

Amperometric Gas SensorsA Review

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Amperometric Gas Sensors—A Review

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1. Introduction

The amperometric gas sensor, or AGS, belongs to a large and important class of electrochemical gas sensors, and they play an ever-increasing role in environmental monitoring, medical and health applications, industrial safety, security, surveillance, and the automotive industry. The fundamental

principles and constituents of the AGS sensor device as well as some important events in the design and development of the AGS technology are reviewed herein. The modern AGS is based on a series of scientific discoveries, and it has contributed much to society in its rich history.

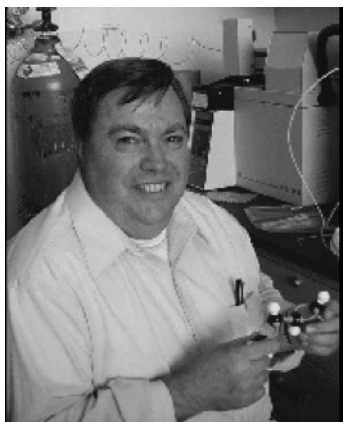
Amperometric gas sensors (AGSs) are best divided by the temperature at which they operate and can be represented by two well-known commercial gas sensors that include the ambient-temperature liquid electrolyte gas sensors used for medical and industrial hygiene applications and the high-temperature solid electrolyte O₂ sensor used in automotive, process, and stack gas applications. The AGS can operate at low or high temperatures, ranging from below freezing to over 1000 °C, and the materials of construction, including the electrolyte, change significantly. The choice of materials can result in totally different designs. The room-temperature AGS uses liquid or polymer electrolytes and is the system of choice for industrial hygiene, health, safety, and medical applications, while the high-temperature AGS using solid electrolytes has been primarily developed for use in automotive exhaust and stack gas process monitoring. This review focuses more on the low-temperature AGS, but some discussions are included on the high-temperature sensors. The fact that the AGS serves many important practical applications speaks to the superb simultaneous combination of features that can be realized with this approach including: low power, low cost, small size, selectivity, stability, sensitivity, and sometimes fast response time. Given these combined characteristics, the AGS is often described as providing relatively high analytical performance at modest cost.

2. Characteristics of Amperometric Gas Sensors

2.1. Electrochemical Gas Sensors

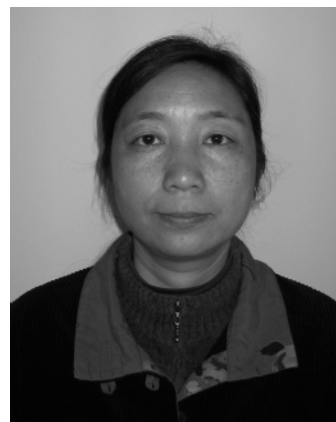
Electrochemical gas sensors can be divided into three main classes according to the operating principle: amperometric, potentiometric, and conductometric sensors. Many sensor types exist within each class. We will not cover potentiometric techniques or conductometric techniques for gas sensors but restrict discussions to amperometric sensors for the gas-phase analytes. In the AGS, the current generated by reaction of an analyte at an electrode is measured as the sensor signal and can be measured at a fixed or variable electrode potential, although it is very common at a fixed applied potential. The reaction rate, reflected by the current at the sensing electrode, occurs at a thermodynamically

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Dr. Joseph R. Stetter obtained a Ph.D. in Physical Chemistry from the University at Buffalo (SUNY) in 1975. In the 1970s, Dr. Stetter was Director of Chemical Research at the Energetics Sciences Division of Becton Dickinson and Company where he developed the first diffusion-type electrochemical CO sensors; the earliest diffusion CO dosimeters; solid-state gas sensors for CO, NO_x, SO₂, and other toxic gases; and an electrochemical hydrazine sensor still in use by NASA. While at the Argonne National Laboratory in Chicago, IL, in the 1980s, he led the development of the first integrated and operational “sensor-array-based” instrument with pattern recognition (now called electronic nose). In the 1980s, Dr Stetter founded TRI (Transducer Research, Inc.), where he developed portable instruments and sensors for CO and CO₂, end-of-service filter indicators, chlorinated hydrocarbon sensors, NO_x sensors, personal protection instruments, and low-cost effective protection equipment for human health and the environment. In the 1990s, he sold TRI and became Professor of Chemistry at the Illinois Institute of Technology, started a sensor research group, and founded the International Center for Sensor Research and Engineering at IIT, mentoring both M.S. and Ph.D. students. He founded Transducer Technology, Inc. (TTI), a start-up company focusing on nanotechnology enabled sensors and instruments in 1999. In 2007, TTI merged with KWJ Engineering, Inc., of Newark, CA, making nanosensors for health, safety, and process control applications. Recently, Dr. Stetter is Director of the Microsystems Innovation Center for SRI International (Menlo Park, CA). R&D focuses on new sensors, unique structures/materials, artificial senses, chem/biosensors, novel MEMS for drug and vaccine delivery, vacuum microelectronics including microelectron and ion sources, and micro/nanostructures and bio-MEMS. Dr. Stetter has published more than 100 refereed scientific and technical articles and has more than 25 domestic and foreign patents. He has served as Chairman of the Electrochemical Society Sensor Division and served on the boards of national and international technical societies. He has organized national and international scientific meetings and symposia in his field and serves as editor and reviewer for scientific and engineering journals. His awards include three IR-100 Awards for new product development; the Federal Laboratory Consortium Special Award for Excellence in Technology Transfer; the Argonne National Laboratory Inventor’s award; the Technology Management Association of Chicago’s 2002 “Entrepreneur-of-the-Year” award; and two NASA New Technology Awards. He is on the board of directors for several start-up companies.

determined potential for any given reaction and, when operated under appropriate diffusion-limited conditions, is simply proportional to the concentration of the analyte. The relationship between current and concentration is linear, typically over 3 orders of magnitude, and measurements with high sensitivity (ppm and ppb) are possible with excellent measurement accuracy under constant potential conditions. Faraday’s Law is often applied to the observed currents, and the design of the sensor is chosen to control many kinetic factors including mass transfer of the analyte to the electrode as well as the electrocatalytic activity of the electrode material. The geometry and dimensions of the sensor device have a profound effect on the AGS analytical performance, including the observed sensitivity, selectivity, response time, and signal stability.



Dr. Jing Li received her Ph.D. in Materials Science in 1996 from University of Utah in Salt Lake City. She is currently a Principal Investigator in NASA Ames Nanotechnology Branch. She leads the effort and has developed a space-qualified nanochemical sensor unit for flight demonstration in a satellite that has been launched and operated successfully since March 2007. The nanotechnology-based chemical sensor platform that she developed has drawn interest from other NASA centers, many industry partners, and government Labs. She is a principle investigator (PI) on the Nano ChemSensor Unit project, which won 2007 NASA Ames Center Honor Award. She worked with a team at NASA on nanoelectronic devices that resulted in a NASA TGIR Award (2002). She is an internationally known expert in the field of chemical sensors. Her research focus is on the chemical sensor development utilizing the nanostructured materials and a sensor array with signal processing techniques for intelligent sensor systems. Prior to joining NASA Ames, she was a lead scientist at Cyran Science, Inc., where she developed polymer-based chemical sensors for an electronic nose instrument. Dr. Jing Li worked at Pacific Northwest National Lab as a DOE postdoc fellow on the chemical sensor development for waste tank monitoring. She has extensive experience of both research and commercialization in developing chemical sensors and intelligent sensing systems, which includes the following: (1) investigating the sensing materials such as nanostructured carbon nanotube and metal, metal oxides nanowires, and their intercalation in polymers as composites; (2) studying the sensing mechanisms in scope of the charge transfer (first and secondary) interaction and diffusion/partition process between sensing materials and analytes characterized by electrical, electrochemical, and spectroscopic techniques such as UV–vis, FTIR, Raman, work function measurements with Kelvin probe, and adsorption/absorption measurement with quartz crystal microbalance and Micromeritics; and (3) developing the signal-processing techniques (i.e., pattern recognition) for a chemical sensor array to be used as an intelligent system for digitizing the chemical information. She is currently a vice chair for Sensor Division in the Electrochemical Society. Her research interests are chemical sensors and intelligent sensing systems for space applications and terrestrial applications.

Table 1. Comparison of Amperometric and Potentiometric Sensors

electrochemical class	sensor signal vs [analyte]	principle
amperometric, AGS	$i = kP$	kinetic, Faraday law
potentiometric	$E = E_c + k \ln P$	thermodynamic, Nernst law

In a potentiometric electrochemical class of sensor, the open-circuit potential between two electrodes is monitored, and this potential is typically proportional to the logarithm of the concentration of analyte. The relationship is often expressed by the Nernst equation, as shown in Table 1. A potentiometric sensor can measure analyte concentrations over a very wide range, often more than 10 decades, and the sensing principle is thermodynamic, i.e., it assumes that all reactions relating to the sensing are at equilibrium. In potentiometry, the chemical and diffusion processes must be at equilibrium conditions in the sensor for a thermody-

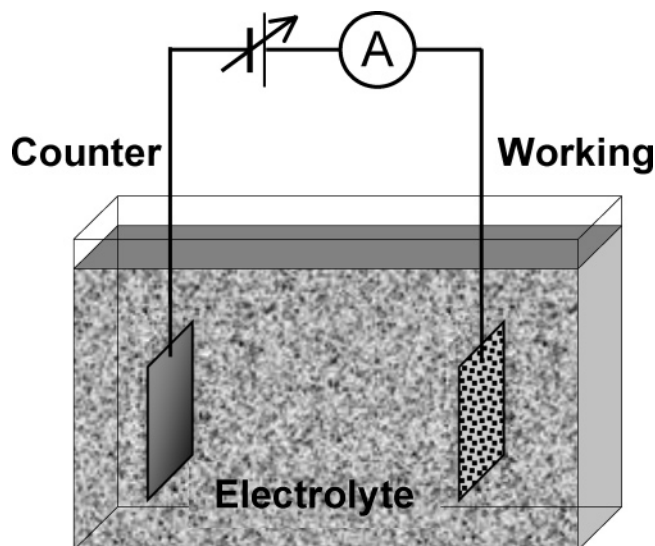


Figure 1. Illustration of amperometric sensor with two-electrode configuration for liquids.

namically accurate signal to be observed, while the amperometric sensors rely on Faraday's law and a dynamic reaction achieving a steady-state condition in the sensor. As may be implied, the amperometric sensor signal will get smaller with the size of the electrode and the rate of analyte reacting at the electrode surface, while the potentiometric sensor assumes a thermodynamic potential independent of size of the electrode. This situation becomes interesting in light of nanostructures wherein the thermodynamic potential is characteristic of aggregates of atoms, while the amperometric sensor reaction rate is typically enhanced by the high surface areas afforded by nanostructured electrode materials.

