Solid-State Gas Sensors: A Review

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ABSTRACT

During the past three decades, gas sensors based either on the surface characteristics or the bulk electrolytic properties of ceramics, have been the subject of extensive research and development. The application of these sensors range from air-to-fuel ratio control in combustion processes such as in automotive engines and industrial furnaces to the detection of leakage of inflammable and toxic gases in domestic and industrial environments. While the solid-state physical sensors, measuring pressure, temperature, and other physical parameters have been commercially successful, less success has been achieved by their chemical analogs, to measure moderate to very low concentrations of gases of importance. These gases include: O₂, H₂, CO, CO₂, NOₓ, SOₓ, propane, methane, ethanol, and so on. The semiconductor-based chemical sensors owe their popularity to their small size, simple operation, high sensitivity, and relatively simple associated electronics. However, most of them still suffer from none selectivity. They also have poor shelf-life and are relatively less stable at higher temperatures. The sensing characteristics and performance of some of the solid-state gas sensors are reviewed in this paper, together with their sensing mechanism, which still is a gray area and has not been fully understood.

The recent emergence of concern over environmental pollution and efficiency in a variety of combustion processes and of increased awareness over a need to monitor potentially hazardous gases has stimulated substantial research and development in the field of gas sensors. These gases include, CO, CO₂, NOₓ (x = 0.5, 1, and 2), SOₓ (x = 2 and 3), a fraction of unburned hydrocarbons [including liquefied petroleum gas (LPG) also known as cooking or town gas] and hydrogen. Requirements to detect and monitor these gases has already led to the development of a wide variety of devices and methods, as evidenced by a large number of instruments now available commercially. The majority of these detection and/or metering devices involve the application of surface or bulk chemical and physical properties of materials and can, therefore, be called solid-state chemical sensors.¹² However, before addressing the topic of these gas sensors, it is appropriate to briefly outline some of the environmental concerns.

LP gas can form explosive mixture with ambient air and can lead to personal injury upon continuous exposure, even in small concentrations. A number of industrially important catalytic processes require either producer gas (CO + H₂) in various compositions or H₂ and CO separately as feed stocks. The producer gas is synthesized by the steam reforming of natural gases and other hydrocarbons under conditions of high temperatures and pressures. The accidental escape or leak of either CO or H₂ from such a high temperature and pressure system can be a source of explosion and health hazard.

The combustion of hydrocarbon fuels is a widely used method of obtaining useful energy in various industries. Burning of fossil fuel in the “lean-burn combustion” manner is regarded as the most fuel and energy efficient mode of fuel utilization, since under these conditions, the hydrocarbons in the fuel are fully converted into CO₂ and H₂O. However, the compositional analysis of the flue gases in most of the combustion furnaces, indicates the presence of CH₄/CO/CO₂/H₂ in the final reaction product, in accordance with the thermodynamic predictions under the conditions of these processes. This could be attributed to the occurrence of the following reactions side-by-side

CH₄ + (1 + x/4) O₂ → CO + (x/2) H₂O [1]

CH₂ + H₂O → CO + (1 + x/2) H₂ [2]

CH₂ + CO₂ → 2CO + (x/2) H₂ [3]

Thus, if there is excess fuel (fuel-rich region), CO would be the main residue product of combustion, together with a small amount of hydrogen, while if there is excess air (fuel-lean region), free oxygen would be present in the exhaust gas, together with carbon dioxide and steam. This situation exists in most conventional fossil-fuel-fired furnaces and automobile engines. At this point, it is worth mentioning that in most of the under-developed and developing countries, coal is still the most viable source of energy. At the same time, it is also the biggest source of air pollutants. Coal, when fed into furnaces, is first distilled, giving out gaseous hydrocarbons, CO, H₂ etc., leaving behind carbon, which on insufficient combustion produces smoke.¹³ Additionally, during combustion SO₂ and NO₂ are formed, both of which contribute to air and soil pollution by way of “acid rain.”

Oxides of sulfur (SO₂ and SO₃) are produced during the combustion of fossil fuels and during smelting of many nonferrous ores.¹⁴ It is necessary to monitor the concentration of these gases escaping into the atmosphere, both for process control and reduction of environmental pollution by way of forming acidic precipitant. Nitrogen oxides, NO and NO₂ (generally represented as NOₓ) are the most common and dangerous pollutants of the atmosphere.¹⁵ Nitrogen oxides are produced during the burning process (mainly energy production and transport) under high temperatures and do not decompose easily at room temperatures. Nitric oxide (NO) constitutes about 98% of the total NOₓ in the automobile emission¹⁶; though not the major emittant in exhaust gases, it is one of the most difficult to control. Together with the oxides of sulfur, these compounds contribute to the formation of acid rain, which experts very harmful environmental effects. Photolytic decomposition of NOₓ by cosmic radiations results in ozone formation, which when combined with hydrocarbons, forms smog.¹⁷ Anthropogenic sources of NOₓ are of more concern than the natural ones, because they are localized and lead to high concentration of this pollutant in ambient air.

The ultimate accumulation of carbon dioxide by fuel burning under “lean” conditions in combustion furnaces and in automobile engines, has been anticipated as the main reason for “global warming” and “greenhouse effects.”¹⁸ Rapid increase in deforestation and urbanization
has made this problem more acute than ever. It is reported that the greenhouse effect makes the Earth’s surface 33°C warmer than it would be otherwise.13 From space, the Earth would appear to be at an average temperature of −18°C. This is because long wavelength radiations from the Earth’s surface are absorbed by clouds and greenhouse gases, and much of that is back-radiated toward the Earth, making the true surface temperature about 15°C on average. The two largest contributors to the greenhouse effect are water vapor and carbon dioxide. Other gases which contribute an additional 50% of the warming of CO₂, include methane, nitrous oxides, ozone, and chlorofluorocarbons (CFCs).14 Arrhenius had estimated a 4-6°C increase in the average temperature due to CO₂ doubling in the atmosphere. Some of the numerical models show that for CO₂ doubling, European temperatures could increase by 2-8°C in the summer and by 4-16°C in the winter.15 Another model predicts summer temperatures in the U.S. warmer up to 8°C.17 Higher growth rates of plants under increased CO₂ may help, as the plants will incorporate more CO₂, but increased radiation due to the thinning of ozone layer may substantially nullify that benefit.

