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# Electrochemical Sensors for Monitoring of Indoor and Outdoor Air Pollution

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Additional information is available at the end of the chapter

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## Abstract

This chapter aims a comprehensive presentation of the most common electrochemical sensors used in the real monitoring applications of air purity testing. Oxygen, hydrogen, hydrogen sulfide, nitrogen oxides, carbon monoxide and carbon dioxide are gases, which can be accurately detected and measured. Too high or too low oxygen concentration levels make the air improper for breathing. Hydrogen sulfide and carbon monoxide are dangerous species; any leakage needs to be pinpointed. A calibrated network of sensors for monitoring gas detection makes it possible to easily locate the source of gas escape during indoor air monitoring. The air quality monitoring stations based on electrochemical sensors are nowadays used to determine the global pollution index of the atmospheric air, in order to prevent the risks toward the human health and damage of environment, especially in the highly populated and industrialized urban areas.

**Keywords:** electrochemical sensors, sensing mechanism, semiconductive oxides, sensing surface, nanoparticles

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## 1. Introduction

Some dramatic changes in the atmospheric chemistry occurred in the last few decades in tight connection with the intense economic overall development of the human society. The highest advances are noticed in the field of energy, transportation, communications and production of numerous daily commodities as cosmetics, hygiene and care products, and pharmaceuticals. This progress had to pay a high price on the quality of the environment in terms of atmosphere, soil and water pollution, climate changes induced by human activities, deforestation and contribution to global warming.

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The detection of various gas species with polluting effects as carbon monoxide, hydrogen sulfide, nitrogen and sulfur oxide, ozone, in both indoor and outdoor air, is a challenging priority worldwide, due to their complex and destructive effects on the environment. Even low concentration values of these species are associated with risks toward human health and generalized damage to ecosystems. Therefore, the detection of gases using electrochemical sensors earns continuous popularity. “Four S” requirements can be formulated and related to chemical sensing: sensitivity, selectivity, stability and speed of response. Nowadays, sensors also bring high reproducibility, robustness, relatively simple setup and involve low electricity consumption for the detection of various gaseous species and concentrations over a wide range of operation conditions, for indoor and outdoor air [1].

On an electrochemical gas sensor surface, the detected molecules undergo a redox reaction on a suitable electrode, generating an electrical current depending on the gas concentration. The sensitive layer from the sensing surface plays the role of a *receptor*. Specific functional surface groups allow the adsorption or chemisorption of the detected species, sometimes followed by combustion or other chemical reactions involving electron transfer. The receptor is connected to a *transducer*, a device which transforms the atomic scale interaction to an electrical measurable response. The changes of the physical properties of the receptor surface due to the interaction with the sensed molecules refer to electron density, optical properties and mass or temperature. The receptor of most electrochemical sensor systems is based on semiconductive metallic oxides (SMO) and the changes during the interaction of a gas involve changes of the electronic charge density and charge carrier mobility [2].

The complex requirements connected to the need of fast and reliable measurement of various gas species, using portable devices if possible, switched the designers and manufacturers interest toward miniaturized setups, usually embedded in so-called sensor arrays. An important advantage of these devices is their extremely high selectivity, possible to reach by performing the signal processing with appropriate software. These advances became possible due to the application of advanced microelectronic and microelectromechanical systems (MEMS) processing.

Different nanomaterials (mainly nanoparticles and nanowires) have also been used in the last few decades in the formulation of sensing layers for the electrochemical sensors. These structures have, on one part, high surface areas and, on another part, the nanosize of the particles or wires from the sensing structure, which makes it possible to be a special matching between the surface and the adsorbed chemical analytes. This fact makes it possible to be used for the manufacturing of sensors with high improvement of the sensitivity level.

A sensor's response to a chemical compound is usually expressed by comparing the signal in the presence of an analyte with the signal in pure air or in an inert gas. The response can thus be the difference or the ratio between the signal values in the absence and presence of the sensed species, as well as the derivative or integrative change with time of the initial signal associated with the presence of a chemical species [2, 3].

In this chapter, a brief description will be given about the sensing mechanisms; then the most popular materials used in the chemical sensing, outlining the role of the nanoporous structure

of the sensing layer will be reviewed, and finally, some examples of practical applications of chemical sensors for dangerous gases will be displayed.

## 2. The principles of gas sensing

During the detection process, some physical or chemical interactions occur between the measured gas and certain specific sites from the surface of the sensor. Sometimes, the changes are even deeper, so the electronic structure of the bulk phase of the sensing material is also affected. In most cases, while the gas interacts with specific sites from the sensing surface, the electronic structure of the solid is highly perturbed and can be converted to measurable electrical properties. It is important to mention, especially for the sensors based on sensing nanostructures (nanoparticles, nanowires, quantum dots), that the interactions take place at atomic level. The sensing layer, which is in direct contact with the gas, is called *receptor*. The interaction between the receptor and the gas induces several changes in measurable parameters of the layer as electrical charge, polarizability, electrical potential or initiating heat generation, changes in mass (detected by measuring the resonating frequency) or optical properties. The signal from the receptor is transformed in a measurable output by a *transducer*. The transducer's role highlights the importance of the receptor microstructure, since the packing extent of the particles has an overwhelming influence on the quality of the signal.

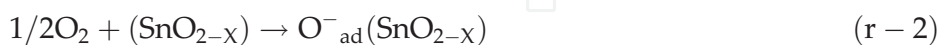
The physical parameters used as output signal are very diverse and depend on the sensed species and receptor composition, transducer's detailed structure, detected species concentration range, required sensor accuracy in detecting and/or measuring, detailed design of the sensing device, working conditions, possible interfering between the target species and other gases from the environment, allowed energy consummation, etc.

A classification of the types of sensor systems, based on the sensing mechanisms, indicates the following categories [2]:

1. Measuring the electrical resistance or impedance changes occurring on thick film metals or metal oxides or conducting polymers, printed on interdigitated electrodes;
2. Amperometric and potentiometric sensors, based on electrical current changes;
3. Capacitive sensors, measuring the electrical capacitance of the layer of metal oxide semiconductor;
4. Field effect transistors (FETs), based on the changes of the work function or polarization of the layer;
5. Acoustic wave resonators, by measuring the mass changes of the bulk or of the surface;
6. Pellistors, thermistors or thermopiles, based on temperature changes;
7. Optical sensors, following the changes of the optical adsorption or reflection due to changes in refractive index and optical layer thickness;

8. Surface plasmon resonance (SPR) sensors, measuring changes in the incidence angle for the start of a surface plasmon, due to changes in refractive index.

The most common parameter modified during the gas exposure of the sensing layer is the value of electrical resistance of the layer. The reason for this behavior is the chemical reaction between a reductive gas species, chemisorbed on the sensor surface, and oxygen from its network. Typically, tin or titanium oxides are appropriate providers of oxygen. The sensors are effective at relatively high temperatures (150–500°C), where the semiconductive oxides become quite good conductors. The reductive gas could be hydrogen or carbon monoxide.



