Sensors for Toxic Gas Detection

PLATINUM METALS PERFORM AN IMPORTANT ROLE

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The utilisation of advanced sensing techniques for detecting, indicating and monitoring toxic gases in industry and the environment is very important for health and safety. In this paper, the application of electrochemical, semiconductor, catalytic field effect and catalytic gas sensors for the detection of toxic gases, and the role of platinum group metals in these devices, is discussed.

It is very important that precise and rapid detection, alerting, and monitoring of toxic gases should be available to prevent or minimise accidents involving poisoning or explosions. Toxic gases, including carbon monoxide, hydrogen sulphide, chlorine, bromine, hydrogen chloride, hydrogen fluoride, nitric oxide, nitrogen dioxide, sulphur dioxide, ammonia, hydrogen cyanide, phosgene, benzene, formaldehyde, methyl bromide, arsine, phosphine, boranes, silane, germane, are found in a wide variety of situations, varying from industry: chemical, heavy, petroleum, electronic, coal, gas, mines, to warehouses, enclosed parking areas, vehicles, sewerage, waste disposal, the atmosphere, houses, and even battle fields. In the past certain colour changing reagents were adopted to detect these gases by tedious and time-consuming colorimetric, or more complicated chromatographic methods (1–3). However, in the last ten to twenty years techniques have progressed rapidly and more sensors have been developed for the fast precise detection of various toxic gases (4–8). Four kinds of sensors will be discussed here.

Electrochemical sensors are of two types, namely, galvanic cell and constant potential electrolysis. With the constant potential electrolysis sensor, it is possible to select the external applied voltage, and the type of electrode for different work and reference voltages, so that it is suitable for detecting carbon monoxide, nitric oxide, phosgene, hydrogen cyanide, arsine, phosphine, boranes, silane, germane, etc., and also for certain components in mixtures of gases (8, 9). The electrode, as the key part, is a gas diffusion electrode made of noble metals. In this device the electric current between the working electrode and the opposing electrode is proportional to the concentration of the toxic gas. This sensor has been widely used in detecting the gases mentioned above, especially in both fixed site and portable detectors.

Semiconductor sensors are prepared as sintered, thick or thin films by the deposition of noble metal catalysts, such as platinum, palladium, ruthenium, gold, etc., onto semiconductor materials, such as ferric oxide, zinc oxide, stannic oxide or indium oxide (10–14). A change in the resistance occurs as soon as the toxic gas is adsorbed on the surface of the semiconductor, thus enabling the gas to be determined. The sensors possess high sensitivity for detecting gas concentrations as low as the ppb level, which makes them widely used for leak detection.

Initially catalytic field effect sensors were only used to detect hydrogen, now however gases such as hydrogen sulphide, ammonia and hydrogen cyanide, which can be dissociated on a palladium grid, can also be determined. Recently there have been improvements in the palladium grid, so that it is now possible to detect gases which do not contain hydrogen, for example carbon monoxide. In addition the output from these sensors can be microprocessed and the sensors can be incorporated into detection systems.

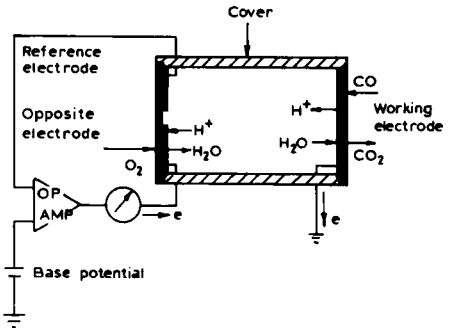

Fig. 1 The constant potential electrolysis sensor has very high sensitivity and selectivity and can detect gases to the ppm level or lower. The external circuit maintains constant voltage at the working electrode, and by amplifying the current produced inside the sensor with an external amplifier, the toxic gas concentration can be measured

Consequently for these sensors the areas of application are continuously growing.

In catalytic sensors the toxic gas is oxidised catalytically on a coiled noble metal wire, which releases heat and causes an increase in the resistance of the wire. The electric signal output resulting from the change in resistance can be utilised to measure precisely the concentration of the toxic gas. Accurate measurement of toxic gases is being undertaken along with the development of the gas sensors, especially for gas concentrations in the range 100 ppm to several ten thousand ppm.

Constant Potential Electrolysis Sensors

At the beginning of the 1980s, constant potential electrolysis sensors developed rapidly (8, 9). This detector, of low concentrations of toxic gases, is now widely available commercially. The sensitivity of the constant potential electrolysis sensor is very high, and can detect gases at the ppm level and even much lower; its selectivity is excellent and it is also energy efficient. The structure of the detector is shown in Figure 1.