In view of these facts, monitoring the progress and control of combustion processes and from the viewpoints of anthropogeneous, industrial, and automobile exhaust pollution control, reliable and long-life sensors capable of detecting and measuring gases in the ambient and at the generating source are needed. Techniques such as gas chromatography and infrared absorption are widely used for accurate analysis and detection of these gases. However, installation of these conventional instruments is costly, requires a sampling system and complicated maintenance, and in situ continuous monitoring in most gaseous environments becomes time consuming and unreliable. During the past three decades, rapid growth has been seen in the sensor technology encompassing a broad spectrum covering safety, fuel economy, pollution control, medical engineering, and industrial processes. Most of the advances in the gas sensors (except, perhaps, for O₂) has been sustained by development based on rather empirical methods, and consequently a reasonable understanding of the gas sensing mechanisms is lacking in the published literature. Moreover, these sensors are often subject to deterioration with time (low shelf-life) and also to interference by other coexisting gases. From a practical standpoint, a gas sensor is useful only if it can detect the desired active component in the presence of noninterfering background constituents. That is, the sensor must be selective and must function according to the acceptable and controllable levels of sensitivity and detectability. Much work is being devoted to the development of sensitive, reliable, and low-cost expensive sensors, capable of detecting even low concentrations (tenths or hundreds of a percent) of gases such as CO, CO₂, O₂, H₂, NOx, SO₂, natural gases (CH₄), propane (C₃H₈), alcohol (C₂H₅OH) and so on.16,34–36

The objective of this paper is to review the development field of chemical sensors, with special emphasis on those based on semiconducting materials, for toxic gases and to analyze the performance and basic working principles of these sensors.

### Solid-State Gas Sensors

Based on the sensing principles, gas sensors can be classified in the following three categories: (i) solid electrolyte gas sensors, (ii) catalytic combustion gas sensors, and (iii) semiconductor gas sensors.

**Solid electrolyte sensors.**—The solid-electrolyte-based sensors owe their usefulness to the exceptionally high ionic conductivity of the solid electrolyte material in the temperature range of 773 to 1573 K. These have only one mobile species, the ion of the oxide electrolyte, and no electronic charge, and zirconia, they find wide applications. An oxygen sensor works on the principle of a concentration cell in which oxygen ion conductor (stabilized zirconia) acts as the solid electrolyte and also as a separator for the two compartments with gaseous mixtures having different oxygen potentials or partial pressures. The galvanic cell

\[ P_{O_2} \quad \text{(ref.)}, \quad Pt/YO_x-ZrO_2/Pt, \quad P_{O_2} \quad \text{(test)} \]

would develop an open-circuit electrochemical potential (EMP) by virtue of the following half-cell reactions

\[ 4e^- + O_2 (P_{O_2}) \rightarrow 2O_2^- \quad \text{(5a)} \]

and

\[ 2O_2^- \rightarrow O_2 (P_{O_2}) + 4e^- \quad \text{(5b)} \]

resulting in the net cell reaction

\[ O_2 (P_{O_2}) \rightarrow O_2 (P_{O_2}) \quad \text{(6)} \]

According to the Nernst equation, the EMP of the cell could be represented as

\[ E = (RT/4F) \ln (P_{O_2}/P_{O_2}) \quad \text{(7)} \]

The \( P_{O_2} \) in the test gas could thus be evaluated by measuring the equilibrium EMP \( E \) at a given temperature, \( T \).

Oxygen sensors based on the above principle are widely used for combustion control in heat-treatment furnaces, glass tank furnaces, ceramic kilns, boilers, oil and gas stoves and for oxygen control in steel and copper melts.39,12 However, the largest single use (>50%) of oxygen sensors is in the automobiles to improve the fuel efficiency and to control CO and NOx content in the exhaust gas.39,12 A single manufacturer (Nippon-Denso) is reported to be producing nearly 100,000,000 zirconia oxygen sensors per year, covering 70% of the Japanese market.39 The schematic of such a zirconia-based sensor is shown in Fig. 1. The basic design consists of a yttria-stabilized zirconia ceramic thimble, which is coated with porous platinum electrode on both sides. The sensor is located in the exhaust pipe, so that the exterior of the sensor is exposed to the exhaust gases and the inside is exposed to the air reference. Sometimes \( YO_x \) is partially replaced by MgO to lower the cost and increase the thermal shock resistance.39–41 The advantages of these sensors are: (i) quick and continuous monitoring, (ii) the sensor output being an electrical signal, can be easily modulated for electronic control device, (iii) accuracy, (iv) simple design, (v) weak temperature dependence, and (vi) wide range of zirconia compositions.39

These sensors, however, measure the equilibrium partial pressure of oxygen and not the true oxygen concentration, and they exhibit very poor sensitivity when the difference between \( P_{O_2} \) and \( P_{O_2} \) is small.33 It may be noted that the response of the sensor (Fig. 2), where fuel/air ratio is expressed as a mass ratio, does not entirely follow the Nernst law (Eq. 7), with the voltage being 15% lower in rich fuel/air mixtures and 10% higher in lean mixtures.39,42 This departure could be due to the fact that in a car engine, the working environment is very demanding with a life-time of several thousand hours, rapidly changing temperature, high velocity gases containing fine abrasive particles, and lead compounds (even in nominally lead-free fuels), which can poison the electrodes. Thus, in order to improve the performance and life-time of the sensors, the electrolyte is usually protected with a porous plasma ceramic coating (of spinel, alumina, or metallic shroud), which acts as a gas diffusion barrier and helps to minimize the degradation of outer electrode by the constituents of the exhaust gases.

Substantial progress has been made in recent years in overcoming the above-mentioned limitations. The most significant of these has been the development of diffusion-controlled limiting-current-type oxygen sensors based on the conventional stabilized zirconia (YSZ) as well as the tetragonal zirconia polycrystal (TZP) electrolytes.6,11 The latter appear to be more attractive, both electrochemically and mechanically, due to their higher oxygen conductivity at lower temperatures and greater durability towards thermal shocks.41 The basic configuration of the limiting current (also known as polarographic or amperometric)43–45 sensors is shown in Fig. 3. The zirconia pellet is coated with porous platinum electrodes. The cathode is enclosed except for a small hole by a porous layer of zirconia, spinel or...
alumina to let air in. A production type, resembling a conventional zirconia sensor has a built-in heater. An external voltage is applied to pump oxygen from cathode to anode. The gas sensing mechanism is believed to be virtually dominated by the diffusion of the gaseous species through the small aperture, and the limiting current is realized owing to the artificial oxygen overpotential at the cathode. Figure 4 shows the voltage-current characteristics of a typical limiting-current sensor. These I-V characteristics could be classified into three regions (i) at small voltages, the oxide ion ($O_2^-$) diffusion through the zirconia electrolyte has been assumed to be the rate-determining step; (ii) at intermediate voltages (regime of limiting current plateau), the current is proportional to oxygen concentration. The rate-determining step in this region is the diffusion of molecular oxygen through the hole; and (iii) at sufficiently high voltages (third region), the increase in current is caused by the electrochemical decomposition of zirconia itself. These sensors have been reported to be sensitive to $H_2$, $NO$, and humidity as well. In the case of hydrogen, the current is associated with the gas concentration, in $H_2$-$N_2$ mixtures, by way of the following two mechanisms: (i) reaction between the hydrogen and oxygen ions in zirconia electrolyte

$$H_2 + O_2 \rightarrow H_2O + V_0 + 2e^-$$

(ii) diffusion of interstitial hydrogen ions (protons)

$$H_2 \rightarrow 2H^+ + 2e^-$$

In analogy to the oxygen sensing, the diffusion of gaseous hydrogen through the diffusion hole is assumed to be the rate-determining step.