When the combustible (reducing) gas consumes the oxygen from the semiconductive material, the amount of oxygen ions from the oxide network decreases and so does the value of the electrical resistance. As soon as the environment of the sensor gets enriched in oxygen, it oxidizes the SnO to SnO<sub>2</sub> again (**Figure 1**).

The electrochemical cells, operating in the potentiometric or amperometric mode, are nowadays the most common gas sensors.

In both cases, the gas diffuses to the working electrode to the sensing area of the sensor through a porous membrane. On the electrode, the gas reacts by oxidation or reduction reactions, giving rise to an electric current, which is taken as a signal by the external circuit. In case of amperometric sensors (**Figure 2**) (two electrode sensor), the measured signal is amplified and further processed, while maintaining a voltage between the working and counter electrodes. In case of potentiometric sensors, the work function requires a three-electrode sensor and the voltage is kept between the working and reference electrodes for a three electrode cell (**Figure 2**). The oxidation and reduction reactions occur in opposite pairs, so if at the working electrode takes place an oxidation; at the counter electrode will take place a reduction.

The amperometric sensors are the most used electrochemical gas sensors, due to linear dependence of the generated current with the gas concentration. In the electrochemical cell, the equilibrium is not established, the current being related to the rate of the electrolytic process occurring at the sensing electrode (named working electrode), whose potential is kept constant using another electrode (named reference electrode). The third electrode is also called counter electrode and is included in an electrochemical sensor (the cell is also called three-electrode sensor). Therefore, the operation of an electrochemical sensor requires a potentiostatic circuit.

The value of the developed current is proportional to the amount of the target gas oxidized on the working electrode. The design of sensors is usually manufactured so that the gas supply to the sensing area is limited by diffusion, in order to obtain a sensor signal linearly proportional to the gas concentration. The signal linearity is an important advantage of the electrochemical sensors compared to other sensor types, in which case, the signal must be linearized. Together with the simplicity of signal interpretation, the linear output allows making more

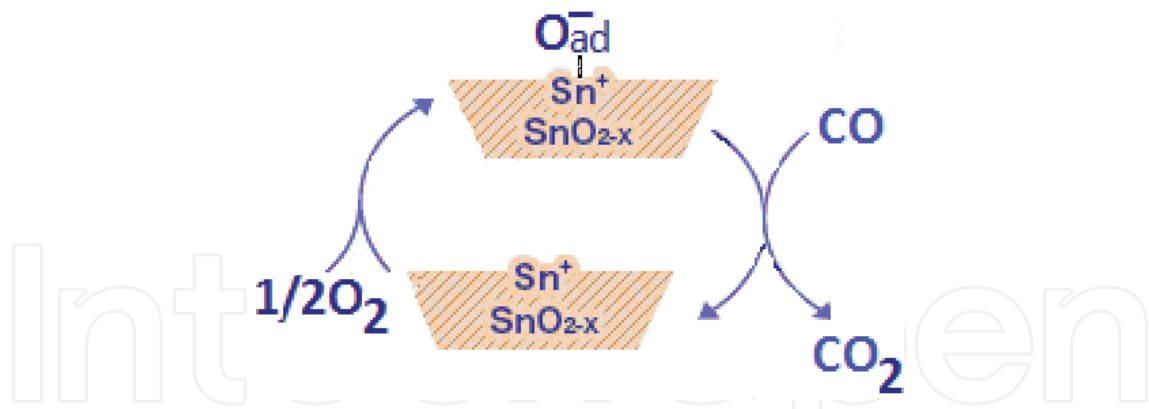


Figure 1. Scheme of the reaction between CO and adsorbed oxygen  $O_{ad}$  on the  $SnO_2$  surface.

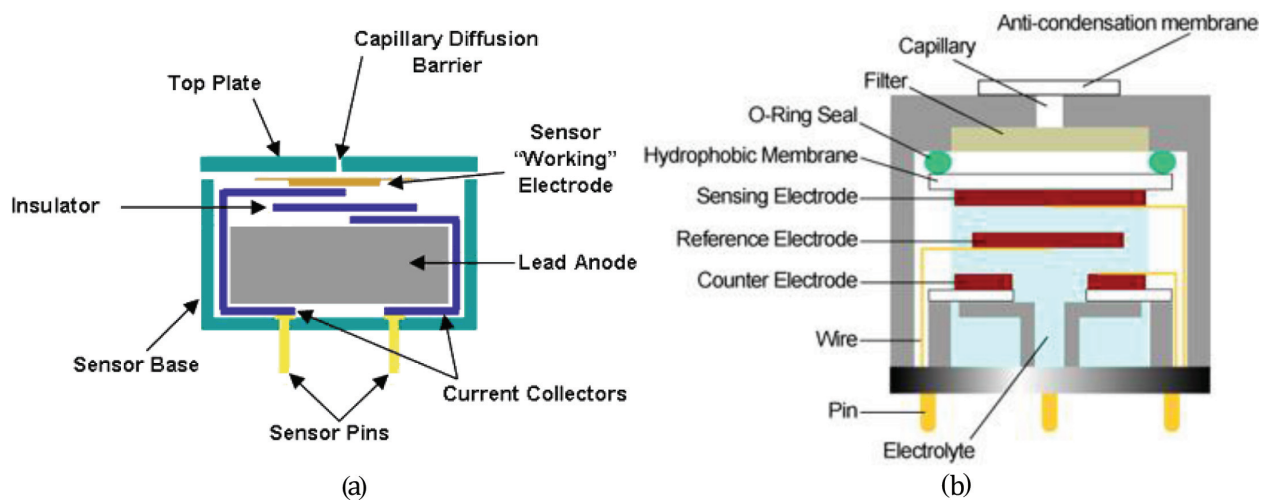


Figure 2. (a) Amperometric cell sensor and (b) potentiostatic cell sensor.

precise measurements at low gas concentrations and the calibration procedure becomes a lot simpler calibration. The diffusion control also allows the sensor manufacturer to tune the sensor to a particular target gas concentration range by simply changing the diffusion barrier. Finally, the calibration of electrochemical sensors could be more stable on time and decrease the operation costs due to less maintenance needs. The sensor sensitivity could be calculated based on the diffusion properties of the gas path into the sensor. However, attention has to be paid to the possible experimental errors in the measurement of diffusion properties [4].

The detailed manufacturing of these electrochemical sensors comprises the use of a membrane filter (MEMBRAPOR), which performs a preliminary cleaning of the target gas molecules from dust and water vapors; then the gas flow is directed through a capillary to a second filter and finally through a hydrophobic membrane, before reaching the sensing electrode surface. On the sensing electrode, the detected molecules are readily oxidized or reduced on the active catalytic sites from the surface, generating or taking electrons according to the behavior of the species to be detected (reducing or oxidizer gas) and generating an electric current. This approach is used to control mechanically the amount of gas molecules entering the sensor by



diffusion through the capillaries. The simple principle of electrochemical detection is respected, and the sensing optimization can be done in line with the desired measurement range, by regulating the gas amount reaching the sensing area till the electrical signal value considered adequate is obtained.