The sensor is composed of three gas diffusion electrodes each of which consists of a waterproofing layer, a charge collecting net made of noble metals and a catalytic layer of noble metals. The principle it works on for detecting gases is that the analyte, such as carbon monoxide, passes through the waterproofing layer of the working electrode to reach the catalytic layer where the carbon monoxide reacts with water in the electrolyte, forming carbon dioxide and releasing electrons. The electrons are then gathered by the collecting net. Meanwhile the reaction of oxygen with hydrogen ions takes place on the opposite electrode, taking up electrons and forming water. The reaction may be illustrated as follows:

$$CO + H_2O = CO_2 + 2H^+ + 2e$$

(on the working electrode)

$$\tfrac{1}{2}O_2 + 2H^+ + 2e = H_2O$$

(on the opposite electrode)

$$CO + \tfrac{1}{2}O_2 = CO_2 \qquad \text{(in total)} \quad \text{(i)}$$

Reaction (i) can be driven by the presence of an applied external voltage. The magnitude of the voltage applied to the electrode affects the oxidation of the carbon monoxide to such an extent that the potential of the working electrode must be kept at 0.9–1.1 V, to maintain the reaction proceeding smoothly; therefore, a device is required in the external circuit to maintain a constant voltage at the working electrode (the basic definition of the constant potential). On amplifying the current produced by the sensor with an external amplifier, the toxic gas concentration can thus be measured, and the amplified current I = nFADC/d, is proportional to the concentration, C, of toxic gas for a specified electrode (n = number of electrons in the reaction, F is the faraday constant, D is the coefficient of diffusion of the gas, d and A are parameters related to thickness and area of the electrode, respectively). This is the principle for measuring toxic gases by the constant potential electrolysis sensor.

The electrode potential needed to detect the maximum electrolytic current for each toxic gas is different, so by selecting a suitable electrode potential, different gases may be measured clearly, without interference. By changing the composition or structure of the catalyst, the

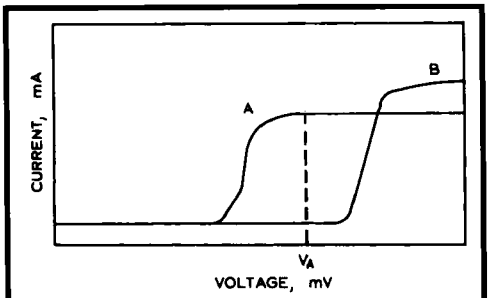

Fig. 2 Voltage V_A is chosen as the working voltage to detect gas A in the constant potential electrolysis sensor

catalytic reaction to a toxic gas can be varied, thus it is possible to measure different gases. If the resulting currents produced by toxic gases, **A** and **B**, under different electrode potentials are as shown in Figure 2, then potential V_A would be selected for the electrode to measure **A**, to avoid interference from gas **B**.

This kind of sensor has been widely applied for the accurate measurement of many toxic gases, but its further development may be limited as the electrolyte will need to be renewed and there is difficulty in achieving sufficient microminiaturisation and integration.

Metal Oxide Semiconductor Gas Sensors

Highly sensitive devices have been available since the beginning of the 1970s for detecting flammable gases by the addition of a noble metal catalyst to a stannic oxide semiconductor. The electrical resistance of a semiconductor material changes on adsorption of some gases, and this change in resistance can be used to detect toxic gases, which even in very low concentrations can profoundly injure the human body. Much attention has been drawn to the convenience in use and cheapness of this sensor, which has resulted in its rapid development.

Nowadays semiconductor gas sensors are generally of three types, namely, sintered, thick film and thin film, of which the side heated thick film type is the one most used. The sensor is made of an alumina tube, usually of 1 mm diameter on which a layer of platinum, ruthenium or gold is deposited as the electrode, with a platinum wire acting as the lead to the electrode. A layer of platinum group metal-containing semiconductor material (stannic oxide or zinc oxide, etc.) is then deposited on the ceramic tube surface. After firing, a heating element is threaded through the core of the tube, and this is soldered with the electrode lead to the element support to form a complete sensor unit (11–14). When the semiconductor comes into contact with a toxic gas it produces a measurable electric response, due to a change in its resistance. Toxic gases at levels of ppm or even ppb may be detected with this type of sensor. However, difficulties are encountered when measuring mixtures of gases, and the linear response for quantitative measurements of this type of sensor is poor and the selectivity is inferior. After many years of investigating different surface treatment techniques for semiconductor materials and catalysts (15, 16), and applying different temperatures for different gases (16), and of using a molecular sieve as a selective filter for certain gases on the catalyst surface (16), the problem of selectivity has still not been resolved.

However, in recent years a combination of various semiconductor sensors, an alteration in working temperature, and the introduction of computer pattern recognition techniques have been tried for solving the long-term problem of qualitative and quantitative measurement of mixtures of gases. The prospects are very attractive for a breakthrough in the use of semiconductor gas sensors for detecting hazardous gases (17).

Metal Oxide Semiconductor Field Effect Sensors

Lundström in Sweden prepared hydrogen-sensitive metal oxide semiconductor (MOS) field effects sensors by using a palladium metal grid material (18, 19), and later Armagarth found that this structure is also sensitive in some degree to hydrogen sulphide and ammonia (20). As this is suitable for microprocessing and integration widespread interest has been aroused (21–23).