In the case of $N_2O$-sensing in $N_2O$-$O_2$ and $N_2O$-$N_2$ mixtures, use is made of its thermal decomposition into oxygen and nitrogen above 600 K

$$N_2O \rightarrow N_2 + 1/2 O_2$$

Therefore, by operating a limiting current oxygen sensor at temperatures well above the decomposition temperature of $N_2O$, its concentration in gas mixtures could be computed from the value of oxygen concentration. However, the selectivity of these polarographic sensors for a given gas in a mixture of two or more reactive gases is debatable. Some of the representative developments in this area are summarized in Table I. Maeda and Nagao have used $ZrMgO$ as the electrode on the test gas side in a galvanic cell configuration with YSZ as the electrolyte and have correlated the EMF response of the cell to the ratio of $CO/O_2$. 

$$\text{Current}$$

$$\text{Anode}$$

$$\text{ZrO}_2-Y_2O_3$$

$$\text{O}_2$$

$$\text{Cathode}$$

$$\text{ZrO}_2-Y_2O_3$$

$$\text{Fig. 3. Structure of a limiting current oxygen sensor with pinhole.}$$
Table I. Solid electrolyte sensors.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Composition</th>
<th>T (°C)</th>
<th>Mechanism/Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>YSZ + ZrMozO~ electrode</td>
<td>500</td>
<td>Ratio of CO/O~ is measured</td>
<td>53</td>
</tr>
<tr>
<td>H<del>2//H</del>2O</td>
<td>CaZr0.4In0.6O~ solid electrolyte</td>
<td>500</td>
<td>Limiting current type</td>
<td>37</td>
</tr>
<tr>
<td>O~2</td>
<td>YSZ</td>
<td>500</td>
<td>Applicable only to N~2O/ inert gas mixtures</td>
<td>51</td>
</tr>
<tr>
<td>H~2</td>
<td>YSZ oxygen sensor</td>
<td>500</td>
<td>Applicable only to H~2/inert gas mixtures</td>
<td>52</td>
</tr>
<tr>
<td>O~2</td>
<td>YSZ</td>
<td>650-1000</td>
<td>Pt + CeO~ electrode material for high temps</td>
<td>174</td>
</tr>
<tr>
<td>CO~2</td>
<td>Nasicon with Li-based mixed carbonate electrodes</td>
<td>800-1000</td>
<td>Working mechanism not clear</td>
<td>106</td>
</tr>
<tr>
<td>H~2</td>
<td>Antimonic acid</td>
<td>0-50</td>
<td>Protonic conduction</td>
<td>176</td>
</tr>
<tr>
<td>CO~2</td>
<td>Li§ lithium aluminotitano-phosphate</td>
<td>650</td>
<td>80 ppm to 1% CO~2 detection</td>
<td>104, 105</td>
</tr>
</tbody>
</table>

expressed in terms of the magnitude of incomplete combustion. Although the sensing mechanism of this sensor is not yet understood or theoretically explained, a further understanding and development of these or similar electrode materials might result in reliable combustion control sensors.

Yet another gas sensor for the direct, continuous, and fast measurement of hydrogen and/or steam concentrations in high-temperature gases, in situ, based on a high temperature proton conductor as a solid electrolyte, holds promise. The principle of hydrogen concentration cell is same as that of the solid-state oxygen cells and is shown in Fig. 5. The differential hydrogen partial pressures across the electrolyte give rise to a theoretical EMF represented by

$$E = (RT/2F) \ln \left( \frac{P_{H_2}^{II}}{P_{H_2}^{I}} \right)$$

where, $P_{H_2}^{I}$ and $P_{H_2}^{II}$ are the partial pressures of hydrogen in compartment I and II, respectively. A number of good proton conducting solids (such as HUO$_2$PO$_4$·4H$_2$O, H$_2$MO$_3$PO$_4$·29 H$_2$O, NH$_2$ substituted-β-gallia and β'-alumina, H$_2$O$^+$ substituted-β- and β' alumina, etc.), have been investigated, but they are unstable at high temperatures and decompose with invariable liberation of water. None of these are stable above about 673 K. Iwahara and coworkers$^{40,41}$ have found that the perovskite-type oxides based on SrCeO$_3$ and BaCeO$_3$ with partial substitution of Ce$^{4+}$ by some of the rare-earth ions (Ln$^{3+}$), are excellent high temperature proton conductors. SrCe$_{0.95}$Yb$_{0.05}$O$_3$ and BaCe$_{0.90}$Nd$_{0.10}$O$_3$ belong to this class of conductors. The EMF response of the hydrogen sensor as a function of hydrogen partial pressure, in the range from 473 to 1173 K is shown in Fig. 6. It was found that the relation between the EMF and $P_{H_2}$ was Nernstian down to about 10$^{-3}$ atm of H$_2$ in the entire temperature range.

The proton conduction in these oxides has been envisaged to be a consequence of electron holes, initially present in the crystal as native intrinsic defects. It is believed that the holes and the counter oxygen ion vacancies play an important role in the formation of hydrogen ions within the lattice and that the conduction is not influenced by the grain boundaries but by the bulk of the crystal itself. Other materials such as Cu$_2$O$^{48}$ ThO$_2$-based,$^{63}$ and LaYO$_3$-based$^{64}$ oxides, have also been studied, but their proton conductivities are much lower than those of SrCeO$_3$- or BaCeO$_3$-based oxides. Moreover, the conductivity measurements on Y$_2$O$_3$$^{67}$ and KTaO$_3$$^{68}$ also have shown these
compounds to be potential candidates for use as hydrogen sensors.

There is no report yet in the published literature, regarding the development of solid-state NO₂ sensors. However, by making use of the decomposition characteristics of NO and NO₂, indirect measurement can be envisaged in terms of NO₂ concentration by the limiting current-type cells. Gur and Huggins²⁵ had studied the decomposition of NO into nitrogen and oxygen on 8 mole percent (m/o) scandia-stabilized zirconia at 1173 K according to the reaction

\[
\text{NO} \rightarrow 1/2 \text{N}_2 + 1/2 \text{O}_2 \quad [12]
\]

The oxygen concentration from the i-V characteristic of the amperometric sensor could be used to compute the NO₂ concentration.

Another area of application of solid electrolytes is the development of SO₂ sensors. However, the measurement of sulfur or sulfur oxides (SO₂ and SO₃) is not as straightforward as the detection and measurement of oxygen, since the electrolyte are neither as stable nor as conducting. Schmalzriedt²⁶ first proposed sulfur sensors based on CaF₂ (fluoride ion conductor) and stabilized zirconia. Because of the complicated nature of electrode reactions, however, the attainment of equilibrium was sluggish and incomplete.

Since then, several modifications of the electrolytes, including those based on CaO + Ca₂O-3O₂ and Na₂S + β-alumina, have been employed. In the case of NO₂ measurement, β-alumina,²⁶⁻²⁷ Nasicon,²³⁻²⁶ and alkali metal sulfates²⁸⁻³⁰ have been widely used.