The role of the catalytically active surface is expected to reach a high reactivity toward the target gas and inhibit the possible undesired interfering responses; therefore, the chemical composition, preparation method and activation of the sensitive solid are crucial in designing the sensing electrode.

An important advantage of the MEMBRAPOR gas sensor is that the signal obtained is connected rather to the target gas concentration than to its partial pressure. So, the sensor can be used at different altitudes (even underground) and the results are independent of the pressure when the device was calibrated.

One of the most common and widely used amperometric sensors is the technical device installed currently on the exhaust pipe from automobiles, named lambda probe. The role of the device is to measure the oxygen concentration after the engine. This value is related to the correct air-to-fuel ratio in the engine and determines the pollution level of the combustion. The air-to-fuel ratio can be regulated by the air admission in the engine and is controlled by the electronic control unit of the car. The proper air-to-fuel ratio (as near as possible to the stoichiometric ratio) is necessary to settle, in order to avoid both the nitrogen oxides formation from the air oxygen and nitrogen, on one hand, and for the complete burning of the fuel, on the other hand.

The working principle of the lambda probe is the measurement of the electromotive force (EMF) generated across a layer of ion solid electrolyte (usually, yttria-stabilized zirconia, YSZ) included in an electric circuit. The trivalent dopant from the framework of the tetravalent zirconium oxide generates oxygen vacancies, on which oxygen can be adsorbed as  $O^{2-}$  ion at temperatures above  $300^{\circ}C$ :



The solid structure of the semiconductive material allows a high mobility of the  $O^{2-}$  ions (behaving as a solid electrolyte), so they migrate through the YSZ layer from one face to the opposite one, where they lose the captured electrons and desorb as  $O_2$  molecules.



This couple of reactions can be valorized in terms of sensor signal either by a potentiometric device or by the amperometric method.

The electromotive force (E) induced across the electrolyte can be expressed by the relation:

$$E = \frac{kT}{nq} \int t_{ion} d(\ln P_{O_2}) \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $n$  is the number of transferred electrons,  $q$  is the electron charge, and  $t_{ion}$  is the ionic transference number. The expression can be simplified for the equations above to the form:

$$E = \frac{RT}{4F} \ln \frac{p_1}{p_2} \quad (2)$$

where  $R$  is the universal gas constant,  $F$  is the Faraday number, and  $p_1$  and  $p_2$  are the partial pressures of oxygen on the two sides of the electrolyte. This relation is known as the Nernst equation.

When the oxygen concentration is measured by the potentiometric method, the electromotive voltage  $U$  associated to the oxygen ions circulation within the sensing layer generates is measured. The value of  $U$  is of course proportional with the difference between the partial pressure of oxygen on the two sides of the zirconia layer [5].

When the amperometric method is used, a current applied between the two sides of the sensing layer crossed by oxygen intensifies the circulation of the  $O^{2-}$  ions and the intensity due to their migration can be measured. Zirconium oxide doped with yttrium oxide is thus used as an "oxygen pump" transporting the gas from one face of the sensing layer to the other. The current intensity thus generated is a measure of the amount of oxygen transported through the layer [6].

The adequacy of a potentiometric oxygen sensor versus an amperometric one depends on the expected oxygen concentration. When the concentration range is wide (case of gasoline engines, where the oxygen ratio must be near the stoichiometric ratio), potentiometric sensors are preferred, despite their intrinsically low sensitivity. In the case of Diesel engines, in order to avoid soot formation, a lean-burn ratio is used; therefore, an amperometric mode is utilized for oxygen detection. This relies on the fact that a limiting current, proportional to the partial pressure of the gas, but independent of applied voltage, is reached when mass transfer across the electrolyte becomes limited by diffusive flux of gas toward the electrode, where the electrochemical reaction takes place, generating this current. The sensing principle is sketched in **Figure 3**.

Sensors based on this principle are now being applied in diesel-engine equipped cars operating under lean-burn conditions. A key challenge for such sensors is that the limiting current depends on the morphology and catalytic activity of the electrodes, which change in time, during operation.

This type of sensor has a good reproducibility, adapts easily to various design versions and works in a wide range of oxygen pressure values. Drawbacks and limitations include the high temperature required for a good working function, the difficulties connected to the sealing of the measuring cell and the interference of other gases possibly present in a real environment mixture. Another attention reason is that the concentration of partial pressure of oxygen in the exhaust gas from engines changes very much (several orders of magnitude). This type of sensor is usually included as the so-called lambda sensor to eventually detect the remaining oxygen in the exhaust gases from automotives. The information from the lambda probe is



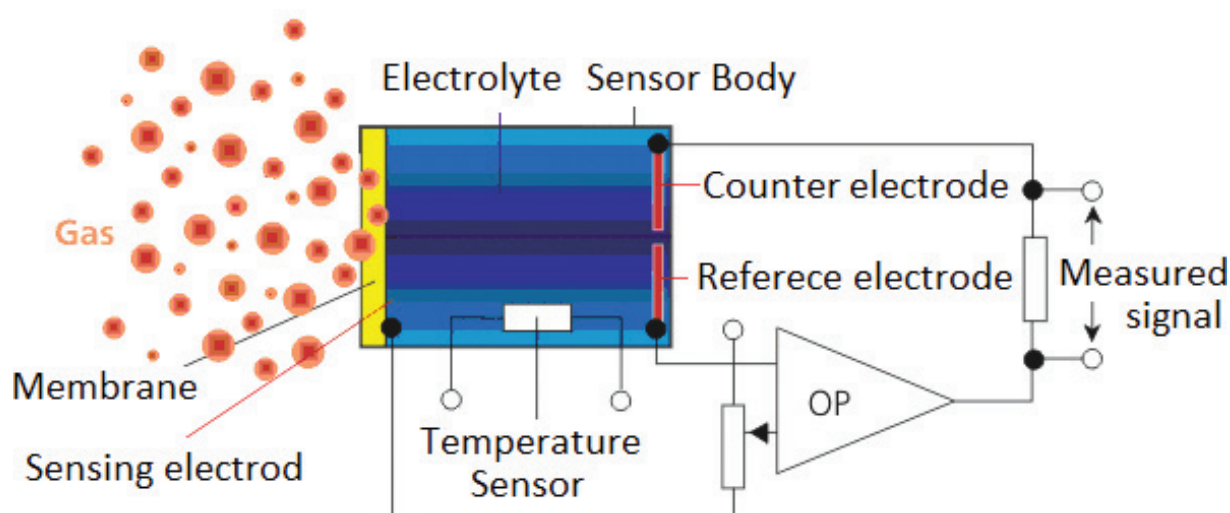


Figure 3. Sensor for automotive exhaust gases.

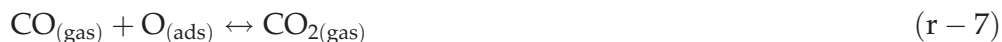
transmitted to the electronic control unit (ECU) of the automotive, which regulates the air-to-fuel ratio in the engine. Therefore, the sensor response must be as fast and sensitive as possible.