2.2. Amperometry

Amperometry is a conventional electroanalytical technique that encompasses coulometry, voltammetry, and constant-potential techniques and is widely used to identify and quantify electroactive species in the liquid or gas phase. For liquid-phase analytes, the electrodes and analytes are immersed in a common electrolyte solution. In contrast, application of amperometry to gas-phase analytes involves a unique gas/liquid/solid boundary (analyte–electrolyte–electrode) and an interfacial transport process that frequently controls the response characteristics and analytical performance of the AGS. A major consideration in the specific design of the sensor device is to choose a geometry and porosity/composition of materials to enable the gaseous analyte to effectively and efficiently transport to the interface of the electrode/electrolyte where a fast, reversible, redox reaction can occur. This interfacial redox reaction provides the charge-transfer reaction of the analyte and the analyte's characteristic sensor signal.

2.3. Amperometric Gas Sensors

Amperometric gas sensors are sometimes called voltammetric, microfuel cell, polarographic, amperostatic, potentiostat, limiting current, or other sensor names.^{1,2} The most descriptive name is “amperometric”, and this refers to either constant-potential amperometry or variable-potential amperometry. A simple amperometric cell with two-electrode configuration is illustrated in Figure 1 wherein the electrochemical system consists of two electrodes, i.e., a working

electrode and a counterelectrode, and the electrolyte solution in which the two electrodes are immersed. Missing from this for the moment is an interface to enable a gaseous analyte to contact the working electrode, but this is discussed later.

When applying a proper potential between the two electrodes, electroactive species in the electrolyte solution will participate in electrochemical reactions on the surfaces of each of the electrodes. A reduction reaction occurs at the cathode and can be expressed as shown in eq 1, and at the same time, an oxidation reaction takes place at the anode and can be written generally as shown in eq 2:



The cathode reaction takes electrons from the cathode and combines them with an oxidized species, O1, to produce a reduced species, R1. At the anode, a reduced species, R2, reacts to produce an oxidized species, O2, and electrons are given to the anode. The electrons on the anode or lack of electrons on the cathode would build up a charge on the electrode surface, except that the electrodes are conductors and are connected in an external circuit in which the electrons flow. This is an illustration of Faraday's Law in that an exact number of electrons are generated or used per each analyte molecule and so the charge (the number of electrons or Coulombs of charge) is exactly related to the number of analyte molecules reacting in the system and the current (electron flow) at the electrode is exactly related to the rate of the electrochemical reactions (current is Coulombs/s). In the AGS, typically the current under diffusion-limited reaction conditions is directly related to the rate of electrode reaction taking place on the electrode surface and, hence, as discussed in more detail below, the rate of the electrode reaction is proportional to the concentration of reactant, i.e., the analyte. Consequently, the electrical charge or current can be used as a sensor signal and will be related to the concentration of the analyte in an AGS.

The common characteristic of all AGSs is that measurements are made by recording the current in the electrochemical cell between the working electrodes and counterelectrodes over time as a function of the analyte concentration. When this experiment is performed at a fixed potential controlled by a potentiostatic circuit, the technique should be properly called “constant-potential amperometry.” The AGS produces a current when exposed to a gas/vapor containing an electroactive analyte because the analyte diffuses into the electrochemical cell, to the working electrode surface, and thereon participates in an electrochemical reaction that either produces or consumes electrons (i.e., a redox reaction).

Selectivity to certain gaseous analytes is an important consideration for sensing applications. For the AGS, selectivity can be realized by optimizing the electrode material to facilitate or catalyze only selected reactions or by control of the sensing electrode potential to select an applied bias that thermodynamically favors either the oxidation reaction or the reduction reaction for a particular analyte. Noble metals such as gold and platinum, mostly in porous or high surface area designs, have been used for the working or sensing electrode in the AGS because of their excellent chemical stability in electrolyte solutions and high electrocatalytic activity toward analytes like CO, H₂S, O₂, Cl₂, and NO. The applied potential between working and reference electrodes set by the potentiostat fixes the thermodynamic operating

potential for the working electrode reaction and is critical for both the observed sensitivity and the selectivity of the sensor. The selection of operating potential provides an effective way to change or optimize the performance of the sensor.

2.4. Theory of the Limiting Current

The observed current in the AGS can depend on many factors, and the resultant mathematical expression relating the current, potential, and concentration can be complex. There are two special operating conditions, called limiting conditions, that can be used to simplify the resulting expression for relating the rate of an electrode reaction (r_r) and the rate of mass transport, e.g., by diffusion (r_d), of the reactant to the electrode surface. These conditions include the situation where $r_r \ll r_d$ (eq 1) and the situation where $r_r \gg r_d$ (eq 2). Both cases are important for sensor applications, and in both these cases, the electrode process can be easily understood and the resulting expression can be simplified. The current obtained at the two rate-limiting conditions is called the limiting current.

In the first case, where $r_r \ll r_d$, i.e., the rate of reaction at the electrode surface is the rate-limiting step, the limiting current is controlled by the rate of the electrode kinetics. In this case, the analyte reaches the surface much faster than it is reacted, and so the concentration at the electrode surface is the same as in the bulk of the solution and the gas surrounding the electrode and the expression for the current will take the form of eq 3,

$$i_{\text{lim}} = nFkAC \exp(\alpha nFE/RT) \quad (3)$$

where k represents the standard rate constant, F is the faraday constant, R is the gas constant, T is the Kelvin temperature, A is the area of the electrode, C is the concentration, n represent the number of electrons per molecule reacting, and α and E are the transfer coefficient and overvoltage of the electrode reaction, respectively. If all conditions are held constant, the limiting current is proportional to the concentration (C) of analyte with an exponential temperature coefficient, and the derivation of this expression can be found in many textbooks.^{3,4} The limiting current that is obtained in this kinetically controlled electrochemical region, however, is not always stable because of the degradation of the electrode's catalytic activity and can be problematic for a practical AGS.

This drawback can be overcome by operating the AGS in the region of diffusion control rather than the electrode's kinetic control. Under this condition, where $r_r \gg r_d$, the rate of diffusion of the reactant toward the electrode surface is much slower than the rate of reaction and now the limiting current is controlled by the diffusion of analyte. In this case, the concentration of the analyte at the electrode surface is virtually zero and every molecule of analyte that reaches the surface is immediately reacted. Under these conditions, the rate of electrode reaction may be limited by the rate of diffusion through a gas membrane or a capillary that is placed somewhere between the bulk analyte sample (e.g., the air containing the analyte) and the catalyst layer of the electrode. On the basis of Fick's diffusion law, the limiting current, i_{lim} , should now be governed by the rate at which the analyte transports to the surface, and this can usually be written as shown by eq 4,

$$i_{\text{lim}} = k[\text{CO}]_{\text{gas}} \quad (4)$$

where the current is directly proportional to the gaseous concentration in some convenient units like ppmv (parts per million by volume). The current can also be limited by the rate of diffusion across the diffusion layer in solution, and an expression similar to eq 4 is also obtained.

Figure 2 illustrates the two limiting conditions described above wherein the concentration of the analyte is plotted vs the distance from the electrode surface. When the current is limited by the rate of the electrode reaction, the analyte supply is much faster than its consumption and the analyte concentration is almost the same in the bulk and at the electrode surface. For a mass transport (diffusion) limited electrode reaction, the analyte supply is much slower than its consumption by reaction at electrode surface, the analyte concentration falls to zero at electrode surface, and the current is now limited by the supply of analyte. This condition is often preferred by the designer of the AGS since the physical control of the analyte supply by diffusion allows one to build a more stable sensor with the square root temperature dependence of the signal.

When operating the AGS using a potentiostat, the sensor can be operated at an electrochemical potential where the reaction is facilitated, and in this case, the magnitude of the sensor signal is practically independent of the electrode potential. In theory, the limiting current region can be achieved in any case when the rate-limiting step is a step prior to electron transfer. Typically, an electrode with relatively high electrocatalytic activity is sought, and the benefits of a stable long-lasting sensor are realized.

2.5. Structure and Geometry of an AGS

Figure 3 illustrates the design of a typical three-electrode AGS for CO sensing having a working electrode (WE) reaction $[\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-]$ and counter-electrode (CE) reaction $[\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}]$ and reference electrode (RE) embedded within the cell. The WE, CE, and RE are in electrolytic contact (all touch the electrolyte), and the overall cell reaction is $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$. The common feature of the typical gas sensor is an interface at the working electrode that facilitates transport of the gas to the WE/electrolyte interface. This inlet can be simple diffusion or aided by a small air pump that transports the sample to the backside of a gas porous membrane through which the analyte diffuses/permeates. The gas membrane can be used to control the gas flow into the sensor and it can aid selectivity, allowing only the analyte gas to pass as well as providing a barrier to prevent the leakage of the electrolyte from the interior of the sensor. The design and materials chosen for each part of the sensor are critical and determined, to a large part, by the application and the desired analytical performance. In the following paragraphs, we discuss alternative materials and designs that are used to provide different performance capabilities.