Salzano and Newman²⁸ were the first to use a sulfate electrolyte for the measurement of p₅0₂ in gases, employing a Li₂SO₄-Na₂SO₄-K₂SO₄-based molten salt electrolyte. However, the high chemical reactivity of melt salts with the electrodes as well as with the container material, together with the need to frequently monitor the change (if any) in the reference concentration, limits the application of such molten salt electrolytes. On the other hand, the solid alkali-metal sulfates are good ionic conductors, with exceptionally high conductivities (typically at 973 K, 4 x 10⁻³, 2 x 10⁻³ and 1.8 x₁⁻¹ cm⁻¹ for K₂SO₄, ²⁷ Na₂SO₄, ²⁸ and Li₂SO₄, ²⁹ respectively). However, all of these sulfates undergo phase transformations attended by large enthalpy and volume changes. As a result, microcracks are generated in the electrolyte, causing permeation of the gas. Lithium sulfate has a very large enthalpy change at the transformation temperature of Na₂SO₄, cracks develop in the protective layer, providing direct access of the gas to the Nasicon or β-alumina. Nevertheless, a layer of Na₂SO₄ is formed on the electrolyte surface. The most successful solid reference electrode for a SO₂ and/or SO₃ sensor is the Ag-Ag₂SO₄ mixture.²⁹⁻³² The Ag-S-O system is unique in that silver and Ag₂SO₄ exist as the adjacent equilibrium phases, in contrast to the usually encountered situation where an oxide phase invariably separates the metal from the corresponding sulfate. This simplifies the electrode processes to a great extent, making the reactions leading to equilibrium, very facile.

Recently, Jacob et al.²³⁻³⁵ have reported the use of CaF₂ electrolyte along with CaSO₄, as the auxiliary electrode for SO₂ measurements. However, the response was found to be very sluggish, suggesting the approach to equilibrium in this configuration to be very slow. In the case where Nasicon and β-alumina have been employed for SO₂ measurements, it was assumed that sodium sulfate forms on the surface of these electrolytes.²³ Nevertheless, once a layer of Na₂SO₄ is formed, the rate of reaction is slow and since Na₂SO₄ is a sodium ion conductor, the diffusion flux through it is limited by the trace concentration of electrons and holes. As pointed out earlier, if such a cell is cycled through the transformation temperature of Na₂SO₄, cracks develop in the protective layer, providing direct access of the gas to the Nasicon or β-alumina. This might give rise to a continuous depletion of Na₂O from the electrolyte, causing compositional, mechanical, and electrical deterioration of the solid electrolyte over long exposures. Akila and Jacob²³ have recently used the two-phase Nasicon/Na₂SO₄ couple to overcome the above mentioned problems. The possible use of K₂CO₃ and Ba(NO₃)₂ as CO₂ and NO₂ sensors, respectively, has been suggested.³⁰⁻³¹ The following cells were employed to measure the equilibrium partial pressure of CO₂ in a gaseous mixture

\[
\begin{align*}
\text{Pt, CO}_2, \text{O}_2/\text{K}_2\text{CO}_3/\text{Ag}_2\text{SO}_4/\text{Ag} & \quad [17] \\
\text{Au, CO}_2, \text{O}_2/\text{K}_2\text{CO}_3/\text{CO}_2 & \quad [18]
\end{align*}
\]

By analogy with the sensing mechanism of the alkali metal sulfates, it is assumed that the following reactions take place at the two electrodes

\[
\begin{align*}
1/2 \text{O}_2 + 2e^- & \rightarrow \text{O}^2^- & [19] \\
\text{CO}_2 + \text{O}^2- & \rightarrow \text{CO}_3^2- & [20]
\end{align*}
\]

leading to the overall cell reaction

\[
\text{CO}_2 + 1/2 \text{O}_2 + 2e^- \rightarrow \text{CO}_3^2- & & [21]
\]

Thus the Nernst equation for the EMF of the carbonate cell is

\[
E = (RT/2F) \ln (p_{\text{CO}_2}/p_{\text{CO}_3}) + (RT/4F) \ln (p_{\text{O}_2}/p_{\text{O}_3}) & & [22]
\]

If p₀₂ at both the electrodes is same, then Eq. 22 simplifies to

\[
E = (RT/2F) \ln (p_{\text{CO}_2}/p_{\text{CO}_3}) & & [23]
\]

In the case of a nitrogen oxide detector,³⁰ barium nitrate containing 1 m/o of AgCl was used as the solid electrolyte. As indicated in the electrode reaction

\[
\text{NO}_2 + 1/2 \text{O}_2 + e^- \rightarrow \text{NO}_3^- & & [24]
\]
the sensing mechanism was found to be a one-electron transfer process \((n = 1.22)\). Recently, Aono et al.\(^{11,12}\) and Imanaka et al.\(^{13-16}\) have reported the use of lithium titanophosphate as the Li-conducting electrolyte for CO\(_2\) measurements, with CaCO\(_3\) + CaO as the solid reference electrode. This material was found to be superior to Nasicon\(^{16,17}\) with respect to its chemical stability in humid and SO\(_2\) containing atmosphere. Yao et al.\(^{18}\) have reported a Nasicon-based CO\(_2\) sensor with a Li\(_2\)CO\(_3\)-CaCO\(_3\) eutectic mixture as the auxiliary electrode, showing a very fast response with response times of about 8 s or less. However, the sensing mechanisms of these CO\(_2\) sensors are not quite well understood at this stage, and a detailed work in this direction is an important area of investigation.

**Catalytic combustion sensors.**—A catalytic (or contact) combustion sensor is a single-port device, wherein the sensing material also acts as a heater. The sensor is fabricated by sintering porous, active alumina beads with a certain amount of highly dispersed catalyst (Pt, Pd, Rh, etc.). Each bead is mounted on a platinum coil. The structure of such a sensor is shown in Fig. 7. When a combustible gas is admitted, it reacts with the catalyst and burns on the platinum coil, heated to about 673-723 K by passing a current through it. The evolved heat of combustion of the gas results in further rise of temperature of the sensing element. This in turn increases its resistance. The resistance increase is then correlated to the concentration of the inflammable gas.\(^{19,20}\) The choice of platinum is due to excellent durability against high specific resistance with temperature rise, resulting in larger changes in resistance than some other high melting metals such as Ir, Pd, or Rh. These catalyst-supported sensors are more sensitive to \(\text{C}_2\text{H}_2\) than to \(\text{CH}_4\), \(\text{C}_2\text{H}_4\text{OH}\), \(\text{CO}\), or \(\text{H}_2\), and hence are mostly used for the leak detection of LP gas or town gases.

Some of the rare-earth-based perovskite-type oxides of transition metals such as Ln\(_2\)CuO\(_4\), LnMnO\(_3\), LnFeO\(_3\), and LnCrO\(_3\) have also been shown sensitive to methanol and ethanol.\(^{12,13}\) The recent advances in the development of the catalytic combustion sensors are summarized in Table II.