### 3. Influence of the sensing surface micro- or nanostructure

When the sensing layer acts as a catalyst that can promote a reaction between species from the gaseous environment of the sensor, the receptor will suffer changes in the layer charge, due to the electron transfer associated with the chemical reaction. These changes can be transformed by the transducer in a measurable signal. Usually, combustion reactions of several organic species or carbon monoxide generate high values of the thermal effect; therefore the reaction heat can also be measured and used to deduce the amount of combustible sensed species. In the combustion process, the oxygen reacts in adsorbed state.

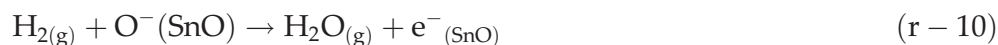
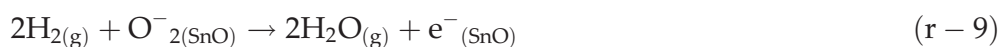
Most sensors based on semiconductive oxides show improvement when doped with noble metals. Thus, a so-call "triple-phase boundary" (TPB) is formed where the gas phase meets both semiconductor oxide and metal. The interface between oxide and metal has different extents of incomplete orbitals or electrons which can be transferred to appropriate species. Thus, oxygen can transform on the active sites (\*) at the interface in electrophilic  $O_2^-$ ,  $O_2^{2-}$  or in nucleophilic  $O^{2-}$ . The sensing mechanism highly depends on the nature of the adsorbed oxygen [7, 8]. When a reducing species exists in the gas to be detected/measured, this species could react with the adsorbed oxygen directly from gas phase (Elley-Rideal mechanism) and form carbon dioxide. The electrons provided by  $O^{2-}$  existing as a mobile species in the solid electrolyte will be released and the solid conductivity increases. The following reactions can be written to support the above statements:



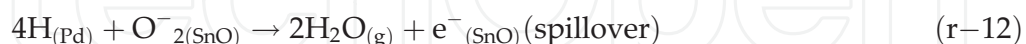


In a sensor for CO, since (r-7) is a cathodic reaction and (r-8) is an anodic one, the transducer transmits, in fact, the sum of signals due to oxygen adsorption and CO oxidation. In these cases, it is important to prepare the material in an appropriate manner so that the metal-oxide joining in the TPB improves and preserves the sensitivity and selectivity of the sensor.

This kind of practical approach can also be used in hydrogen and ammonia sensors, since these species can decompose on Pt, Pd or Au due to the spillover of hydrogen atoms to the metal oxide. This hypothesis is supported by Barbosa et al. [9], which prepared SnO<sub>2</sub> micro-disks made of tin oxide nanoparticles from the bulk oxide and carbon black, following a thermal treatment at 1135°C, then doped the resulted material with Ag or with Pd. Two distinctive mechanisms were proposed for the detection on the pure and doped oxide, since the ability of Pd to split in atoms of the hydrogen molecule involves its participation in adsorbed state. Thus, for pristine SnO<sub>2</sub>, the proposed reactions are:

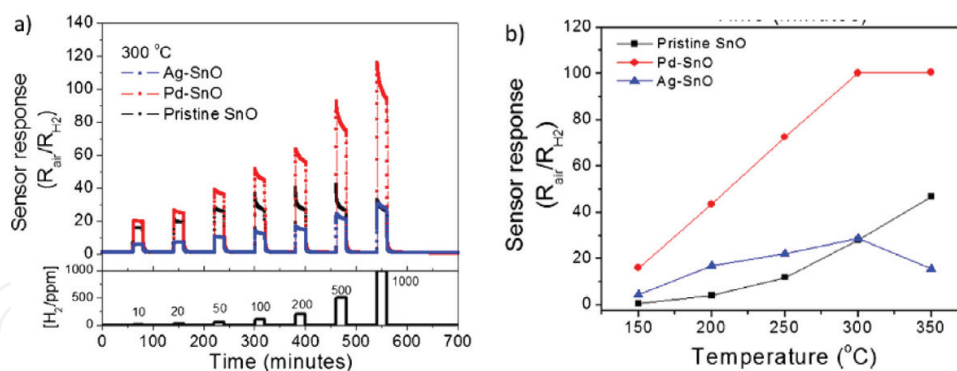


The nature of ionic oxygen species from the solid surface depends on an important factor, on the temperature value; at low temperature, the O<sub>2</sub><sup>-</sup> species predominates, while at higher values, O<sup>-</sup> is the major species. Hydrogen as free gas can be easily oxidized by the adsorbed oxygen. The released electron decreases the resistance value of the sensing layer, so the R<sub>air</sub>/R<sub>H<sub>2</sub></sub> ratio increases proportionally with the hydrogen concentration (**Figure 4**). Sensor response when SnO<sub>2</sub> was doped with Ag was insignificantly modified, while when doping was made with Pd, the sensitivity toward hydrogen increased a lot. Therefore, the authors propose another mechanism for the sensing process, based on the hydrogen splitting on Pd sites, followed by the oxidation on SnO sites and release of a higher number of electrons, suffering a spillover effect:



The sensor response is a lot higher in terms of R<sub>air</sub>/R<sub>H<sub>2</sub></sub> ratio on Pd-doped SnO<sub>2</sub> and is highly favored by the temperature increase up to 300°C; this is in fact the upper value allowing the hydrogen adsorption.

The detection of nitrogen oxide is of crucial importance in the environment monitoring. Nitrogen oxides, NO and NO<sub>2</sub>, denoted generally as NO<sub>x</sub>, are formed during the fuel burning in stationary sources (energy plants) and in the automotives' engines, from the elements of the air, in the harsh conditions (high temperatures, especially in case of Diesel engines). NO has



**Figure 4.** Hydrogen sensing on SnO<sub>2</sub> and Pd-doped SnO<sub>2</sub> disks of nanoparticles. (a) Sensor response at 300°C at 1000 ppm hydrogen. (b) Temperature dependence of the sensor response.

