the hydrogen concentration exceeds that of oxygen, the bridge output suddenly changes polarity, indicating a drop in sensor temperature; this is accompanied by marked changes of up to three orders of magnitude in bead sensitivity. A similar trend in sensitivity and bridge output is also observed when CO is used, though the magnitude of the observed changes is not as great. Interestingly, in the case of methane, the bead sensitivity actually decreases as P_{O_2} is reduced, while a significant cooling of the sensor occurs, especially when the reducing-gas concentration exceeds that of
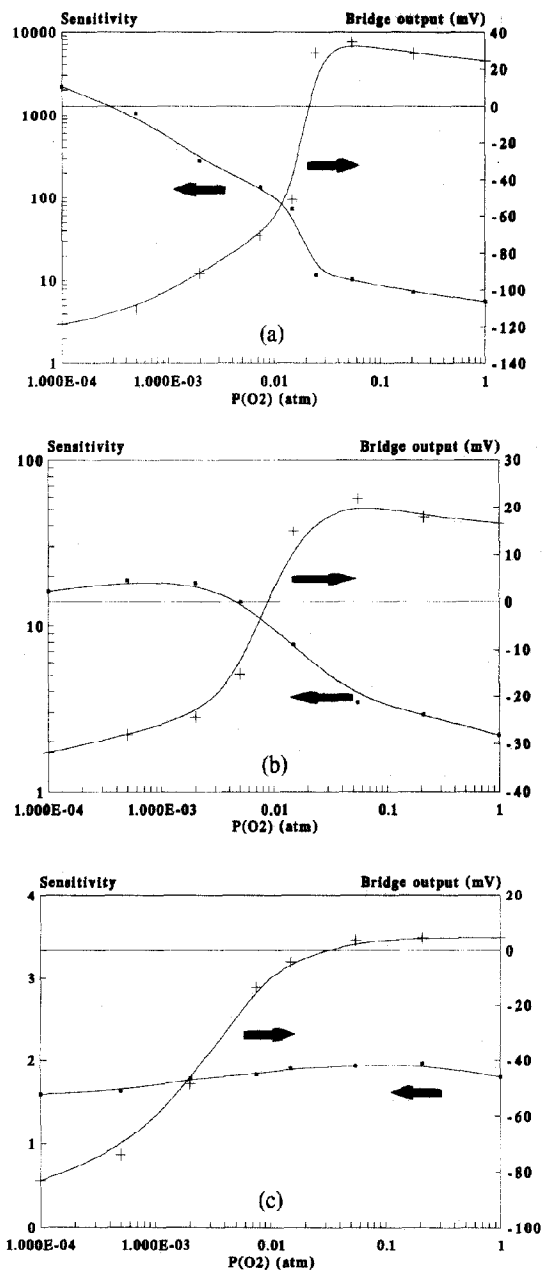

Fig. 4. The effect of oxygen partial pressure on the bead sensitivity and bridge output of a sensor based on undoped SnO_2 upon exposure to 1% v/v concentrations of: (a) hydrogen, (b) carbon monoxide and (c) methane at operating temperatures of 320, 290 and 460 °C, respectively.

oxygen. This result may have particular significance since it forms the basis of a method of differentiating between methane and other reducing gases such as hydrogen under oxygen-depleted conditions. The SnO_2 bead undergoes substantial cooling in the presence of both gases but only displays marked resistance response ($i_0/i_{gas} > 100$) in the presence of hydrogen.

It therefore appears that a change in the detection mechanism occurs when the reducing-gas concentration exceeds the oxygen concentration in the test atmosphere at which point the surface reactions become endothermic in nature. Such reactions may include the direct reduction of SnO_2 to SnO by the reducing-gas mixtures in the absence of sufficient oxygen for the conventional sensing mechanism to occur. Evidence for this has been obtained by exposing the undoped SnO_2 sensor to a high concentration of H_2 (1% v/v) in nitrogen, whereupon the oxide bead assumes a dark grey colour indicating the presence of SnO, which disappears upon the introduction of air.

In separate experiments involving an undoped SnO_2 sensor, the effect of temperature on reducing-gas response under oxygen-deficient conditions ($P(O_2) = 10^{-4}$ atm) was studied and the results were compared to the characteristics obtained in air. Results show that the endothermic changes experienced by the sensors when exposed to reducing gases in oxygen-deficient conditions are temperature dependent and are only observed if the operating temperature exceeds a certain threshold value. The limiting temperature also appears to be dependent on the reducing gas, i.e., endothermic changes in H_2 occur at a significantly lower temperature than in CO. These observations support the theory that direct reduction of the SnO_2 by the reducing gas is responsible for increased sensitivity under oxygen-depleted conditions. A thermodynamic approach to evaluating the feasibility of these reactions via Gibbs free-energy calculations estimates that sensor reduction should only become a favoured process above a threshold temperature (e.g., for CO this corresponds to approximately 300 °C) [6].

4. Conclusions

It has been demonstrated that considerable information regarding sensor operation, especially under conditions of varying oxygen partial pressure, can be obtained from prototype SnO_2-based devices employing a Pt wire coil to measure temperature changes and an additional contact to the bead surface to enable active material sensitivity measurements. When operated in dry air, resistance changes occurring within the active sensing material upon the introduction of reducing gases such as H_2 or CO are matched by the release of heat. However, under oxygen-depleted conditions, sensor exposure to reducing gases leads to substantially increased resistance response and this is accompanied by a significant cooling of the SnO_2 bead, indicating that endothermic processes are taking place.

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