2.5.1. Gas Membrane

Several types of porous and gas-permeable membranes exist and can be made of polymeric or inorganic materials. Most of them are commercially available very thin solid Teflon films, microporous Teflon films, or silicone membranes. Issues concerning the choice of membrane include permeability to the analyte of interest, ability to prevent electrolyte leakage, manufacturability, and the thickness and

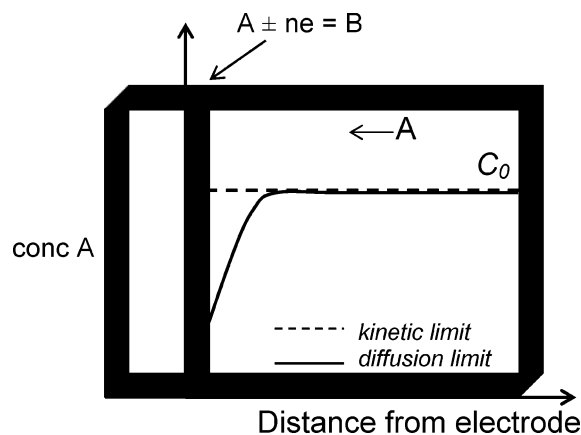


Figure 2. Concentration distribution of analyte (A) for different current limit conditions.

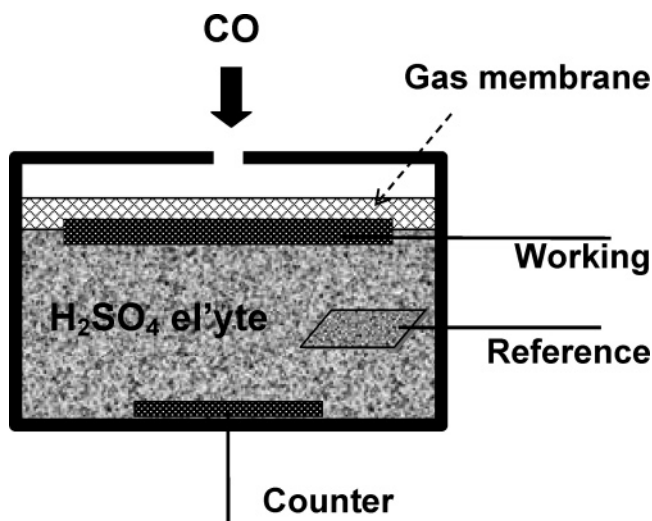


Figure 3. Illustration of amperometric gas sensor for CO with three-electrode configuration.

durability of the membrane. For example, a semipermeable membrane composed of an acrylonitrile butadiene copolymer can be used to selectively detect the partial pressure of oxygen in blood samples by allowing oxygen transport and effectively preventing the transport of the other species present in the sample. In a number of cases, the rate of mass transport through the membrane controls the limiting current and, hence, the sensitivity of the AGS. An ideal gas membrane will have a constant permeability to the target gaseous analyte during sensor operation over a wide temperature range and possess mechanical, chemical, and environmental stability.

2.5.2. Electrolyte

The role of the electrolyte is to transport charge within the sensor, contact all electrodes effectively, solubilize the reactants and products for efficient transport, and be stable chemically and physically under all conditions of sensor operation. The electrolyte is an ionically conducting medium that ionically transports charge within the cell. Examples of commonly used electrolytes include the following: aqueous electrolytes, such as sulfuric acid, sodium hydroxide, and potassium chloride; nonaqueous electrolytes, such as propylene carbonate with lithium perchlorate; and solid electrolytes, such as the polymer Nafion when wet and, for high-temperature sensors, yttria-stabilized zirconia or YSZ,

β -alumina, and NASICON. For AGS applications, the electrolyte solution needs to support both counterelectrode and sensing electrode reactions, form a stable reference potential with the reference electrode, be compatible with the materials of construction, and be stable over long periods of time under various operating conditions. In some cases, hydrogels or an electrolyte inside a porous matrix are used to replace free liquid electrolytes to raise viscosity, lower evaporation rates, and resist leakage of the electrolyte from sensor devices. The polymers or hydrogels can prevent the evaporation of electrolyte during sensor fabrication, especially for microsensor devices where very small amounts of electrolyte are used. Solid electrolytes (polymers and high-temperature ionic materials) allow fabrication of a solid-state sensor, which avoids the danger of leakage of liquid electrolytes entirely. In order to get sufficient ionic conductivity, elevated operating temperatures may be required. High-temperature operation can be an advantage for operation in harsh environments, in an internal combustion engine control system, or for exhaust gas monitoring.

2.5.3. Electrodes

The electrode reaction, i.e., electron-transfer reaction at the WE, involves several steps,^{1,2} including adsorption of the analyte onto the surface, electroreaction, and desorption of products from the electrode surface. Typically, the working electrode is made from a noble metal, such as platinum or gold, which is capable of making a defined interface with the electrolyte in the cell and is porous to allow efficient diffusion of the gas phase to a large and reactive electrode/electrolyte interface. The noble metals generally exhibit excellent stability under polarized potentials that may be corrosive to other metals. The noble metals are also excellent catalysts for many analyte reactions. Carbons, including graphite and glassy carbon, are also popular materials for working electrodes, especially for sensing bioanalytes since many forms of carbon are biocompatible. The selection of the WE material is, therefore, based on the electrochemical and electrocatalytic properties as well as its stability and manufacturability.

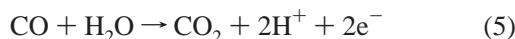
The counterelectrode must also be stable in the electrolyte and efficiently perform the complementary half-cell reaction that is opposite of the analyte reaction.² A Pt electrode is very often used as the CE in an AGS. In addition to the working electrodes and counterelectrodes, a reference electrode is also present when a potentiostat is used.¹ The reference electrode must form a stable potential with the electrolyte, be compatible with the sensor manufacture, and, generally, not be sensitive to temperature (T), pressure (P), relative humidity (RH), or other contaminants or reactants in the sensor system. The RE must be able to maintain the WE at a constant electrochemical potential during the sensing application. An Ag/AgCl reference electrode, which shows good reversibility, is commonly used for this purpose. The other popular reference electrode is a Pt/air electrode, which is not a classical reference electrode but is sometimes called a pseudo-reference electrode because, while it forms a stable potential, the potential is not that of a well-defined thermodynamic reaction and the electrode must be calibrated with an electrode of known potential. In a two-electrode system, a single electrode, called the auxiliary electrode, can function as both the RE and the CE for the purposes of a given analytical experiment.

Table 2. Example Electrode Reactions for Aqueous Electrolyte Amperometric Gas Sensors

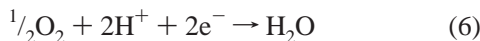
target gas	electrode reaction
H ₂	H ₂ + 2OH ⁻ = 2H ₂ O + 2e ⁻
CO	CO + H ₂ O = CO ₂ + 2H ⁺ + 2e ⁻
O ₂	O ₂ + 4H ⁺ + 4e ⁻ = 2H ₂ O
NO ₂	NO ₂ + 2H ⁺ + 2e ⁻ = NO + H ₂ O
NO	NO + 2H ₂ O = NO ₃ ²⁻ + 4H ⁺ + 3e ⁻
H ₂ S	H ₂ S + 4H ₂ O = SO ₄ ²⁻ + 10H ⁺ + 8e ⁻
SO ₂	SO ₂ + 2H ₂ O = SO ₄ ²⁻ + 4H ⁺ + 2e ⁻

2.6. Electrode Reactions

For an example of electrode electrochemical reactions, the typical room-temperature liquid electrolyte CO sensor is considered. The CO sensor has an H₂SO₄ electrolyte and three Pt electrodes, typically made with high-surface-area Pt powder. The fundamental process for the electrochemical reaction is the transfer of electrons from the reacting CO and H₂O to the WE surface and the formation of some H⁺ to transport the charge in the cell and the formation of one additional oxygen-carbon chemical bond changing the valence of the carbon atom:



In order to maintain charge neutrality in the electrochemical cell, a second reaction, the reduction of oxygen to water, will occur at the CE that uses the acid and electrons to form water:



The WE current generated in the electrochemical cell is related to the rate of CO oxidation at the working electrode and is directly proportional to the rate of CO arriving at the working electrode.

Upon completion of the electrochemical reaction, the products must desorb from the electrode surface. Following desorption, reaction products (CO₂) diffuse away from the electrode area. If the products of the reaction are sensor poisons, the sensor lifetime or response characteristics may be severely limited. Thus, the choice of materials and methods for the electroanalytical processes are critical in the sensor design. Table 2 lists electrochemical reactions for gas analysis. However, the actual electrode reaction at the electrode surface is dependent on the nature of the electrode material, the electrolyte solution, the thermodynamic potential, the interface of the electrode-electrolyte, and, of course, the analyte.

To be complete, each of these analyte reactions is balanced with a second half-cell reaction that occurs at the CE, and this was discussed in the electrolyte section. The counter-reaction is important to consider because it can limit the overall performance of the resulting sensor. It is typically chosen to be a fast, reversible, and noninterfering reaction. This is not always easily achieved and has limited some successful commercialization of amperometric sensors.

2.7. Analytes

Many gases can be measured with an appropriately designed AGS, such as H₂, O₂, CO, NO₂, NO, O₃, SO₂, H₂S, and organic vapors with electroactive functional groups like alcohols or aldehydes. Each sensor can have a unique design and a different set of materials and geometries for mem-

branes, electrolytes, and electrodes in order to take advantage of chemical properties of a specific target analyte and survive under various operating conditions. This use of a variety of materials, unique geometries or structures, and different methods is what gives the sensors their analytical properties and allows them to serve diverse applications. It is because of the discovery of unique combinations of materials, geometries, and methods that the AGS keeps improving and the widespread use of the AGS for industrial safety, biochemistry, clinical chemistry, health and medicine, agriculture, food safety, environmental protection, automotive technology, space exploration, military threat detection, and process control continues to grow. The next section presents a historical perspective on the development of AGS technology and its path to becoming one of the most widely used gas-sensing devices.