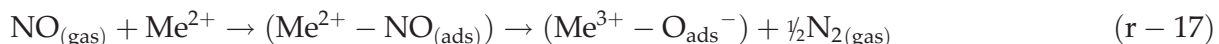
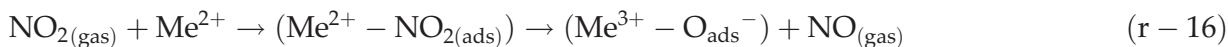
character of reducing agent and NO<sub>2</sub> acts rather as an oxidant. The NO detection mechanism supposes the participation of O<sup>2-</sup> by the reaction:



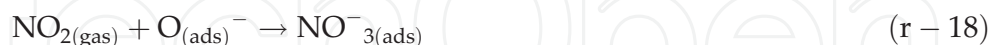
while NO<sub>2</sub> decomposes to NO, it can be detected in the same manner:



If the sensing layer contains basic sites (In<sup>2+</sup> and Sn<sup>2+</sup> ions, for instance), NO<sub>2</sub> is adsorbed as an acid anhydride and decomposed to NO and nitrogen:



The reactions occur better on stronger basic sites, because of the competition between the two oxygen species O<sub>2(ads)</sub><sup>-</sup> and O<sub>(ads)</sub><sup>-</sup> and NO<sub>2</sub>. On less basic sites, NO<sub>2</sub> can be oxidized to NO<sub>3</sub><sup>-</sup>:

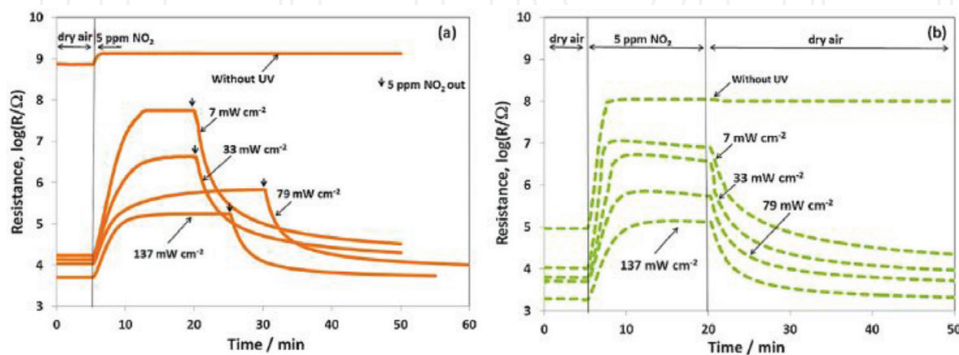
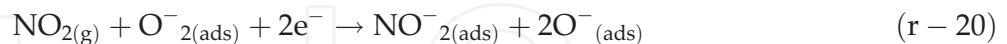


Indium oxide has a somehow basic character, so its sites will act rather as adsorption sites for NO<sub>2</sub>. On the contrary, on SnO<sub>2</sub> the reaction between NO<sub>2</sub> and O<sub>(ads)</sub><sup>-</sup> is by far preferred. The prevalence of these two reactions depends on the temperature value. The role of the basic sites is more significant at low temperatures. The mixed indium and tin oxide (ITO) brings the advantages of both components: conductivity (due to the presence of the two metallic species) and high defect density, bringing active adsorption and reaction sites.

Saboor et al. [10] prepared nanoparticles of SnO<sub>2</sub> to be used as sensing material and stimulated the chemical interaction between the solid and the sensed species (NO<sub>2</sub>) by UV irradiation. The tin oxide samples were prepared from SnCl<sub>2</sub> or SnCl<sub>4</sub>, by precipitation in hydrothermal conditions at 190 and 240°C, using ethanol and/or NaOH solution to initiate precipitation, or

by the action of microwaves on a mixture of  $\text{SnCl}_4$ ,  $\text{NaOH}$ , and ethanol. The samples were used either as-synthesized or after calcination at 400 or 500°C. The resulted powders were screen-printed on interdigitated electrodes deposited on alumina substrates. The sensing properties were tested by measuring the electrical resistance of the  $\text{SnO}_2$  material deposited between the metallic contacts in the presence of 5 ppm  $\text{NO}_2$ , in comparison with pure air, and the response was expressed as the resistance ratio  $R_{\text{gas}}/R_{\text{air}}$ . For a sensing material, it is also important to investigate the recovery time after sensing, i.e., the time needed for the baseline to return to the initial value, after cutting off the contact with the sensed species; generally, the recovery time is the time value needed to decrease 80–90% of the response value.

The results in the sensing procedure indicate that pristine  $\text{SnO}_2$  gave almost no signal without UV light, while the signal magnitude depended strongly on the irradiation intensity. This effect must be explained in connection with the sensing surface microstructure (which is correlated with the value of the specific surface area and free pore volume), more precisely, by the presence of a high number of grain boundaries and by the role of UV light in the charge carriers generation during the irradiation of a semiconductive material. The experimental results indicate that the semiconductive properties of tin oxide depend on the sample structure and morphology, i.e., on the preparative method. The  $\text{SnO}_2$  surface is covered with adsorbed oxygen species  $\text{O}_2^-$ ,  $\text{O}^-$  and  $\text{O}^{2-}$ , the first being predominant at temperatures below 100°C. Under UV irradiation, on one hand, the oxygen adsorption is favored, and on the other hand, the electron-hole pairs' formation and separation, characteristic to the semiconductive oxide photo-generated charge separation, is stimulated by the built-in electric field near the surface of  $\text{SnO}_2$  nanoparticles. This increase in the number of charge carriers is reflected because of a drastic decrease in the electrical resistance in air. When  $\text{NO}_2$ -containing air flows on the sensor area, the molecules pick up electrons from the surface and therefore, decrease the number of free carriers, i.e., decrease the electrical resistance value. The following reactions occurring on the surface can explain the observed transient responses, as well as the effect of irradiation on the sensing signal magnitude (Figure 5).



**Figure 5.** Values of the electrical resistance in time on 5 ppm  $\text{NO}_2$  exposure under UV irradiation, on as-synthesized (a) and calcined (b)  $\text{SnO}_2$  prepared hydrothermally from  $\text{SnCl}_4$ .

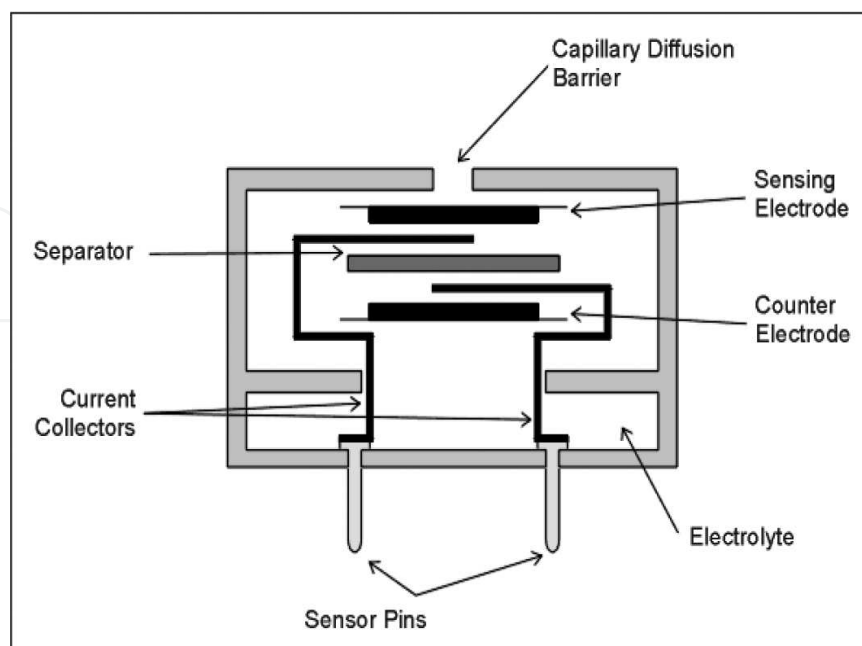
The results indicate that the sensing is favored only when the sensor area is irradiated by low intensity UV light, in terms of both sensing performance and recovery time of the sensor. The explanation lies in the moderate activation of the surface by UV light, in terms of formation of active species of oxygen. The higher UV light intensity may contribute to the desorption of the chemisorbed oxygen.