**Table II. Catalytic combustion sensors.**

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Composition</th>
<th>(T (^\circ\text{C}))</th>
<th>Mechanism/Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4\text{OH})</td>
<td>LaNiFeO(_3), Sn(_2)Sr(_2)FeO(_5)</td>
<td>150-400</td>
<td>Catalytic combustion of ethanol</td>
<td>112</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>Pt/Al(_2)O(_3)/Th(_2)O(_3)/Pd</td>
<td>500-600</td>
<td>Catalytic oxidation “pellistor” type</td>
<td>117</td>
</tr>
<tr>
<td>(\text{H}_2\text{C} = \text{CH}_2)</td>
<td>Al(_2)O(_3)/Pd</td>
<td>400-500</td>
<td>Highly sensitive to (\text{CH}_4)</td>
<td>118</td>
</tr>
<tr>
<td>(\gamma)-Al(_2)O(_3), 5% RH</td>
<td>180</td>
<td>Catalytic combustion type</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>(\text{SnO}_2) with hydrophobic catalyst</td>
<td>100-200</td>
<td>Catalytic combustion type</td>
<td>120</td>
</tr>
<tr>
<td>(\text{CH}_2\text{OH})</td>
<td>(\text{SmCrO}_3)</td>
<td>500-600</td>
<td>Adsorption and oxidation</td>
<td>121</td>
</tr>
<tr>
<td>(\text{CH}_3\text{OH})</td>
<td>(\text{GaFeO}_3)</td>
<td>400-500</td>
<td>Catalytic combustion</td>
<td>117, 118</td>
</tr>
</tbody>
</table>

**Semiconductor gas sensors.**—The third and the most widely studied area of solid-state gas sensors is that based on semiconductor oxides. It has been long known that adsorption of a foreign species on a semiconducting surface provides surface states, and the electrical properties of these surfaces change as a result of adsorption and/or reaction.\(^{12,13}\) Significant progress has been made to utilize this change in the semiconductor property to quantify the presence of a specific reactive gas in a gaseous mixture. Compared to the organic (\(\beta\)-napthol, phenanthrene, poly-p-dimethylaminophenyl acetylene, polybenzimidole, polyaniline, polyimidazole, etc., polypyrrole, etc.) and metal oxide counterparts have been more successfully employed as sensing devices for the detection and metering of a host of gases such as \(\text{CO}, \text{CO}_2, \text{H}_2\text{O}, \text{NH}_3, \text{SO}_2, \text{NO}_x\), etc., with varying degree of commercial success.\(^{14}\) A recent monograph by Madou and Morrison\(^{15}\) has dealt with the subject of chemical sensing by semiconducting oxides in considerable depth and detail.

The report on a ZnO-based thin film gas sensor by Sieyama et al.\(^{16}\) in 1982, gave rise to unprecedented development and commercialization of a host of semiconductor oxides, for the detection of a variety of gases over a wide range of composition. Simultaneous efforts were also made to improve the selectivity, sensitivity, and response characteristics by modifying the surface chemistry by means of catalysts.\(^{16}\) Listing all the developments in this fast growing area of detection technology in a chronological order would occupy a large volume of this paper; nevertheless, ample references will be made to most of the significant and epoch-making contributions to date. Special emphasis will be put on the aspect of sensing mechanisms of these sensors, which still is a gray area and not fully understood.

The working principle of the sensor devised by Sieyama et al. is believed to be based on the idea that, besides by the reaction with oxygen, the surface and grain boundary resistance of the oxide species on a semiconducting surface changes as a result of adsorption or desorption of a foreign species. Moreover, the chemical adsorption is very selective for different reactive gases. The experimental setup used by them is shown in Fig. 8. This sensor could detect toluene, benzene, ethyl ether, ethanol, propylene, and \(\text{CO}\) in the concentration range of 1 to 50 ppm. The sensor, however, is nonselective. Figure 9 shows the cross section of an SnO\(_2\)-based gas sensor, constructed and used by Oyabu et al.\(^{17}\) The sensor was fabricated by vacuum deposition of a thin film of tin followed by high temperature oxidation on a polished ferrite substrate with a thick \(\text{RuO}_2\) film as the heater. To increase the sensitivity of the sensor, 0.2 weight percent (w/o) Pd was added to the sensor material. This sensor could detect ethanol and carbon monoxide as shown in Fig. 10. Following this, a number of investigations were reported to enhance the sensitivity and selectivity of sensors by means of additives. Some of the specific sensor/gas systems with and without additives (catalysts) reported in the literature summarized in Table III.

In general, semiconductor materials are used as sensors of reducing agents, gases oxidizable by atmospheric oxy-
Table III. Semiconductor sensors.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Composition</th>
<th>T (°C)</th>
<th>Mechanism/Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>TiO₂ with Al, Ga, Sc, In</td>
<td>450</td>
<td>Trivalent dopants: sensitivity selectivity, fast response</td>
<td>165, 179</td>
</tr>
<tr>
<td>NO₃</td>
<td>WO₃</td>
<td>300</td>
<td>Low concentration of NO and NO₃</td>
<td>168</td>
</tr>
<tr>
<td>H₂</td>
<td>SnO₂/Figaro type</td>
<td>300-400</td>
<td>Good agreement with conventional measurements</td>
<td>180</td>
</tr>
<tr>
<td>H₂</td>
<td>TiO₂</td>
<td>25-200</td>
<td>H₂ diffusion in the lattice</td>
<td>186</td>
</tr>
<tr>
<td>CO, CH₄</td>
<td>SnO₂ pellet</td>
<td>200-300</td>
<td>Taguchi type: good for alarms</td>
<td>2</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂ + Pd</td>
<td>350</td>
<td>High operating temp: CH₄</td>
<td>28</td>
</tr>
<tr>
<td>CH₄</td>
<td>SnO₂/Figaro type</td>
<td>100-500</td>
<td>Low operating temp: CO</td>
<td>28</td>
</tr>
<tr>
<td>CO, H₂, C₂H₄OH</td>
<td>SnO₂</td>
<td>200-400</td>
<td>Operating temp. critical for selectivity</td>
<td>148</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂ with Al and Sb</td>
<td>200-400</td>
<td>Temperature pulsing</td>
<td>181</td>
</tr>
<tr>
<td>CO</td>
<td>Pt/SnO₂/In</td>
<td>40-90</td>
<td>90°C sensitive to H₂</td>
<td>182</td>
</tr>
<tr>
<td>CO</td>
<td>Pd-doped SnO₂</td>
<td>200</td>
<td>90°C sensitive to CO</td>
<td>182</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂ by spray pyrolysis</td>
<td>400</td>
<td>Higher sensitivity in thick film</td>
<td>154</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂-Ag Pd, Pt, ZnO</td>
<td>400</td>
<td>Short response time</td>
<td>125</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂ + La₂O₃</td>
<td>400</td>
<td>Sensitivity controlled by operating temp/additives</td>
<td>158</td>
</tr>
<tr>
<td>CO</td>
<td>BaMnO₃ (M = Ti, Sn)/(Cu, Pb, Ca, Ba) oxide</td>
<td>800</td>
<td>High sensitivity, quick response</td>
<td>170</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂/Pt/SnO₂/Pd</td>
<td>400</td>
<td>Change in capacitance</td>
<td>172, 172</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂</td>
<td>300-500</td>
<td>Sensitivity to CH₄/H₂ affected by % of Pt, SiO₂, Pd</td>
<td>183</td>
</tr>
<tr>
<td>CO</td>
<td>Pd-SnO₂</td>
<td>300-500</td>
<td>Temp. pulsing/doping with Sb improves CO selectivity</td>
<td>184</td>
</tr>
<tr>
<td>CH₄</td>
<td>SnO₂</td>
<td>500</td>
<td>Selectivity to CO enhanced by increasing SnO₂ layer thickness</td>
<td>185</td>
</tr>
<tr>
<td>CO</td>
<td>SnO₂</td>
<td>140-180</td>
<td>Sensitivity to CO unaffected by the presence of CO₂ and NO₂</td>
<td>185</td>
</tr>
</tbody>
</table>