3. Survey of Old and New Amperometric Gas Sensors

In general, the AGS technology results from the basic understanding of electrochemistry arising from the works of Nernst, Faraday, and Heyrovsky as well as the understanding of mass transport and electrochemical reactions provided by Fick, Cottrell, Buttler-Volmer, and Levich. Their fundamental scientific advances allow us to make sensors and understand the many dynamic aspects of the observed AGS signals.^{3,4}

3.1. Working Electrode and Sensor Design

3.1.1. Clark Sensor

The earliest successful AGS was developed by Clark et al. in 1953 for oxygen determination.⁵ The original Clark sensor was first introduced to measure the oxygen content in blood samples, and the major innovation was to cover the shiny platinum button WE cathode with cellophane. Unlike previously designed O₂ sensors, which employed a bare platinum electrode, the Clark sensor showed enhanced selectivity for oxygen due to the presence of the cellophane membrane, which allowed O₂ to penetrate but prevented interferences from red blood cells and some other gases. The success of the Clark sensor eventually resulted in the use of cellophane-covered platinum electrodes to regulate the oxygen tension in the arterial line of the dispersion oxygenator during total bypass of the heart and lungs.⁵

As demonstrated by Clark, a membrane diffusion barrier for the working electrode offers several advantages over a bare electrode. For instance, the membrane eliminates interferences from ions and other substances to which it is impermeable, thus improving the selectivity for the analyte of interest. Also, the membrane serves as a diffusion layer for gaseous analytes. By appropriate selection of the membrane material and size, one can control the analytical characteristics of a sensor, permitting the analysis of several analytes over a wide range of concentrations. The earliest Teflon-bonded diffusion electrodes were prepared by Niedrach and Alford⁶ for use in fuel cells. Later, we will also show a method to use bare electrodes with a polymer electrolyte and thereby eliminate the membrane to improve response times.⁷

In 1958, Sawyer et al. investigated sensing of several gases such as oxygen, nitrogen, chlorine, bromine, sulfur dioxide, nitrogen dioxide, nitrous oxide, hydrogen, carbon monoxide,

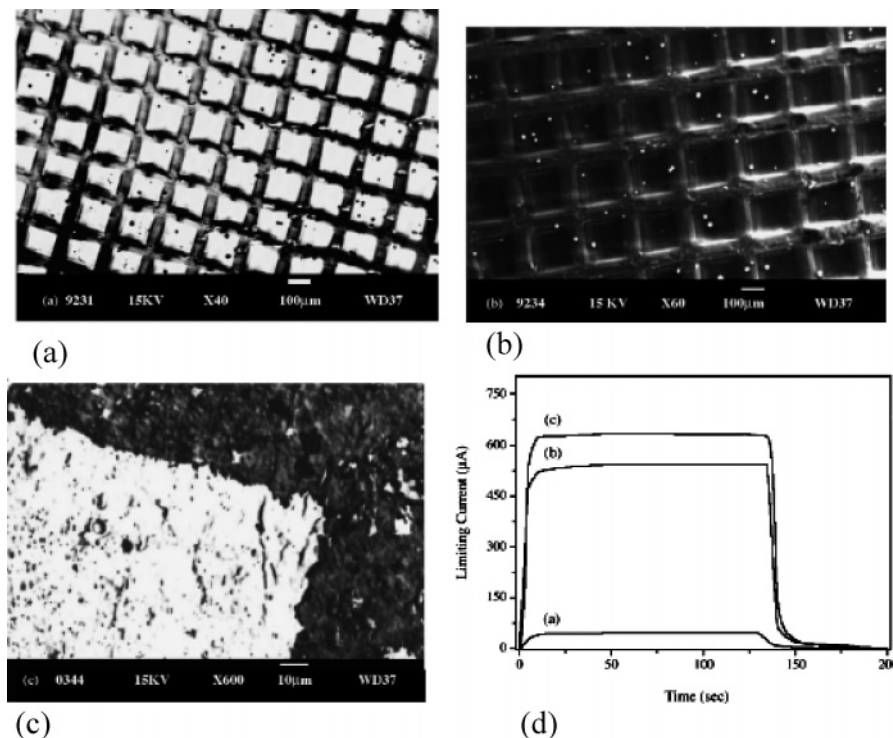


Figure 4. SEM micrographs of KrF laser patterned PTFE membrane electrodes: (a) PTFE-bonded platinum black layer irradiated with a fluence of 500 mJ/cm^2 ; (b) gold film irradiated with a fluence of 60 mJ/cm^2 ; (c) the edge of the electrode as shown in (a); and (d) time-dependent limiting currents of the SO_2 sensors with different pattern sizes compared to the unpatterned sensor. The concentration of the SO_2 gas is 998 ppm: (a) unpatterned sensor, (b) patterned sensor with the pattern size of $100 \mu\text{m}$, and (c) patterned sensor with the pattern size of $60 \mu\text{m}$. Reprinted with permission from Qin, Z.; Wang, P. N.; Wang, J. *Sens. Actuators, B* **2005**, *107*, 805. Copyright 2005 Elsevier Science.

hydrogen sulfide, and hydrogen cyanide with a membrane-coated platinum electrode.⁸ The best performance characteristics were achieved using polyethylene, as opposed to saran, Mylar, and natural rubber, as the membrane material. As shown by their results, the incorporation of the membrane into the sensor system greatly enhanced the overall practicality of the sensor, leading to many new applications. However, it remained difficult to construct practical gas sensors at that time because there was no convenient way to package the electrodes for field use.

Modern Clark electrodes are fitted with a porous poly(tetrafluoroethylene) (PTFE) membrane. Because of the hydrophobicity of the material, the pores (typical diameter $10 \mu\text{m}$) are not wetted by the aqueous solution but allow the transport of dissolved gases to the electrode–electrolyte interface.⁹ As the mass-transfer rate of the analyte is slow compared to electron transfer, the Faradaic current is controlled by diffusion rather than the kinetics of the electrode reaction, and this assures a linear dependence of the current on concentration of the dissolved oxygen. The arrangement can be used for the measurement of other dissolved electroactive gases, most notably for the determination of chlorine in swimming pools. The layer of electrolyte solution between membrane and electrode is kept thin in order not to compromise sensitivity and response time. This design is, in principle, suitable for measurements in the gas phase, but in practice it is found that the cell is not stable because of variations in the thickness of the thin liquid film used in the Clark design, most likely because of evaporation of the water used as a solvent for the electrolyte. For the measurement of electroactive species in the gas phase, designs derived more from fuel cell technology have been

adopted. PTFE membranes can be coated with vacuum-evaporated metals for improved sensitivity.¹⁰

The potential drop across any given sensor cell includes the potentials of the working electrodes and counterelectrodes and the potential over the galvanic cell's internal resistance. For a given material of working electrode, the sensitivity of the galvanic cell depends on the surface area on which the electrochemical reaction takes place.^{11–15} The assembly must provide as large a surface area as possible for the three-phase boundary (TPB = interface between the gas, the electrode, and the electrolyte), because the electrode reaction is assumed to take place primarily in this region. The particular “hair morphology” of a catalyst surface, e.g., nanostructures, can dramatically increase the three-phase boundary area, followed by an enhancement of the sensor's sensitivity. A further improvement of the sensitivity from ppm to ppb gas concentration levels can be obtained using the new membrane–electrode assembly composed of a PTFE membrane and a nanocomposite material of carbon nanotubes and PTFE. Carbon nanotubes can greatly increase the surface area of the TPB because the carbon nanotubes have very high surface area, e.g., single-walled carbon nanotubes can achieve $1600 \text{ m}^2/\text{g}$ Brunauer–Emmett–Teller (BET) value.^{16,17} The catalyst is deposited electrochemically on the membrane in order to get a nanostructured surface and to increase the TPB area.^{18–20} Wang's group developed a method to pattern the PTFE membrane electrodes by KrF laser ablation²¹ (see Figure 4). Patterning of the sensing electrode can be well-controlled and is expected to increase the sensitivity of the sensor because the sidewall of the patterned catalyst layer can be considered as the effective TPB. Compared with the unpatterned sensor, the sensitivity of the sensor with a pattern

size of 60 μm was improved by 14 times, and the response time is reduced half.