## 4. Main types of electrochemical sensors used in practical applications

### 4.1. Sensors for toxic gases

Electrochemical sensors destined for toxic gases detection and measuring work as micro fuel cells, are designed as maintenance-free and stable devices for long periods. A simple sensor with this purpose consists of two electrodes, a sensing and a counter one, allowing placing a thin layer of electrolyte between them (**Figure 6**). The electrodes are accommodated in a plastic box with a capillary opening to allow the gas entry to the sensing electrode. The electrodes are connected through two pins going to the external interface and thus allow the sensor connection in a resistor circuit for measuring the voltage drop resulting from any current flow.

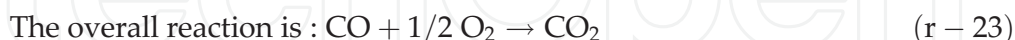
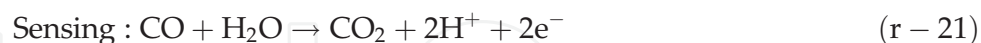
The molecules of the target gas diffuse into the sensor and are oxidized or reduced on the sensing electrode. On the other hand, on the electrode takes place the corresponding inverse reaction, and consequently, a current is generated in the external circuit. The amount of gas entering in the sensor depends on the capillary diffusion barrier. The current generated in the circuit is proportional to its concentration, so that the sensor gives a direct measure of the interesting species of toxic gas; the response depends rather on the volume or concentration of gas than on its partial pressure.



**Figure 6.** Toxic gas sensor.



The key feature of this sensor design is thus the gas diffusion barrier, whose role is to control/limit the amount of gas reaching the sensing electrode. On the electrode, all target gas admitted inside the cell will practically react. Common commercial products for measuring various toxic gases are the CiTiceL sensors. The reactions occurring at the electrodes in sensor exposed to a gas flow containing carbon monoxide are:



The detection principle for other toxic gases which can be oxidized electrochemically is similar. The reactions (r-21)–(r-23) above indicate that the oxygen is necessary on the counter electrode to generate the current. Usually, the sample stream readily contains oxygen. The sensor exposure to an anaerobic sample gas may result in signal drift; therefore, the toxic gas sensors should never be immersed in an anaerobic gas mixture. In some applications, the sensors could be frequently exposed to high concentrations of analytes; in this case, it is necessary to ensure an additional oxygen source near the counter electrode. In the gas sensing procedure, it is important to make sure that the rate-limiting step is the gas diffusion through the capillary, while all other stages are a lot faster. A way to achieve this goal is to use electrode material as solid with high catalytic activity for the electrochemical reactions based on the sensor.

#### 4.2. Three- and four-electrode sensors

The simplicity of design of the two-electrode sensors, however, brings a major drawback: the polarization of the counter electrode, which limits the measuring range. This effect could be eliminated by using a third electrode, named reference electrode, having a stable potential. It is held at a fixed potential relative to the reference electrode (no current is drawn from it), so both keep a constant potential. The counter electrode can still polarize but will not affect the sensing electrode. The three-electrode sensors are generally used in the electrochemical sensors for detecting toxic gases.

In some applications, however, the presence of the third sensor brings changes that compromise the sensor behavior, as the cross-interfering gases or zero-offset changes with temperature. In this case, the introduction of a fourth “auxiliary” sensor allows the sensor performance to be kept in order to allow the simultaneous measurement of two gases.

#### 4.3. Overcoming cross interference

The fourth auxiliary electrode can be useful in preventing the cross-sensitivity to other gases. For example, the sensing reactions involved in carbon monoxide sensors are similar in terms of electrical changes of the sensing area to those found in the hydrogen gas sensing. Therefore, if hydrogen is present in a gas mixture containing carbon monoxide, the response of hydrogen damages accurate measurement of CO. In this case, the fourth-auxiliary electrode has the role to measure the hydrogen, while CO and some of the H<sub>2</sub> reacts on the sensing electrode. The

signal from the fourth electrode is used as a compensating signal, which is subtracted from the signal of the sensing electrode using a microprocessor with appropriate software.

#### 4.4. Overcoming temperature effects

The temperature effect is due to the important increase of the signal when temperature changes. A 10°C rise of temperature almost doubles the baseline signal of most electrochemical sensors. The effects are significant especially when measuring low concentrations of gases, such as ozone and carbon monoxide. Since the signals from both sensing electrode and auxiliary electrode give similar responses to changes in temperature, the signal from the auxiliary electrode can simply be subtracted from that of sensing electrode to compensate the temperature effect.

#### 4.5. Dual/multiple gas sensor

The multiple sensor modules find applications in the monitoring of the urban atmosphere, the environment associated with energy plants or other industrial units, the unorganized emissions, the emergency monitoring, the land monitoring using portable gas detector for various gas detection equipment as well as smart home appliance.

An example of sensor widely applied in gas monitoring is the **4COSH CiTiceL** four-electrode sensor, manufactured by City Technology company from the Great Britain [11]. It allows measuring CO and H<sub>2</sub>S simultaneously with one sensor with a portable instrument. The sensor has wide ranges of measurable gas concentration values: 0–500 ppm CO and 0–200 ppm H<sub>2</sub>S, at resolution values of ±1 ppm for CO and ±0.5 ppm for H<sub>2</sub>S in a relative humidity range of 15–90%. It is important to mention that the declared signal loss is 5% per year. The weight is only 5 g, and the gauge size is only 2 × 1.6 cm.

The sensor includes two sensing electrodes, one for CO and the other for H<sub>2</sub>S. On the first sensing electrode, hydrogen sulfide is oxidized completely and CO diffuses through the sensor being oxidized on the second electrode. This sensor obtains two separate signals, one for each gas, but allows two gases to be measured with one sensor.

**ZE10** (Figure 7) is a multispecies, high-performance electrochemical device for gas sensing, able to detect CO, SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub>, with good selectivity and stability, produced by Winsen Company (China) [12]. It has a built-in temperature sensor for thermal compensation. It combines the electrochemical detection principle with sophisticated electrical circuit design, aiming to meet different detection requirements from customers. The detection resolution is up to 10 ppb, the response time 30 s, the humidity range 15–90%. In Figure 8, the electrical diagram for a potentiostatic sensor is presented.

In Table 1, the technical data about the sulfur dioxide and nitrogen dioxide sensors are exemplified.

The Figaro company (USA) is producing various types of gas sensors: metal oxide sensors (MOS), catalytic sensors, and electrochemical sensors. Figaro electrochemical sensors are amperometric fuel cells with two electrodes, the working (sensing) electrode and the counter



Figure 7. Multielectrode electrochemical sensors for detection of H<sub>2</sub>S and CO.