Gen and gases such as H₂, CO, hydrocarbons, and other organic gases and vapors. Most of these sensors are believed to operate by adsorption of oxygen on the surface, leading to a high resistance (for n-type semiconductors such as ZnO, SnO₂, TiO₂, etc.), and the resistance is lowered when a reducing agent reacts with this surface. On the other hand, on a p-type semiconductor, reaction of the reducing gaseous species with the adsorbed oxygen, results in an overall electron donation to the substrate and causes decrease in conductivity and, therefore, increase in resistance. The other important oxygen removal process of interest and relevance is the dissociation of the lattice or by virtue of the presence of lattice defects. For this, imperfections (e.g., oxygen interstitials or anionic/cationic vacancies) must be mobile at the temperature of application. Being endothermic in nature, this occurs at low oxygen partial pressures and/or high temperatures.

As pointed out in the section on Solid electrolyte sensors, the largest market and use of solid-state gas sensors is in the automobile industry, where ZrO₂-Y₂O₃ solid electrolyte is still the material of choice for the detection of the air/fuel ratio in the automobile exhausts. The second type of oxygen sensor used for stoichiometric A/F control is the resistive-type sensor, consisting of TiO₂ material, whose resistance depends on temperature and oxygen partial pressure in the ambient atmosphere as

\[
R = R_0 P_{O_2} \exp \left( \frac{E}{kT} \right)
\]  

[25]

Thus, at a given temperature, resistance of TiO₂ is a function of \( P_{O_2} \) alone. The use of titania in an internal combustion engine was first reported by Ford Motor Co. in 1975, followed by the use of a TiO₂ pellet sensor by Nissan Motor Co. in 1982, and a heated thick film type in 1985. Since the resistance of TiO₂ depends exponentially on temperature, the sensor requires either a heater or a thermistor for temperature compensation. Porous titanium dioxide ceramic pellets embedded with Pt wires, essentially make up the sensor; porosity facilitates faster equilibration, and the response time could be considerably shortened by impregnating the sensor with Pt. Figure 11 shows the dependence of the output of a TiO₂ sensor when the thermistor is also used as a load resistor. The introduction of thick film technology in the fabrication of TiO₂ sensors has yielded the fastest A/F sensors and has also made the incorporation of heaters in the sensor structure for improved performance and durability, simple. The advantages of this sensor are the small size, simplest design (since no reference electrode is required), and low cost. As was also pointed earlier, when leaded gasoline is used, lead deposits poison the Pt electrode of the zirconia sensor, making the triple-point ief-
ective for oxygen exchange; low melting lead glasses may also form. Under such circumstances, the TiO\textsubscript{2} sensor performs better than the zirconia counterpart.

Semiconducting CoO, \textsuperscript{151} CoO-MgO, \textsuperscript{156} SrTiO\textsubscript{3} (doped with Al\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, or MgO) \textsuperscript{111} have also been proposed as lean-burn oxygen sensors. Another potential material under study for A/F control is Nb\textsubscript{2}O\textsubscript{5}. \textsuperscript{189} Semiconducting Nb\textsubscript{2}O\textsubscript{5} thin film sensors appear to possess lower temperatures, may desorb or transform to O\textsuperscript{-}. \textsuperscript{39,40} The reduction of oxygen in ZnO in accordance with the reaction represented by Eq. 26. The effect of hydrogen and oxygen chemisorption, on the electrical conductivity of ZnO has been extensively studied in the literature. \textsuperscript{148-154} It has been shown that the chemisorption properties and the resistivity characteristics of ZnO are very sensitive functions of the type of sample (pellet or powder) and kind of pretreatment given to the oxide. The resistivity values even at room temperatures are different within a batch of samples, prepared under identical conditions. Moreover, the temperature-programmed desorption and other measurements show that the O\textsubscript{ad} to O\textsubscript{ds} conversion occurs at about 473 K, O\textsubscript{ad} desorption at 523 K, and the lattice oxygen may be removed at a slightly higher temperature under vacuum. \textsuperscript{155} Another problem is the hydrogen diffusion, since the bulk diffusion of hydrogen in ZnO might cause slow (and sometimes irreversible) changes in bulk resistivity.

Titania becomes semiconducting when at high temperatures Ti\textsuperscript{4+} and Ti\textsuperscript{3+} ions coexist in the lattice. \textsuperscript{147}
Even though, in most of these sensors the primary mechanism of operation is through the changes introduced in the surface conductivity by chemical reactions occurring on the surface, the change in conductance depends a great deal on the physical nature of the sensor element. For example, for sintered pellets or powders, the changes in conductance are greatest at the grain boundaries. For thin films, the oxygen-induced depletion width might involve the entire film, but thick films where this does not occur, may involve a combination of factors.147