The dramatic increase of the limiting current and the shortening of the response time were obtained from the increase of the TPB area and the rapid gas diffusion through the membrane electrode. Other nanostructures are used for this purpose as well, such as composites of $\text{Gd}_{0.7}\text{Ca}_{0.3}\text{CoO}_{3-\delta}$ and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ that have potential applications as oxygen-permeable membranes in an amperometric sensor for NO_x detection in exhaust gases.²² In addition, a series of manganites was investigated for membranes with the composition $\text{A}_{0.7}\text{E}_{0.3}\text{MnO}_3$ ($A = \text{Gd}, \text{Y}, \text{and Pr}$ and $E = \text{Ca and Sr}$).²³ The presence of slow diffusion-coupled redox processes could be detected in all manganites at low and high oxygen activities vs an air reference electrode. The oxygen ion conductivity was considerably lower than $10^{-5} \text{ S cm}^{-1}$ in all investigated manganites. Nevertheless, the comparison of results for glass-encapsulated and nonencapsulated microcontacts showed that $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and, in particular, $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are quite active as catalysts for the oxygen electrode reaction at the three-phase boundary air/zirconia/manganite, whereas $\text{Y}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ does not catalyze the oxygen electrode reaction significantly at the surface. Studies have been carried out on the selectivity, mass transfer rates, and effects of temperature on PTFE films as diffusion barriers.²⁴ The advent of using nanostructures has made a significant impact on the design of the modern AGS as it has on other sensors.¹⁹

3.1.2. Diffusion Electrodes

A major achievement in the evolution of the modern AGS occurred in 1965 with the development of the gas-diffusion electrode by Niedrach.⁶ The original Niedrach electrode consisted of a sintered Teflon–Pt catalyst covered with a porous Teflon film. Its performance was evaluated in hydrogen–oxygen and hydrogen–air fuel cells at ambient temperature in 6N KOH and 5N H_2SO_4 . In both cases, it was shown that water was efficiently retained in the electrolytic solutions and did not leak into the gas fuel feed stream. The Niedrach electrode provided a model for the contemporary gas-diffusion electrode, being “semihydrophobic” and allowing an open porous electrode of the finely dispersed metal catalyst yet not allowing complete penetration by the electrolyte. These electrodes are prepared by mixing Teflon emulsion with a high-surface-area noble metal catalyst powder and then depositing the slurry on a metal wire screen or on the surface of a totally hydrophobic porous Teflon film. The electrochemical cell that is based on a gas-diffusion electrode composed of a porous PTFE membrane and a porous electrode is shown in Figure 5. The resulting gas-diffusing electrode consists of highly interlocked matrices of gas pores, electrolyte channels, electronically conducting paths, and electrocatalytic surfaces. It is porous enough to affect efficient gas permeation, has sufficient metal catalyst to be a good electronic conductor, and is hydrophilic enough to make intimate contact with the electrolyte for ionic conduction and facilitation of electrochemical reactions involving gases.

In contrast to the Clark electrode, gas-diffusion electrodes based on back-side metallized porous membranes are not affected by evaporation of water because the porous electrode is directly in contact with the bulk of the electrolyte solution. The mass transfer of analyte from the sample to the working electrode can be faster, resulting in shorter response times

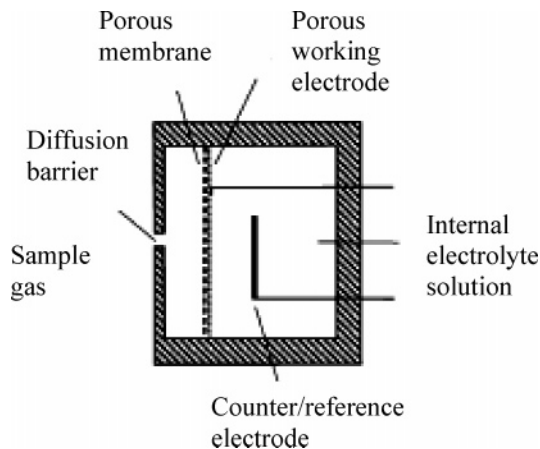


Figure 5. Schematic of a cell based on a gas-diffusion electrode (GDE) composed of a porous PTFE-membrane and a porous electrode. Reprinted with permission from Knake et al., *Analytica Chimica Acta*, **2005**, 549, 1. Copyright 2005 Elsevier Science.

and higher currents that lead to higher sensitivity. Also, the real surface area of the electrode can be several orders of magnitude higher, allowing species with relatively poor electroactivity to produce measurable currents. Therefore, they are especially valuable in those cases when the kinetics of the electrochemical reaction are very slow, such as the oxidation of hydrocarbons and CO. Examples of the earliest of these sensors reveal excellent practical sensor characteristics.^{25–28} A kinetic study of NO gas at the Pt/Nafion electrode with application to the amperometric NO and NO_2 sensing has been carried out by Ho’s group.^{29,30} Sensors based on metallized porous membranes and porous catalytic electrodes have been produced from several manufacturers that are widely used in industrial applications.^{1,2} On the other hand, relatively few publications on this specific structure of electrode have appeared in the scientific literature in the past decade,^{31–33} indicating the maturity of this type device.

The fuel-cell type electrode was never utilized in an AGS until, in 1969, a breakthrough in design combined it with a Pt/air reference electrode to achieve the practical ethanol and CO sensor design introduced by Oswin, Blurton, and co-workers.²⁶ This new design was used to detect various toxic gases, such as ethanol, CO, H_2S , NO_2 , and NO. The sample (an electrochemically oxidizable or reducible species) enters the cell through porous electrodes similar to those used in a fuel cell (see Figure 6);³⁴ hence, the device has been incorrectly called a fuel-cell sensor, although its purpose is not the conversion of chemical to electrical energy. The relationship between the cell current and the concentration of chemical species of interest present in a more or less constant matrix can be established empirically and optimized to be linear in most cases over a fairly broad range of concentrations. In the electrochemical cell that becomes the sensor of Oswin and Blurton,²⁶ the gas was detected from the current generated by the electrochemical reaction at a fixed potential of 0.9–1.5 V vs SHE. This avoided the generation of undesired current from reactions involving the oxygen–water redox couple within the cell. The original Oswin/Blurton cell significantly simplified sensor design and provided a model for several two- and three-electrode sensors that were eventually introduced in the 1970s including ethanol,²⁶ CO, and other gases.²⁸

Recently, a high-temperature solid electrolyte amperometric CO_2 sensor was fabricated using a Pt/NASICON (Na^+ conductor, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$)/Pt cell and a porous Na_2CO_3 –

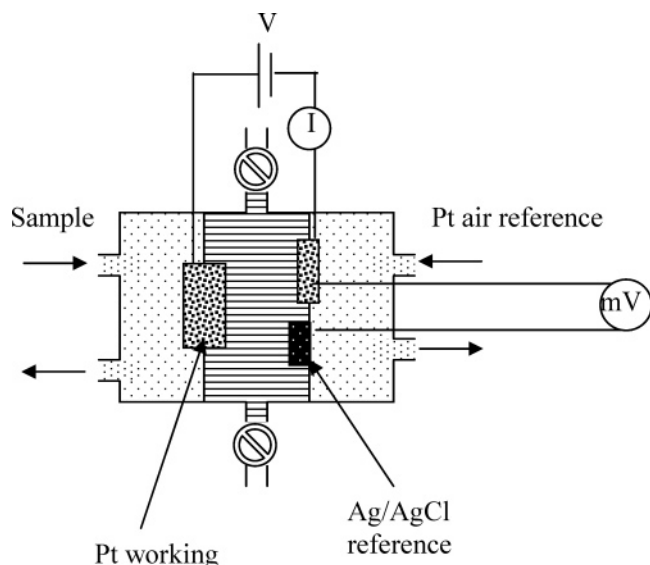


Figure 6. Fuel-cell-type amperometric sensor.

BaCO₃ auxiliary layer.³⁵ A platinum-loaded zeolite electrode was developed for high-temperature measurement of total NO_x in combustion environment.³⁶ A Pt-loaded Y (PtY) is a catalyst electrode for NO_x equilibration with electrochemical oxidation of NO on a yttria-stabilized zirconia (YSZ) electrolyte. By applying a low anodic potential of 80 mV, the NO in the NO_x equilibrated mixture can be oxidized at a Pt working electrode on the YSZ electrolyte at 500 °C. A novel reference electrode for a NO_x sensor was developed that did not require air, and this makes the design simpler and more robust.³⁷ With the advent of nanotechnology, the use of nanostructured materials in fuel-cell sensors to enhance the sensor performance becomes ever more popular. The details will be discussed in the following section.

3.2. Electrolytes

In addition to the progress made in the development of electrodes and sensor geometries, the 1970s witnessed improvements in the use of different electrolytes. Prior to 1970, electrolyte solutions for amperometric sensors were mainly aqueous in nature. Even nowadays the aqueous solutions are still used as the electrolytes for gas sensing, e.g., acid or halide-halate electrolytic solutions are used for acidic gas³⁸ and for other gas-detection applications.³⁹ As illustrated in the preceding examples, aqueous electrolytes are effective in many amperometric gas sensors. However, they are also limited in their specificity, service life, operating temperature range, and electrical potential range. As a result of the problems and limitations associated with aqueous electrolytes, sensor research began to focus on the design and development of alternative electrolytes. By the middle 1970s, nonaqueous and solid polymer electrolytes emerged for the AGS.^{6,40–48} As nanotechnology becomes more prevalent and many nanostructures are developed for use as working electrodes, parallel studies of nanostructures for use as the electrolyte are also being conducted.