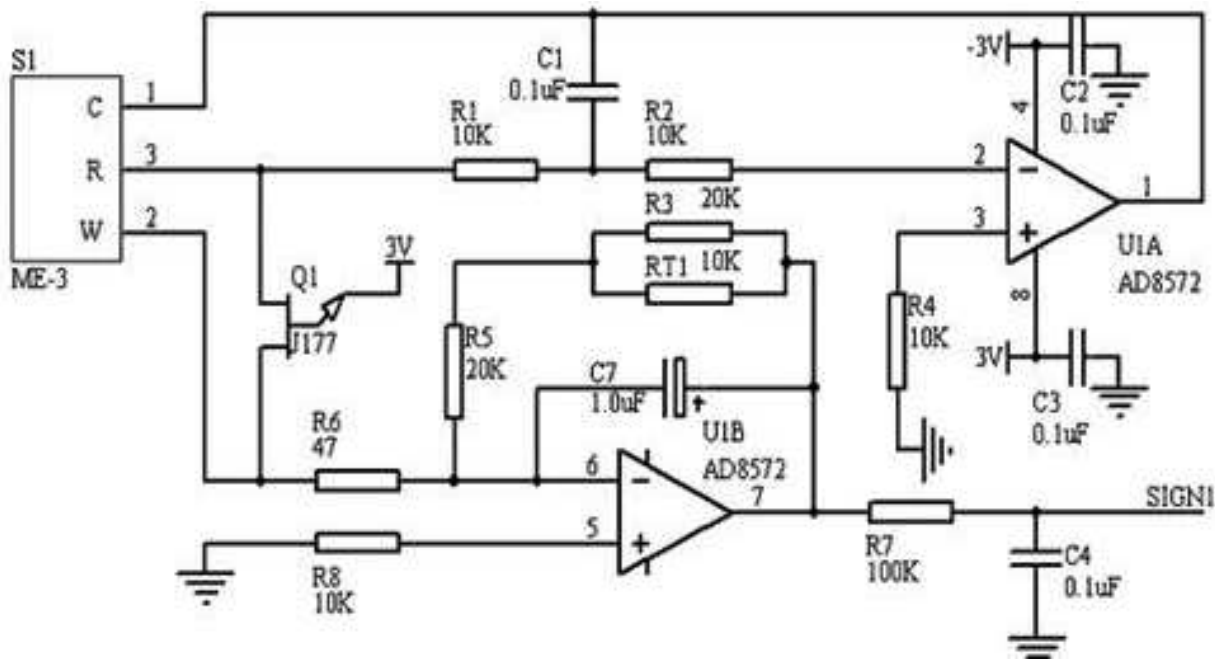


Figure 8. The electrical diagram for the ME-3 potentiostatic sensor (3 electrodes: C, R, and W).

electrode, having placed in between a layer of ion conductor (Figure 9). When a reducing gas (CO) reaches the working electrode, its oxidation will occur on it, with the participation of a water molecules from the surrounding air (r-24).



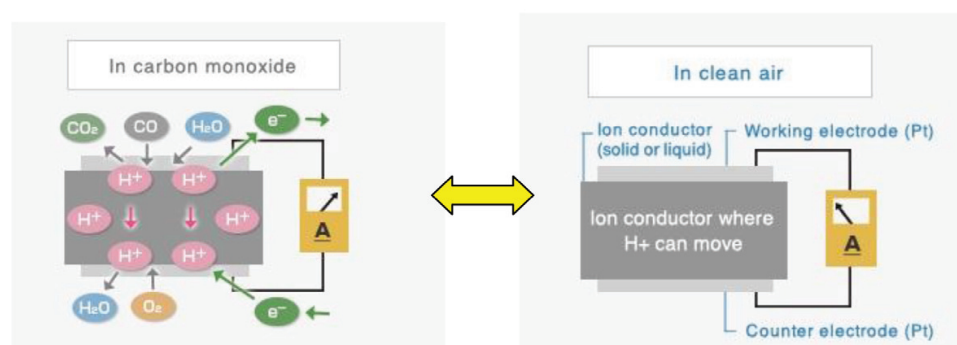
Since the working electrode is connected to the counter electrode, the protons (H<sup>+</sup>) formed by reaction (r-24) will flow toward the counter electrode through the ion conductor and the electrons will move to the counter electrode through the external wiring. The protons and electrons will then react with oxygen from the environmental air (r-25)



The overall reaction is thus:

Parameter	SO <sub>2</sub> sensor, sulfur dioxide	NO <sub>2</sub> sensor, nitrogen dioxide
Measurement range	0–20 ppm	0–20 ppm
Max detecting concentration	150 ppm	150 ppm
Sensitivity	(0.55 ± 0.15) μA/ppm	(0.78 ± 0.42) μA/ppm
Resolution ratio	0.1 ppm	0.1 ppm
Response time (T90)	<30 s	<25 s
Bias voltage	0 mV	0 mV
Load resistance (recommend)	10 Ω	10 Ω
Repeatability	<2% output value	<2% output value
Stability (/month)	<2%	<2%
Output linearity	Linear	Linear
Zero drift (–20–40°C)	≤0.2 ppm	0.2 ppm
Storage temperature	–20–50°C	–20–50°C
Storage humidity	15–90% RH	15–90% RH
Pressure range (kPa)	90–110	90–110
Anticipated using life	2 years (in air)	2 years (in air)

**Table 1.** Technical parameters for some electrochemical gas sensors produced by Winsensor.



**Figure 9.** Changes and moving of the charge carriers in a Figaro electrochemical gas sensor exposed to CO-containing gas and clean air.



The simplicity, robustness and low piece of the Figaro sensor helped it to be present in most domestic and industrial applications, especially for the detection of organic compounds associated with the fuel gas leaking: residential gas detection, leak checkers.

#### 4.6. Electrochemical sensors working at high temperatures

A very important practical application of amperometric method in gas sensing is found in the production of oxygen sensors, able to work at high temperature, to monitor the composition of exhaust gas from automotives. The precise monitoring of the oxygen in the exhaust gas allows

the fine regulation of the air-to-fuel ratio entering in the engine and thus increase the fuel economy, produce lower toxic emissions, and reach best engine performance.