It is usually considered that hydrogen containing compounds, including hydrogen sulphide,

ammonia and hydrogen cyanide, dissociate out atomic hydrogen on the semiconductor grid (palladium or other noble metals) and that atomic hydrogen diffuses into the inner surface of the noble metals grid. A dipole is produced at the metal-insulator interface which causes an increase in the work function of the metal, and this in turn changes the threshold voltage of the semiconductor sensor. The change in work function is proportional to the concentration of the gas measured, and the noble metals mainly act as catalysts for the dissociation and oxidation of the hazardous gases. As the hydrogen ion is much small than other atoms it is easier for it to diffuse through most metals, (including the platinum group metals), to the inner surface. However, obtaining measurements for compounds which do not contain hydrogen is rather difficult.

In order to extend the range of measurements, studies have been undertaken on various grid materials (platinum, palladium, iridium, rhodium, etc.), fabricated by different techniques, and on different grid structures. A MOS sensor cannot usually detect a carbon monoxide molecule, for example, since it is unable to diffuse through the palladium layer to the metal-oxide interface.

In Figures 3 and 4 are shown a recently developed porous palladium layer grid structure and a double layer porous grid structure, respectively. Carbon monoxide can pass into the pores and then diffuse through the boundaries of the pores

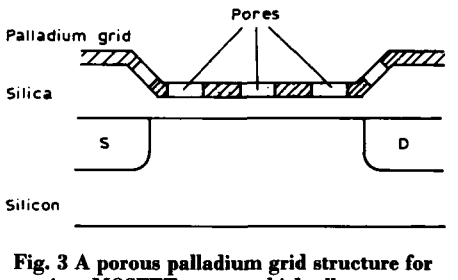

Fig. 3 A porous palladium grid structure for use in a MOSFET sensor, which allows gas to diffuse through to the semiconductor underneath. S is the source electrode and D is the drain electrode

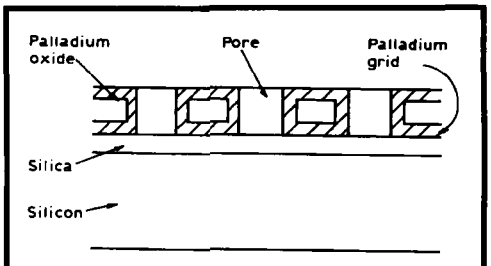

Fig. 4 A double layer porous grid structure of palladium and palladium oxide

to the inner palladium-silica interface, thus causing a change in the threshold voltage which enables the carbon monoxide concentration to be measured. Other compounds not containing hydrogen can also be detected in this way. In the past the MOS sensor has been used mostly for detecting a single component gas only, but through improvements in grid material, grid structure, fabrication techniques, and by using a combination of different sensors, as well as adopting pattern recognition by computer linkage, the detection of mixtures of gases has become possible (24, 25).

Although the MOS gas sensor has only a limited market at present, with the developments outlined above its prospects must be good.

Catalytic Gas Sensors

Most hazardous gases can be catalytically oxidised with the release of heat, therefore an accurate measurement of these gases can be achieved using the catalytic sensor (10, 26). The catalytic sensor is a fine wire wound coil, made of noble metal, usually platinum or platinum-rhodium, of known resistance. A support layer and then a noble metal catalyst is applied to the coil, followed by activation, reduction, ageing and pairing, with the reference element (11, 26). During measurement the toxic gas comes into contact with the sensor, which forms one arm of a Wheatstone bridge, the other arms being composed of a reference element and other two resistors. Catalytic oxidation takes place at a specified working temperature, evolving heat which causes an increase in resistance in the platinum coil, and results in loss of equilibrium in the

Wheatstone bridge, so giving an output of millivolt size. This output is proportional to a wide range of toxic gas concentrations, so precise measurements can be made by adopting suitable circuitry, and detection, in addition to alerting and monitoring, can be performed.

Catalytic sensors have been used for fast accurate detection, alerting to, and monitoring of methane in coal mines, and various flammable gases above ground (10, 11, 26). The lower the number of carbon atoms present in the hydrocarbon, the more difficult it is to oxidise, so that methane which is the most difficult to oxidise is often selected as the standard for measuring the total amount of flammable gases present. Catalytic sensors are not sensitive enough to detect toxic gas present in the atmosphere at very low concentrations. Now a highly sensitive catalytic sensor is being developed which will be able to detect accurately toxic gases in concentrations ranging from as low as 100 ppm to several ten thousand ppm. A much smaller sensor of lower power consumption for detection and alerting is also being developed. The author considers that the problems of qualitative and quantitative measurement of various components in mixtures of gases will be solved when catalytic sensors are linked up to computers, by combinations of several sensors of differing composition and structure, with control of requisite temperatures, and by the adoption of pattern recognition techniques.

It is anticipated that this kind of sensor will play a fuller role in the detection of toxic gases in the near future.

Conclusion

Platinum group metals function as electrodes, collectors, catalysts, grid materials, lead wires and heat-sensitive wires in the four kinds of gas sensors discussed here, for leak detection and the accurate determination of toxic gases under various conditions. They perform electrocatalysis, chemical adsorption, dissociation and catalysis, etc.

The introduction of computer pattern recognition techniques together with sensor development, will improve measuring techniques, especially for the qualitative and quantitative detection of mixtures of gases. Thus the platinum group metals are at the centre of sensor development and will continue to be so.

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