3.2.1. Nonaqueous Electrolyte

One of the earliest amperometric sensors employing a nonaqueous electrolyte was described by Schneider in 1978.⁴⁷ The novel electrochemical cell, used for the detection of chlorine, contained a nonaqueous electrolyte composed of

lithium or sodium perchlorate as supporting electrolyte dissolved in an organic solvent selected from the group consisting of γ -butyrolactone, sulfolan, or propylene carbonate. All these solvents have a high boiling point (>200 °C) and possess a high anodic limit with the Pt electrode. This sensor was superior to previously designed chlorine sensors, which frequently failed because the electrode materials selective to chlorine often dissolved in the aqueous electrolyte medium. The new sensor was effective in detecting chlorine down to the ppm range, had a fast response time of <1 min, and had an extended useful life of >1 year. A word of caution must be added that the use of perchlorates in organic solvents always represents an explosion hazard, particularly when the assembly is, inadvertently, allowed to dry up or be exposed to high temperatures. Similarly, Venkatesetty described the invention of a carbon monoxide sensor incorporating a nonaqueous electrolyte.⁴⁴ This sensor, based on an aprotic electrolyte system, was also used to amperometrically detect toxic gases such as nitrogen oxides, SO₂, and H₂S. Other electrochemical cells employing nonaqueous electrolytes were also introduced during the same time period. These systems were used to fabricate amperometric sensors for several gases such as methane,⁴⁵ hydrazine, and carbon dioxide.⁴⁷

3.2.2. Solid Polymer Electrolytes

Solid polymer electrolytes became important during the mid-1970s because of the inefficiencies and maintenance requirements of liquid electrolytes. Originally, a solid polymer electrolyte (SPE) was described as a solid plastic sheet of perfluorinated sulfuric acid polymer that, when saturated with water, became an excellent ionic conductor. Nafion, a typical solid polymer electrolyte, is a hydrated copolymer of poly(tetrafluoroethylene) (PTFE) and polysulfonfyl fluorine vinyl ether containing pendant sulfonic acid groups (Dupont). Nafion has good proton conductivity, high gas permeability, and chemical stability, and it has been widely used in chloralkalai, fuel-cell, and sensor applications. In the Nafion-based AGS design, Nafion film is used both as the electrolyte and as a support for the electrode structure. The ionic conductivity results from the mobility of the hydrated hydrogen ions that move through the polymer sheet by passing from one sulfuric acid group to another.¹⁹ An early amperometric gas sensor incorporating a solid polymer electrolyte was described by LaConti and later improved by Sedlak et al. The sensor, originally used to detect carbon monoxide,⁴³ employed Nafion. Being a cation-exchange membrane, Nafion permitted the passage of cations and blocked the passage of anions. Thus, the hydrogen ions produced at the working electrode through oxidation of carbon monoxide were transported through the ion-exchange membrane to the counterelectrode, where they reduced oxygen with the addition of electrons to produce molecular water. In addition to its excellent ion-exchange capacity, the Nafion electrolyte exhibited other positive features, such as high structural stability, resistance to acids and strong oxidants, and good thermal stability. As a result of its useful characteristics, Nafion has been used to detect gases other than carbon monoxide,^{49,50} such as CO₂ and NH₃,⁵¹ NO_x,^{52,53} hydrogen,^{54–56} H₂S,⁵⁷ SO₂,⁵⁸ O₂,^{59,60} O₃,^{61,62} and alcohol vapors.⁶³ The only limitation for field use was the issue of the water in the Nafion freezing at low temperatures.

In addition, Kuwata et al. illustrated two different amperometric oxygen sensors using a Nafion membrane opera-

tive at room temperature.^{64,65} Also, Alberti and Casicola presented an amperometric three-electrode sensor for CO operating at room temperature and using thin layers of α -zirconium phosphate as a solid electrolyte.⁴¹

3.2.3. Ceramic Solid Electrolytes at Elevated Temperature

The use of ceramic solid electrolytes in amperometric gas sensors at elevated temperatures allows for the detection of different gases under harsh conditions. There is an increasing need for rugged and reliable gas sensors capable of monitoring carbon monoxide, nitric oxides, sulfur oxides, and hydrocarbons from automotive exhausts. Because of such harsh environments, e.g., high temperature and high pressure, aqueous electrolytes, liquids, or polymeric materials cannot be used in sensor designs. Ceramic solid electrolyte sensors are typically designed for high-temperature applications such as stack gas, combustion process, and automotive engine exhaust. The solid electrolyte provides ionic conduction and also supports the electrodes. The interface between the solid electrolyte and the electrode plays an important role in the resulting gas sensor's analytical characteristics.

Liu and Weppner described amperometric gas sensors using solid electrolytes such as NASICON, cubic stabilized zirconium oxide, and polycrystals of tetragonal zirconium oxide to selectively detect the partial pressures of several gases.⁶⁶ An AGS incorporating solid electrolytes made from rare earth elements was also designed for high temperature, and Stetter and Cao⁶⁷ described an amperometric sensor for the detection of halogenated compounds such as chloropentafluorobenzene, chlorobenzene, bromobenzene, and iodobenzene. This sensor, which used a bead of sodium lanthanum fluoride silicate as the solid electrolyte, was shown to operate around 550 °C.⁶⁷ Similarly, Coillard et al. discussed a sensor employing commercial zirconia lambda gauge for the amperometric detection of NO in automobile exhausts at high temperature.⁶⁸ As a result of their versatility, solid electrolytes have become important components of amperometric gas sensors.

An amperometric NO sensor using a LaGaO₃ solid electrolyte was investigated, and the response was based on the difference of catalytic activity of the electrodes.⁶⁹ It was found that the oxygen pumping current increased upon exposure to NO when Sr_{0.6}La_{0.4}Mn_{0.8}Ni_{0.2}O₃ and La_{0.5}Sr_{0.5}MnO₃ (LSM-55) were used as active and inactive electrodes for NO oxidation, respectively. Compared with various common electrolytes such as YSZ or Sm-doped CeO₂, it was clearly demonstrated that much higher sensitivity in the amperometric mode is achieved by using LaGaO₃-based fast oxide-ion conductors. The fuel-cell configuration was used for the investigation of three types of metallic electrodes for NO detection in the exhaust gases.⁷⁰ Their results show that the cell defined as RhPtAu/YSZ/RhPtAu gives a relatively high NO sensitivity of ~14 nA/ppm and a low O₂ sensitivity of 0.02 nA/ppm. The availability of electrode materials with selectivity opens up possibilities for the development of highly sensitive amperometric NO gas sensors with a single working electrode, i.e., the NO concentration in O₂ and NO containing gas mixtures can be directly measured without oxygen pumping.

3.3. MEMS and Nanotechnology

Microelectrodes (MEMS), especially micro-working electrodes, with a very small electrode surface area, have been used for amperometric gas sensors. In recent years, MEMS

technologies have increasingly been employed to fabricate microelectrode structures. The microelectrodes have shown several advantages of high sensitivities, fast response speeds, small sample amounts, and well-defined and reproducible geometries.

In contrast to the development of sensor parts, such as membranes, electrodes, and electrolytes, which occurred during the 1960s and 1970s, amperometric gas sensor research of the 1980s focused on the production of novel sensor designs. One of the highlights of the 1980s in relation to analytical chemistry was the introduction of microsensors. Microfabrication of electrochemical devices has numerous advantages over standard fabrication procedures. These advantages include precise reduced sensor size, reduced cost, smaller sample size, faster response time, higher concentration sensitivity, well-defined geometrical features, and potential for mass production. These advantages, however, must be obtained without degradation of the signal-to-noise ratio as the sensor size is reduced.

Progress in the development of microamperometric sensors was slow when compared to the production of micropotentiometric sensors. Microamperometric sensors of the early 1980s consisted only of microfabricated electrodes on a suitable substrate. These electrodes were then coated with the liquid electrolyte solution that also carried the sample to the electrode area for analysis. An example of an early microamperometric sensor was presented by Sleszynski and Osteryoung in 1984.⁷¹ The given sensor, which used very small electrodes constructed from nonconductive epoxy and reticulated vitreous carbon (RVC), was shown to yield desirable results as compared to standard fabricated sensors. However, the goal of constructing complete, practical, and commercially successful amperometric gas sensors using the microfabrication approach has still not been achieved.

During the late 1980s, microfabrication technology for the construction of amperometric sensors was investigated with the introduction of novel sensor electrode designs. In 1988, Maclay and co-workers^{72,73} introduced a series of Nafion-based microfabricated amperometric gas sensors using gold sensing electrodes in the shape of a square grid. The newly designed sensors were evaluated by comparing their analytical characteristics with those of conventional sensors. The response time of the miniaturized sensors was >1 order of magnitude faster than conventional sensors, although they had a lower sensitivity. This work also elucidated the fact that the sensitivity of the device depended not only on the chemical nature of the electrode surface but also on the specific structure of the electrocatalytic surface and the interface created by gas/electrode/electrolyte.

In an effort to improve the sensitivity of microamperometric sensors, Buttner et al.⁷³ constructed devices with an integrated design in which the working electrodes, counter-electrodes, and reference electrodes were photolithographically etched onto a gold-coated silicon oxide surface of a silicon wafer and spin-coated with a thin film of a solution of Nafion. The working electrode of the sensor was an ultrafine square grid with evenly spaced regions of gold and holes every 50 μm . The signal observed for the sensor following exposure to gases such as H₂S and NO greatly exceeded the response that would be expected on the basis of simple geometric considerations of microelectrodes.⁷³

The analytical characteristics of microamperometric sensors can also be improved by varying the sensor components, such as electrolyte composition. For example, Hauser et al.³¹

recently described the preparation of a carbon dioxide sensor using mixed organic solvents as the electrolyte. As shown by the results of this study, a mixed acetonitrile/dimethyl sulfoxide solvent enhanced the overall performance of the sensor by producing a large potential window over which the CO₂ reduction currents can be measured.³¹ As illustrated by these examples, advances in microtechnology during the 1980s have resulted in the production of newly designed amperometric gas sensors with characteristics superior to those of conventional sensors.

More recently, gold microelectrodes are used with and without membranes in nonaqueous media for oxygen, carbon dioxide, and nitrous oxide detection simultaneously over a wide concentration range.^{74,75} It is believed that, by using sufficiently small microelectrodes, it should be possible to effectively "outrun" the reaction kinetics by the much faster loss of species from the electrode/electrolyte interface by diffusion, thereby giving rise to independent oxygen and carbon dioxide signals. Hahn and co-workers also conducted the microelectrode studies of isoflourane vapor, an inhalation anesthetic agent, and oxygen mixtures in dimethyl sulfoxide.⁷⁶ However, such sensors never demonstrated the long lifetimes required by field applications nor the low cost and, thus, have not been commercialized for popular use. Very recently, nanosize working electrodes using carbon nanotubes have been reported.