One of the main problems with tin oxide as well, as other gas sensors, is their lack of selectivity; they appear to respond to a wide spectrum of reducing gases, thereby making it difficult to assign the signal to a particular gas of interest in a mixture of several. One method is the use of thermal cycling of the sensor element.148,149 As different reducing gases react at different rates as a function of temperature, varying the temperature in a cyclic manner could lead to unique signatures of the gas of interest. In some cases, thermal cycling has also been reported to cause a great increase in the sensitivity of detection. Besides this, two more techniques have been used for obtaining selectivity to some extent in semiconductor sensors for combustible gases. One is the use of "filters," where only the gas(es) of interest can reach the sensor, while the gases that are of no interest are adsorbed.127 The other, most common approach to selectivity is through the use of catalysts and promoters. In order to promote the gas sensitivity, additives of various kinds have been employed (cf. Table III); these materials effectively influence the semiconducting properties of the sensor material. The reactions may proceed via the additives supported on the semiconductor sensor rather than directly on the sensor surface. Addition of a noble metal (such as Pt, Pd, etc.166), or an alloy of noble metals (such as Pd/Au), has been long known to enhance the sensitivity and selectivity of the sensor elements. While the noble metals Pd and Pt tend to catalyze complete combustion of hydrocarbons to CO2 and H2O, some oxides such as CuO and V2O5 have been reported to cause partial and selective oxidation.127 In some cases, the oxides together with Pt or Pd have been used to impart some selectivity. For example, in the study of Nitta and Haradome152 and Chiou et al.,154 ThO2 was added to increase the sensitivity to CO of a Pd- and MgO-catalyzed SnO2 sensor. These authors reported that the addition of ThO2 increased the CO sensitivity and decreased the hydrogen sensitivity. It was suggested that thoria removed the hydroxyl radicals from the SnO2 surface, allowing more oxygen adsorption to accelerate the CO oxidation rate. However, such a reaction might be facilitated at fairly low temperatures only. In some cases use of elemental Cr and Sb has also been reported to bring about selectivity; nevertheless, the precise role of these additives is not yet known and the explanation for most of the observations are based on pure speculations.155,156 Therefore, low selectivity, poor sensitivity at low gas concentrations, and a lack of clear understanding of the sensing mechanisms are some of the problems associated with semiconductor sensors, and are yet to be resolved.
Yamazoe\textsuperscript{157} has stressed the need to differentiate the receptor function (to interact with the reactive gases) from the transducer function (to transduce the effect of interaction into signals). The receptor function is provided by the semiconductor surface and the foreign metals and/or oxides if present, while the transducer function largely depends on the microstructure of the sensing element, especially on the size of crystallites relative to the Debye length. Nevertheless, both these functions are strongly dependent on various factors (such as the grain size, role of metal sensitizer, and gas-selective sensitization, etc.), which give rise to rather complex outcomes in sensitivity and selectivity. Based on XPS measurements on Pd-modified SnO\textsubscript{2} sensors, Yamazoe \textit{et al.}\textsuperscript{156} have distinguished two types of interactions, chemical and electronic, leading to sensitization. In chemical interaction, the additives assist the redox processes of semiconductive oxides, whereas in electronic interaction, the additives interact electronically with the semiconductor as a sort of electron acceptor or donor. This causes a change in the electronic states of the additive, which in turn causes a change in surface conductivity. Xu \textit{et al.}\textsuperscript{159} have studied the correlation between the gas sensing characteristics of SnO\textsubscript{2}-based sensors, where SnO\textsubscript{2} grain size was controlled by the addition of several dopants. It was found that the gas sensitivity increased with decreasing crystallite size (of the order of 5-10 nm). They interpreted the observed correlation in terms of the relative magnitudes of the crystallite diameter ($D$) and the Debye length ($L$). As $D$ decreases and becomes closer to 2$L$, the space-charge region is believed to become more dominant in each crystallite of the sensing material. Thus the electric resistance would become more sensitive to the reactive gases. In the case of the sensor doped with rare-earth- or alkaline-earth metals or with Ni and Zn (more or less stable valency), the crystallite size was about 5 nm (close to 2$L$; for SnO\textsubscript{2}, reported $L = 3$ nm), and in these cases the gas sensitivity was found to be exceptionally high.

Substantial work has been carried out in the authors’ laboratory to identify new semiconductor oxide materials, or to tune the known semiconductors by proper chemistry variations for their application as CO and H\textsubscript{2} sensors in combustion furnaces and in automobile exhaust systems at temperatures $\sim$773 K and higher. Azad \textit{et al.}\textsuperscript{160} have recently developed a new carbon monoxide gas sensor based on MoO\textsubscript{3}. It was found that the MoO\textsubscript{3} thick films could be used as on/off type detectors, whereas those based on thin films and the two-phase mixture of ZrO\textsubscript{2}-MoO\textsubscript{3} (1:2 molar ratio) could be employed for measuring the concentration of CO gas in the fuel-fired furnaces. Figure 14 compares the patterns of resistance change of MoO\textsubscript{3} film with that of a two-phase binary mixture of ZrO\textsubscript{2} and MoO\textsubscript{3} in the presence of CO. It is evident that the binary mixture showed strikingly different behavior towards CO. In the case of sensor made from pure MoO\textsubscript{3} (both in thick film and sintered pellet configurations), the resistance decreased rapidly in the presence of small concentrations of CO in the gas stream and reached a value which was several orders of magnitude lower than that before the introduction of CO in the furnace. In contrast to this, the resistance of the sensor made from the two-phase mixture of MoO\textsubscript{3} with ZrO\textsubscript{2}, dropped monotonously and gradually with increasing CO concentration and seemed to reach saturation, for concentrations greater than about three volume percent (v/o) of CO. Incidentally, the thin films of MoO\textsubscript{3} deposited on zirconia substrate exhibited similar behavior. Such behavior, according to these authors, might suggest the possibility that zirconia, present as a second phase, plays a definite role. It is believed that zirconia might act as a “low activation energy” diffusion barrier for the oncoming CO, causing the resistance of the sample to drop continuously in a steady fashion. This would continue until saturation level in the resistance is reached for a given CO concentration. In a binary mixture such as this, the grain boundary effects, however, cannot be ruled out. Moreover, there is a possibility that in the case of thin films of MoO\textsubscript{3} on zirconia substrate, the film might actually consist of a two-phase mixture of ultrathin thinness, rather than of pure MoO\textsubscript{3} on an inert substrate.

The sensitivity and response time of MoO\textsubscript{3}-based sensors were greatly improved by the addition of small amounts of palladium, as shown in Fig. 15 and 16. Typically, a 2 w/o...
Pd-doped MoO₃ film took 3 min, compared to 17 min taken by an undoped film, when 0.5 v/o of CO gas was introduced. The XPS analyses of the thick as well as thin film samples of MoO₃ sensor elements after their exposure to CO gas were found to unequivocally establish that the redox processes involved were primarily surface dominated. On the basis of these experimental evidences, a sensing mechanism, operative in MoO₃-based sensors has been postulated,

where the chemical reaction of CO with the lattice oxygen is the predominant factor in governing the resistance change of the sensor. As pointed out earlier, in the gas sensor technology, it is generally accepted that the chemisorption or ionosorption of "nucleophilic" O⁻ ions on the surface of an n-type semiconductor creates a thin layer of high electric resistance. When these chemisorbed or ionosorbed oxygen species are consumed by a reducing gas, the net result is an accumulation of free electrons, which is manifested in the form of increase in conductivity. Oxygen, however, cannot be chemisorbed on undoped stoichiometric n-type oxides. On the other hand, from thermodynamic considerations, a defect structure consisting of bulk oxygen vacancies and interstitial oxygen ions acting as donor species is always present. This allows for either (i) the adsorption of a small fraction of a monolayer of oxygen ions, or (ii) the formation of additional donors near the surface. Based on the experimental evidence, Azad et al. concluded that the latter might be the case with MoO₃-based sensors. A schematic of the defect surface of the sensor is shown in Fig. 17a, for which the following defect equilibrium could be written in terms of the Kröger-Vink notations

\[ O_o \rightleftharpoons O_i^- + V_b \]  

And the reaction of CO with the surface might occur as

\[ CO (g) + O_i^- \rightleftharpoons CO_2 (g) + 2e^- \]  

or

\[ CO (g) + O_o \rightleftharpoons CO_2 (g) + V_0 + 2e^- \]  

where the defect symbols have their usual universal significance.