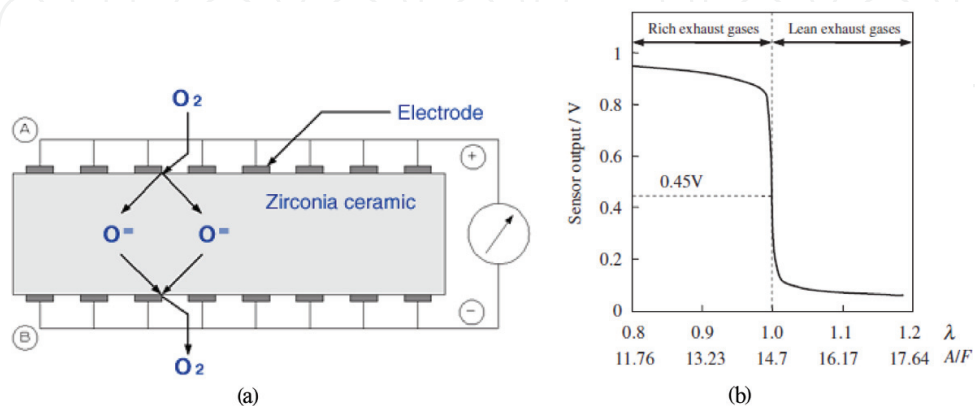
In a simple zirconia cell (**Figure 10a**), the oxygen detection performed by applying the Nernst equation (relation 2) allows to calculate the partial pressure of oxygen,  $p_1$  on one side of a zirconia layer, if the pressure  $p_2$  at the other side is known, by measuring the electromotive force,  $E$  developed between the two sides of zirconia layer [2, 5, 13].

If the electromotive force  $E$  is measured on a wide range of air-to-fuel  $A/F$  ratio (or stoichiometric ratio  $\lambda$ ), **Figure 10b**, one can see that the range, where the variation of  $E$  with  $A/F$  is high, is situated in close neighborhood of the stoichiometric air-to-fuel ratio. The lean or rich mixtures cannot be measured with the simple zirconia cell. In order to increase the range where the measuring of oxygen concentration can be made with a higher accuracy, a dual-cell wide range oxygen sensor was developed (**Figure 11**). The design consists of two cells joined together: a pumping cell and a Nernst cell. The pumping zirconia disc plays the role of an electrochemical oxygen pump: it evacuates or pressurises the sealed chamber, depending on the direction of current applied between the pump and the common electrodes. When the oxygen ions move through the disc from one electrode to the other, the value of  $p_2$  changes.

In the other half of the cell, the sensing one, the difference in oxygen pressure between the two sides of the sensing disc generates a voltage proportional to the ratio of the oxygen ion concentrations, as shown by Nernst equation. Two voltage values, the lowest and the highest, can be associated with the highest and the lowest values of the oxygen pressure, respectively. When the extreme value of the voltage is reached, the current source is reversed and the inverse process begins. In **Figure 11b** is displayed the variation of the current intensity in the pumping cell with the air-to-fuel ( $A/F$ ) ratio.

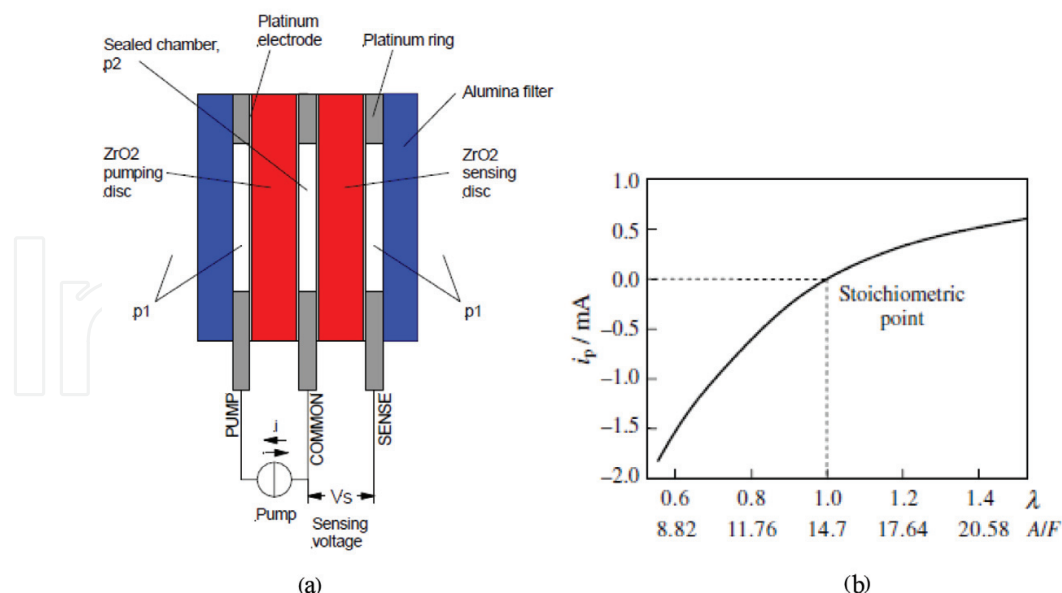
This sensor can work on a large air-to-fuel ratio range, preventing the lean-rich cycling inherent in narrow-band sensors. Thus, the engine control unit can adjust very fast with the fuel delivery and the ignition timing in the engine, improving both fuel efficiency and  $\text{NO}_x$  formation.

The need to develop high-performance  $\text{NO}_x$  sensors arises, on one hand, from the toxic and destroying effects on the environment, and on other hand, due to the constant increase of



**Figure 10.** (a) Simple zirconia cell. (b) Electromotive force from Nernst equation dependence on air-to-fuel ratio.





**Figure 11.** (a) Dual cell oxygen sensor and (b) pumping current value in function of air-to-fuel ratio (from Ref. [12]).

atmospheric NO<sub>x</sub> emitter sources (automotive emissions, especially cold start, and stationary sources, power plants). NO<sub>x</sub> was reported to be responsible for acidic rains, destruction of the protective ozone layer and physiological complex harm to humans and animals. From the economical, practical point of view, there is a strong demand of NO<sub>x</sub> sensors for the continuously increasing automotive industry worldwide and for power plants and industrial boilers. Special requirements can be formulated for commercial combustion NO<sub>x</sub> sensors [13]: fast response and robustness to withstand in harsh environments (600–900°C) for a long time, no sensitivity towards moisture, working properly even in the absence of oxygen, low/affordable price. The sensing of NO<sub>x</sub> is performed by potentiometric or mixed potential type gas sensors based on zirconia.

## 5. Conclusions

The electrochemical gas sensors are nowadays indispensable in the monitoring of the atmosphere quality, especially due to pollutants associated with human activities. Carbon monoxide, sulfur oxides, hydrogen sulfide and nitrogen oxides are only a few of species, which can seriously damage the environment equilibrium by smog formation, acid rain, soil deterioration, water contamination, as well as some direct damages on the human health.

The electrochemical gas sensing is based on gas oxidation or reducing reactions on sensing surfaces with catalytic potential, which suffer noticeable charge changes that can be amplified and processed in order to generate a signal. The electrochemical sensors are fast, reliable, small and cheap; therefore, their use nowadays includes the exhaust systems from automotives, domestic/residential gas detection, and leak checkers.

The detection mechanisms are different from one gas to another and the application of electrochemical methods is not always convenient; the detected gas must be electrochemically active.

Also, a number of recommendations and cautions must be respected, in order to avoid damaging the sensors. In order to prevent the deterioration of the sensor, the users should respect the rated voltage mentioned by the manufacturer and use the sensor in the right temperature range. Moreover, the exposure to excessive humidity, contamination with various chemicals, sudden exposure to extreme temperatures and mechanical shocks are absolutely to avoid for preserving the sensors' work function and accuracy.

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