The advantages of such microsensors are small in size, low cost, low power, high signal-to-noise ratio, and low detecting limit. For the discussion of using the nanostructures for making the microsensors, a sensor array consisted of various highly sensitive carbon nanotube-based sensors developed by Li's group are described here, such as sensors using pristine carbon nanotubes,⁷⁷ carbon nanotubes loaded with metal clusters,^{78,79} and carbon nanotubes coated with polymers.⁸⁰ An interdigitated electrode (IDE) was utilized as a transducer, with many of them on a chip that was fabricated on a silicon wafer.⁸¹ This electrochemical sensor depends on the transfer of charge from one electrode to another electrode. The gases and vapors introduced to this sensor array are NO₂, HCN, HCl, Cl₂, acetone, and benzene in parts per million (ppm) concentration levels in dry air. These are toxic gases and vapors that are of interest to both military and civilian personnel in defense applications, as well as in industry process and environmental monitoring. The detection limit of carbon nanotube sensors can achieve the ppb concentration level.⁸² Carbon nanotubes can be coated with metals to prepare hydrogen sensors⁸³ or with Nafion to make RH sensors.²⁰

For many years, it was generally reported that potentiometric sensors were more easily microfabricated because the signal size did not depend at all on the electrode size while amperometric sensor currents were directly proportional to electrode size. An ideal use of nanostructures to create large surface area in small-sized devices is found here. With the use of nanostructures, the electrode area of the amperometric sensor can be reduced by orders of magnitude while preserving the sensor signal magnitude, and this is a perfect example of the importance of nanostructures in the design and construction of the AGS.

Several other designs for amperometric gas sensors were also introduced during the 1990s. For example, Wallgren and Sotiropoulos reported⁸⁴ the construction of an oxygen sensor based on the planar sensor design. The design consisted of both the working electrodes and the counter-

electrodes being vacuum-deposited as nonporous Au layers on the same face of a Nafion electrolyte and in contact with the gas sample. Potential advantages of this design include faster response times and higher sensitivities per useful electrode area due to the high mass transport rates of the gas to the sensing electrode since no membrane or significant liquid film barrier is present. Also, smaller quantities of precious metal catalyst could be used for the working electrode, and the labor-intensive stacking steps required for the fabrication of conventional-type designs are avoided. As shown by the results of this research, oxygen reduction leads to an exponential current rise over a wide potential range, indicating very high mass transport rates and implying that the electroactive gas reacts at the line formed by the gas/solid electrolyte/metal layer interface.⁸⁴ However, the practicality of the design may be questioned because, in practice, if the water content of the membrane changes, so do the dimensions, and this can lead to stresses that will fracture the electrodes and alter the response.

Berger and Edelman also described the production of a planar sensor used to detect the partial pressure of oxygen in blood samples.⁸⁵ In this sensor, a semipermeable membrane, comprising an acrylonitrile butadiene copolymer or an acrylate-based copolymer, was provided to act as an impermeable barrier for ions and blood constituents other than oxygen.⁸⁵

In 2004, Meyerhoff and co-workers reported a planar amperometric nitric oxide sensor based on platinumized platinum anode.⁸⁶ A microporous poly(tetrafluoroethylene) gas-permeable membrane was used. Platinization of the working platinum electrode surface dramatically improves the analytical performance of the sensor by providing ~10-fold higher sensitivity (0.8–1.3 pA/nM), ~10-fold lower detection limit (≤ 1 nM), and extended (at least 3-fold) stability (>3 d) compared to sensors prepared with bare Pt electrodes. In this article, both experimental results and theory of NO measurements as a function of sensor diameter and distance from a point source were discussed in the context of an investigation of monitoring NO release from diazeniumdiolate-doped polymeric films. By modifying the above-discussed NO amperometric gas sensor with thin hydrophilic polyurethane films containing catalytic Cu(II)/(I) sites, the direct amperometric detection of *S*-nitrosothiol species (RSNOs) is realized.⁸⁷ Catalytic Cu(II)/(I)-mediated decomposition of *S*-nitrosothiols generates NO(g) in the thin polymeric film at the distal tip of the NO sensor.

Another type of planar thick-film sensor with centrosymmetric diffusion geometry for detection of hydrocarbons in oxygen, nitrogen, and hydrocarbon gas mixtures has been developed for monitoring in exhaust gases.⁸⁸ In this work, propene (C₃H₆) is chosen for sensor tests as a model hydrocarbon. The solid-state electrochemical cell based on yttria-stabilized zirconia (YSZ) operates in the amperometric mode. Oxygen is pumped out at the Au/YSZ electrode, and C₃H₆ is oxidized at the Pt/YSZ electrode (see Figure 7). At a gas temperature of 600 °C, the sensitivity is 2 nA/ppm C₃H₆ for this high-temperature amperometric gas sensor design.

3.4. Sensor Array

The 1980s also witnessed the microcomputer revolution, which, coupled with the advent of chemometrics and available AGSs, encouraged the introduction of arrays of gas sensor systems.^{89–93} While the earlier research occurred in

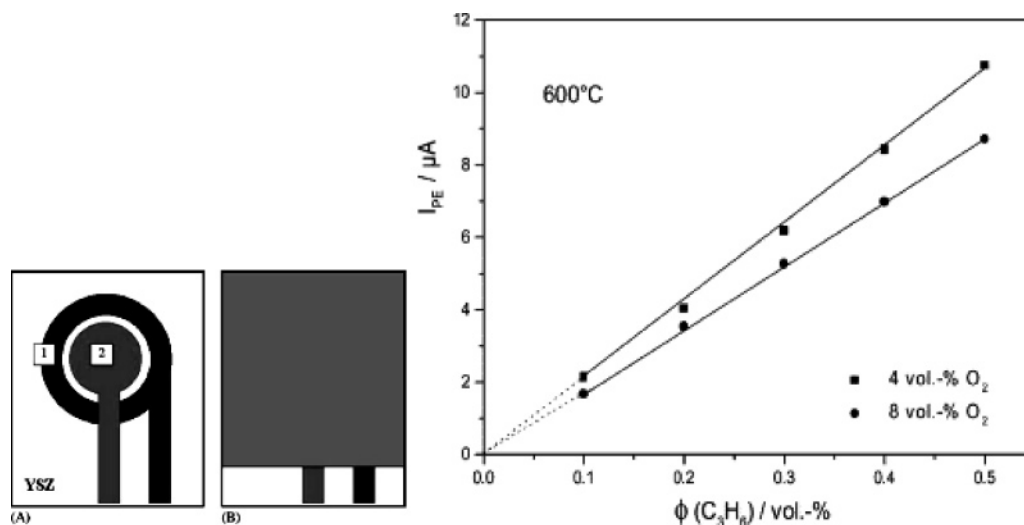


Figure 7. Schematic of the sensor design: (A) one side of the sensor showing the counterelectrodes upon the YSZ substrate, (1) Au/YSZ ring electrode (RE) and (2) Pt/YSZ point electrode (PE); (B) back side of the sensor, showing the diffusion barrier covering the working electrodes; and (C) propene characteristics of the Pt/YSZ point electrode at various oxygen concentrations. Reprinted with permission from Schmidt-Zhang, P.; Guth, U. *Sens. Actuators, B* **2004**, *99*, 258. Copyright 2004 Elsevier Science.

the early 1980s^{93,94} in conjunction with a K-nearest neighbor or KNN algorithm for pattern recognition, a very recent development features an amperometric sensor array for a gas mixture of NO_x , CO, O_2 , and SO_2 detection using Nafion/Pt (or Au)/ceramic plate microelectrodes prepared by micro-fabrication technologies as the sensing electrodes and a backpropagation neural network (BPN) as the pattern-recognition algorithm.^{95,96} The limiting current potentials for anodic oxidation of NO on Au, anodic oxidation of SO_2 and CO on Pt, and cathodic reduction of NO_2 on Au and O_2 on Pt were applied to each of the sensors in the array, respectively. The system was optimized for identifying these gases with their concentrations in the mixture. Sensor array technology has been utilized in chemical detection of gases and is sometimes known as an electronic nose^{97,98} and, when used in liquids, is sometimes known as the electronic tongue.⁹⁹ However, the instrument using a sensor array as a detector has not been fast to get into the commercial analytical market and remains in the stage of a new technology in various application areas. One of the main reasons for the slow introduction of arrays into the market is the difficulty in calibration and in the isolation of the analyte response from the matrix response. Recent conferences, reviews, and books have chronicled progress in sensor arrays incorporating all types of sensors.⁹⁰

A recent renaissance has occurred and provided new interest in sensor-array-based analysis. Much of this interest has to do with important applications like the detection of lung cancer, recently shown to be possible with a gas sensor array.¹⁰⁰ While the relationship of the sensor array signals to lung cancer is undisputed, there is something unsettling about an analytical technique for which the molecular basis for the response is clearly not well-understood if understood at all. Statistically, while we expect the analysis to be somewhat robust and to apply to unknowns, the statistical basis for this can be calculated and the molecular basis is only implied. Thus, the sensor array work often blurs the line between functional dependence and association of a signal and complex endpoint. It will take progress in multivariate calibration, the construction of multivariate models like the net analytical signal recently used for NIR determination of glucose, or the development of another robust

method in order to gain widespread analytical acceptance for routine analytical determinations. What the sensor array has always been good at is the comparison of two complex mixtures, one a standard and one sample or a mixture of standard and a sample to the standard. In analysis, the sensor array can be a highly valuable tool for determination or comparison of complex nonmolecular endpoints like taste, odor, or flavor, and the AGS was one of the earliest contributors.^{93,94} More comparisons of different analytical myths and operational aspects of the electronic nose can be found⁸⁹ for practical applications.

4. AGSs For Practical Applications

The modern AGS can be considered one of the primary methods for field detection of CO in air for industrial hygiene applications since the 1970s, when it was introduced to replace the hopcalite catalyst method.¹⁰¹ The 1970s through the 1990s also brought about many additional applications of amperometric sensors in field analytical use.¹⁰² The AGS provides ppm level sensitivity, stability, low cost, low power, good selectivity, and fast response all at the same time, and this makes for a powerful and versatile sensor. Also, because the analysis is “on the spot”, samples do not have to be preserved or returned to a lab for a slow and costly analysis.