It was concluded that the experimental results were in better conformity with the reaction of CO as per Eq. 33 rather than Eq. 34. At the saturation level, an almost complete consumption of O⁻ species on the surface has been postulated and a hypothetical schematic of the reduced surface (MoO₃₋ₓ ν ≤ 1; in this case ν = 1) is shown in Fig. 17b.

Turning on air or oxygen at this juncture is likely to anneal the oxygen vacancies on the surface, regenerating the original surface. The reoxidation of the oxide lattice may be represented by Eq. 35a-d

\[ O_3 + e^- \rightarrow O_{2,ads} \]  
\[ O_{2,ads} + e^- \rightarrow O_i^-_{,ads} \]  
\[ O_i^-_{,ads} \rightarrow 2 O_{ads} \]  
\[ O_{ads} + V_0 + e^- \rightarrow O_o \]  

Madou and Morrison have also suggested a similar scheme.

The enhanced sensitivity of the Pd-doped MoO₃ sensor was explained by the above mentioned scheme, with the recognition that Pd plays a role of catalyst in the MoO₃ matrix and promotes the sensitivity by providing adsorption sites to the oncoming CO gas, which then reacts with the MoO₃ surface. The following sequence of reactions have been postulated in the presence of Pd

\[ CO (g) \rightarrow CO_{ads}(Pd) + e^- \]  
\[ CO_{ads}(Pd) + O_i^- (MoO_3) \rightarrow COO_{ads} \]  

or

\[ CO_{ads}(Pd) + O_o (MoO_3) \rightarrow COO_{ads} + V_0 \]  
\[ COO_{ads} \rightarrow CO_2 (g) + e^- \]  

The formation of adsorbed carboxylate ion on several oxides has been reported in the literature.

Birkefeld et al. and Akbar et al. have investigated TiO₂-based semiconducting oxides as a potential sensor material for reliable detection of CO and H₂ gas in the temperature range of 773 to 1073 K. They report significant change in the sensing characteristics of the anatase modification of TiO₂ when it was admixed with an insulating second phase such as α-alumina or yttria. In the case of alumina dispersion in the TiO₂ matrix, the sensor response was found to be exclusively dependent on the hydrogen concentration alone in the gas phase; the presence of CO or CO₂ did not affect the sensitivity (Fig. 18). On the other hand, the sensitivity for both CO and H₂ was enhanced when yttria was used as the dispersoid (Fig. 19). Creation of a space-charge region at the interface, the nature of which solely depended on the type of the second phase, is believed to be responsible for the observed beneficial effects.
Several preliminary research works have been reported in the literature to develop NO sensors based on semiconducting oxides and an In dopant. TiO2 sensor has been commercialized. However, these sensors are poor to modest in their sensitivity to either NO or NO2. Recently, Akiyama et al. have identified tungsten oxide (WO3) as a highly sensitive material for NO (0–200 ppm) and NO2 (0–800 ppm) in the temperature range of 473 to 773 K.

There has been relatively much less work on humidity sensors, based on semiconductor principles, where the humidity could be measured by the increase in conductivity due to the "donor-like" behavior of adsorbed water on semiconductors. However, from a chemical point of view, due to the "donor-like" behavior of adsorbed water on midity could be measured by the increase in conductivity in the literature to develop NO sensors based on semiconductors, in the sense that CO2 also happens to be chemically but derives some support from indirect experimental evidence.

in the density of adsorbed negatively charged oxygen ions. The polar water molecule, adsorbing adjacent to oxy-

derived from the valence or conduction band of most of the semiconductors. Morrison has suggested that the electron injection is not from the water molecule but from the adsorbed oxygen ions. The polar water molecule, adsorbing adjacent to oxy-
gen ions changes the energy level and the rate of electron injection and extraction of the latter, resulting in a net loss in the density of adsorbed negatively charged oxygen ions. Such a highly hypothetical model may or may not be valid but derives some support from indirect experimental evidence.

Semiconductor-based sensors for CO2 are like humidity sensors in the sense that CO2 also happens to be chemically stable compound and has little tendency to inject or extract electrons from a semiconductor. From this point of view, semiconductor sensors for CO2 are not so common. On the other hand, CO2 has a tendency to adsorb on oxides with local bonding, making a carbonate-like structure, that may change the intergranular conductance (by changing the conduction band edge, for example) or may change the adsorption site for oxygen. Either of these possibilities could indirectly change the conductance of a pressed semiconductor pellet and thus make it CO2 sensitive. A change in capacitance can be used for CO2 detection, since the dielectric constant of oxides generally differ from that of carbonates. Based on these concepts, Yoshinaka et al. have reported the CO2 sensing capability of metal oxide-modified SnO2 element. Among the various metal oxide dopants used (as many as 16 different oxides were investigated), those based on RuO2 (R = La, Pr, and Nd) were found to be the most efficient in terms of sensitivity and the 90% response time. Recently, Ishihara et al. have demonstrated the potentials of NiO-, CuO-, and PbO- BaSnO3 and CuO- BaSnO3 mixed capacitors as selective carbon dioxide sensors over a wide range of concentrations (50%) and temperatures (400–800 K). However, the application of these sensors is limited to the oxidative environment, since some of the transition metal oxides mixed with BaTiO3 or BaSnO3 (e.g., CuO or NiO) might get reduced to lower oxides (Cu2O) or the respective metal. Ishihara et al. also proposed a three-step detection mechanism, operative in these sensors: adsorption of CO2, carbonation of the second-phase oxide, and the joint grain effect. These workers have also emphasized that the capacitance changes of the sensor element were caused mainly by the carbonation of the oxide, since the optimum operating temperatures of CO2 detection showed a good correlation with the decomposition temperature of the carbonate corresponding to the metal oxide. However, much work needs to be done in this area, since CO2 sensing is an important aspect of environmental safety from the viewpoint of global warming.

Summary

Gas sensors can be broadly categorized as semiconductor sensors, catalytic combustion sensors, and solid electrolyte sensors. A variety of sensors responsive to gases such as CO, CO2, O2, H2O, NO2, CH4, C2H6, C3H8, have been developed. These ceramic sensors are easy to use and offer viable alternatives to several conventional techniques such as gas chromatography and infrared absorption, and they can also be used for hazardous gas alarms and leakage detectors. Sensors measuring the equilibrium as well as the true oxygen concentrations, detectors able to measure the CO to O2 ratio, which is a measure of the degree of combustion, are also available. Although extensive advances have been made in the sensor technology, problems such as poor selectivity with respect to the interference of ambient gases, a lack of understanding of the sensing mechanisms, and aging have to be overcome before reliable instrumentation can be designed. Further research in this area should lead to the development of reliable sensor systems, which when used with the available electronics and software, are anticipated to aid greatly in the design of intelligent industrial processes with efficient emission control.

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