By manipulating the standard three-electrode potentiostat arrangement of amperometric gas sensors, one can design an amperometric detector for various target analytes and conditions in field analysis. Hauser et al. recently described a simplified amperometric detector for capillary electrophoresis. This system employed only two electrodes in total to analyze catecholamines, ascorbic acid, carbohydrates, and heavy metals. Detection was carried out with a single working electrode by using an electrophoretic counterelectrode as a polarized pseudo-reference electrode with an appropriate electronic circuitry. As shown by the results of this study, the amperometric detector achieved similar performance characteristics as compared to the traditional amperometric gas sensor.³¹

The amperometric gas sensor has a long history of development and some of them have produced mature for field applications. With the advent of microfabrication

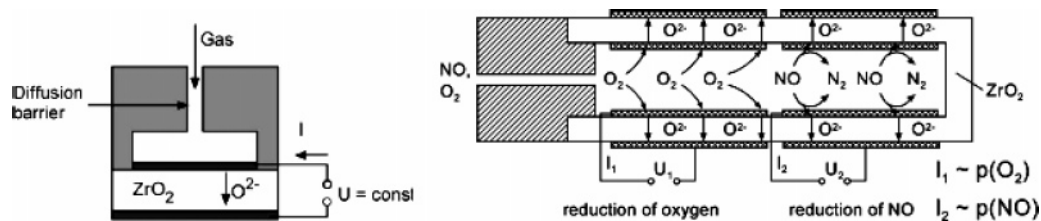


Figure 8. (A) Schematic cross section of a typical amperometric oxygen sensor with a channel-type diffusion barrier and (B) principle of an amperometric two-electrode cell for the simultaneous detection of oxygen and NO. Reprinted with permission from Reinhardt, G.; Mayer, R.; Rosch, M. *Solid State Ionics* **2002**, *150*, 79. Copyright 2002 Elsevier.

technology, computational power in a PC, and nanotechnology, improved sensors with better working electrodes, different types of electrolytes, and miniature design have evolved, and this has expanded the spectrum of real-world applications.¹⁰³ The challenges are common to all applications including the following: inexpensive fabrication steps, sensor robustness, reliability, reproducibility, low power consumption, and easy system integration.

4.1. Industry

AGSs possess high sensitivity, small size, and low power consumption, which can be used to quickly verify incoming raw materials at the delivery point. The AGS technology can significantly reduce the amount of time and money spent analyzing materials in a lab, as well as reduce the amount of material handling. Most changes in chemical processes can be reflected in the changing composition of the vapor phase surrounding or contained within the process. Thus, vapor-phase sensors can enable the quick assessment of the chemical status of most industrial processes. Examples are found across many sectors including food processing (coffee roasting and fermentation), petrochemical (plastics manufacture and gasoline blending), and consumer products (detergents and deodorants). Much like vision inspection is used to assess the visual integrity (color, shape, and size) of products, olfactory inspection assesses the chemical integrity (consistency and presence of contaminants) of products.^{1,2,89,91,109,110,111}

4.2. Environment

Increasing awareness of new regulations for safety and emission control makes environmental monitoring one of the most important applications for reliable gas sensors. Current methods for air quality analysis typically require the use of very costly and bulky analytical equipment. For applications in environmental monitoring or indoor air quality measurement, sensors that are able to selectively detect various gases at concentration levels ranging from a few ppb to hundreds of ppm are valuable. New developments in MEMS sensors are trying to address these difficult measurement tasks.¹⁰³ With unique combined advantages of high sensitivity, small size, and low power consumption, the amperometric gas sensor is uniquely suited for environmental applications, but it is often challenged with sensitivity or selectivity demands not encountered in other applications. For example, the amperometric sensors based on stabilized zirconia have been developed for the detection of oxygen-containing gases like NO_x or combustible gases such as CO, H₂, and hydrocarbons;¹⁰⁴ for NO_x detection;¹⁰⁵ for lean combustion gas control;¹⁰⁶ and for selective detection of propane.¹⁰⁷ Multi-electrode amperometric sensors are able to detect O₂ and NO or O₂ and combustibles at the same time, and such a

multielectrode cell is illustrated in Figure 8. The basic idea is to adjust geometric and working parameters in such a way that, at each electrode, essentially one-electrode reaction takes place. Selectively reacting electrodes are desired to improve sensor performance. Recently, SrTi_{0.65}Fe_{0.35}O_{3-δ} (STF-35) has received considerable attention for use as a resistive oxygen sensor because of its unusual temperature-independent conductivity above 700 °C and pO₂ > 1 Pa.¹⁰⁸ This material has the potential for automotive oxygen sensor applications. Combined with physical sensors for temperature, anemometry, pressure, and humidity monitoring, an AGS system can be built to get comprehensive information for an environment simultaneously.

The Indoor air quality application is just now beginning to emerge as exposure to environmental pollutants in the air is being suspected for many human health issues. The Exposure Biology program at the National Institutes of Health addresses many of these concerns. The application to measure trace levels of pollutant exposure of children and the population at large will require new sensors for measurements as well as new modeling tools (<http://www.gei.nih.gov/exposurebiology/index.asp>). This need for personal measurement sensors at ppb levels for specific pollutants represents a new challenge that is ideally met with the AGS since it has all of the important logistical features of low power, light weight, small size, and low cost. However, the challenge is obtaining increases in sensitivity and selectivity and often response time and stability in the AGS for analytes such as ozone, CO, NO_x, and others.

4.3. Defense and Homeland Security

Chemical sensors like the AGS are suitable for security and defense applications because of their portability and low power consumption. AGS potentially can offer higher sensitivity, specificity, and lower power consumption for toxic gas detection. Some examples include monitoring filter breakthrough (e.g., toluene concentration inside the mask), personnel badge detectors (e.g., toxins accumulation), embedded suit leak-detection sensors (e.g., soldiers' suits for upcoming warfare agents), and other applications. Additionally, a wireless capability with the sensor can be used for networked mobile and fixed-site detection and early warning systems for military bases, work facilities, and battlefield areas. Explosives detection at the airport is recently a priority application for Department of Homeland Security (DHS), and sensors or detectors will require quick detection and a low false-alarm rate. One type of the liquid explosive hazard that is easily detected by amperometry is hydrogen peroxide. The challenges will be to obtain the stability, reproducibility, and low maintenance of the fielded sensors to achieve quick screening and early warning at the airport. The detection of mustard gas and HCN are two specific agents that can be

addressed with the AGS, as well as TNT, when the electrochemical sensors are used in arrays.^{109–116}

4.4. Medical/Biomedical

Chemical sensors will provide physicians with a quicker and more accurate diagnostic tool. Applications will include breath analysis that can provide objective information on the identity of certain chemical compounds such as in exhaled air and in the excreted urine or other body fluids that are directly related to specific metabolic conditions, certain skin diseases, or bacterial infections, such as those common to burn wounds. Additionally, the chemical sensors may also provide more accurate, real-time patient monitoring during anesthesia administration.

An amperometric enzyme/gas-diffusion electrode is developed that combines a porous air-breathing gas-diffusion electrode with an enzyme immobilized on its catalytic layer. The oxygen needed for the enzymatic reaction is supplied to the reaction zone of the electrode in the gas phase through the gas-supplying layer of a gas-diffusion electrode. The performance of a gas-diffusion/enzyme electrode operating in oxygen-containing solutions is practically independent of the concentration of the dissolved oxygen.

5. Summary

Amperometric gas sensors have a long and rich history. The present review shows that AGSs are an important member of the electrochemical class of chemical sensors. Many research and development efforts have resulted in practical life-saving sensors, such as the AGS for CO, H₂S, NO₂, O₂, or other electrochemically active gases that are now routinely used in industrial hygiene and safety monitoring of people and workplaces. There is an ever-expanding list of analyte targets for the AGS, and its use for electroactive materials like TNT will challenge the sensitivity of the amperometric approach. With the advent of arrays, the AGS is contributing to the detection of a diverse set of complex endpoints including toxicity, cancer detection, and off-odor of materials. New applications such as homeland security and defense against threats have arisen and will challenge the sensitivity and selectivity of the electrochemical technique in general and the amperometric approach specifically. As we demand ever-lower detection levels and since the sensor signal in amperometry is directly proportional to the electrode area, the challenge is to maintain and improve the signal/noise ratio for the analyte. However, the challenge of amperometry is to utilize the ability provided by electronics to detect smaller and smaller amounts of charge/current and to use nanostructures to continue to increase the electrode reactive surface area even with less material used in the electrode.

The advancement of MEMS technology and the fast pace of nanotechnology will no doubt enable new AGS designs and materials such that new applications are found for large gas molecules and weakly electroactive gas molecules in applications that will analyze for chemical threats, toxins, food flavors, and fragrances. Much of the modern AGS work focuses on new designs that incorporate microfabrication and nanofabrication to achieve smaller size, low power, lower cost, and portable sensors and sensor arrays with intelligence. New nanomaterials development changes the building blocks that will provide well-organized nanostructures with high surface area, high chemical reactivity at lower temperature,

good mechanical strength, and better thermal stability, leading to new catalysts for selectivity, new electrolytes for higher-temperature operation, multiple working electrodes for self-amplifying sensors, and combinations with bioanalytical approaches for biosensors and enzyme-based sensors.

MEMS technology and nanotechnology combined with new computational power brighten the future of the AGS and its use within analytical chemistry and especially in field analytical measurements. We now begin a new era of AGS development using new materials, new time-resolved and spatially resolved sensor array approaches, and smaller sensor devices. It is clear that the utility of amperometry will continue and will preserve its place in gas-sensor applications now and in the future³⁷ and will continue to serve for the betterment of human health, safety, and the environment.

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