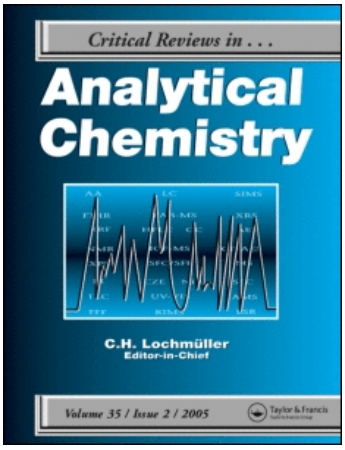

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Amperometric Solid-State Gas Sensors: Materials for Their Active Components

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ABSTRACT: Principal materials used for the active components of amperometric solid-state gas sensors, namely, the electrolytes and electrode materials, are reviewed. Inorganic proton conductors, solid polymers, and hydrogels are the most frequently used electrolytes. Electrode materials are discussed with the respect both to the catalytic activity (pure metals and carbon, catalyst films, and composites) and electrode geometry (the length of the three-phase boundary). Basic properties of the sensors with these materials are discussed briefly.

KEY WORDS: amperometry, gas sensors, solid electrolytes, electrode materials.

I. INTRODUCTION

Amperometric sensors for gases are an important analytical tool and cater for those practical requirements that cannot be adequately satisfied by standard laboratory analytical procedures. First of all, in general, gas sensors usually provide information on the presence and contents of certain gaseous components in the gas or liquid phase much more rapidly than laboratory analysis; second, they are small, readily compatible with microelectronic circuitry and can often work without an external power source; third, they are inexpensive. On the other hand, the laboratory analytical procedures, which are much more expensive, time-consuming, and demanding on space and human labor, mostly provide substantially more reliable results. Therefore, sensors find primary use as sources of real-time, semiquantitative information in automated systems and robots, signal and alarm circuits, and portable monitors. Compared with laboratory analytical procedures (but also to many nonelectrochemical sensors), amperometric sensors have a very simple construction and often can be mass produced cheaply by uncomplicated technologies and used as disposable sensors, attractive to, for example, clinical, pharmaceutical, and environmental laboratories, but also to the general public (see the single-use glucose strips for diabetics).

For the above reasons, amperometric gas sensors are developing rapidly and the field is often reviewed, both generally[1-3] and with respect to their special types, such as solid-state sensors with solid electrolytes operating at elevated temperatures,[4] sensors with solid polymer electrolytes working at ambient temperature,[5-7] or sensors employing analyte preconcentration in a contact liquid phase.[8] Many articles deal with some general properties of sensors; for example, some recent publications discuss the factors affecting the transport of gas from the test bulk toward the working electrode, which affects the sensor static properties (the response magnitude and reproducibility)[9,10] and its dynamic behavior (response time).[11,12]

All amperometric sensors are based on an electrochemical cell containing an indicator and a reference electrode and possibly also an auxiliary electrode; the electrodes are conductively interconnected by an electrolyte. The indicator electrode is exposed to the test gas either directly or through a transport barrier. The sensor functional parameters (sensitivity, selectivity, reliability,

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dynamic range, response rate) and its mechanical properties (size, ruggedness, stability of the cell geometry, lifetime) depends on its design and on the construction materials.

The construction of various sensors and their electrochemical and analytical properties and applications are discussed in the reviews mentioned above.[1-12] The present article aims to demonstrate the range of the materials used for the active components of amperometric sensors, namely, the electrolytes and electrode materials. In fact, the present research and development of new sensors is primarily concentrated on the selection of the construction materials and testing their long-time performance; in this review we only deal with the materials for sensors operating at ambient temperature.

II ELECTROLYTES

A. Inorganic Solid Electrolytes

In solid-state sensors, liquid electrolytes are replaced by solids exhibiting ionic conductivity. The oldest materials of this type are inorganic proton conductors, antimonic acid and zirconium phosphate (as a composite with PTFE) in H_2 and CO sensors.[13,14] They are still used: α zirconium phosphate, $Zr(HPO_4)_2.H_2O$, is contained, as a thin film prepared from a colloidal dispersion, in planar sensors for NO and NO_2[15] and CO.[16-18] (References 16–18 employ an unusual material for the reference and auxiliary electrodes — titanium hydride, TiH_x where $x \approx 1.7$, which is only compatible with sensors containing a proton conductor and no aqueous solution[19]).

Other inorganic proton conductors, dodecamolybdo- or dodecatungsto-phosphoric acid and $Sb_2O_5.2\text{-}4H_2O$, act as electrolytes in galvanic cells sensing H_2;[20] the electrolytes are doped by unspecified polymers in order to suppress the response dependence on humidity. A platinum working electrode is employed, with an auxiliary electrode of a 1:10 composite of carbon and a catalyst containing complexes of the type $CoLCl_2ClO_4$, where L is, for example, 5,7,7,12,14-hexamethyl-1,4,8,11-tetraazocyclotetradecane. Hydrogen is oxidized at the platinum electrode,

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

whereas the oxidation products, electrons and protons, are consumed on the auxiliary electrode,

$$Co(III)L + e^- \rightarrow Co(II)L,$$

the Co(II) formed being rapidly reoxidized by atmospheric oxygen,

$$4Co(II)L + O_2 + 4H^+ \rightarrow 2H_2O + 4Co(III)L.$$

Therefore, the overall reaction in the galvanic cell is

$$2H_2 + O_2 \rightarrow 2H_2O.$$

An analogous cobalt catalyst has also been used for detection of H_2S, but this sensor contains a liquid electrolyte, sulfuric acid.[21]

Among other inorganic solid electrolytes, vanadyl sulfate, $VOSO_4.3H_2O$, can be mentioned that has been used in a two-electrode solid-state sensor for oxygen and sulfur dioxide[22] (carbon has been used for both the working and the pseudoreference electrode), or fast ion conductors α-$PbSnF_4$ and $Ag_6I_4WO_4$ in a galvanic O_2 sensor.[23,24]

B. Solid Polymer Electrolytes

The cation exchanger Nafion, the poly(tetrafluoroethylene) copolymer with poly(sulfonylfluoride vinyl ether) manufactured by DuPont (USA), is an exceptionally important electrolyte for electrochemical technologies (industrial electrolyzers and fuel cells[25-27]); it also is the most common solid electrolyte in amperometric gas sensors operating at ambient temperature.[5-7]

In gas sensors, Nafion membranes or films obtained by evaporating the solvents from Nafion solutions in mixtures of water and lower aliphatic alcohols are used mostly. The polymer is strongly hydrophilic, and thus its geometric dimensions, as well as the transport and electrical properties, depend significantly on the amount of water contained within its structure. The water content in

Nafion varies with varying relative humidity (RH) of the gas with which the polymer is in contact, and thus the response of gas sensors employing Nafion membranes mostly depends not only on the analyte concentration but also on the test gas RH; this is the main problem involved in application of these sensors.

In order to suppress the effect of the RH, measures are taken to maintain the water content within Nafion constant. In one approach, the test gas is humidified in a defined manner prior to its feeding to the sensor[28,29] or an auxiliary humidifying gas is used.[30] Another, more suitable technique[31,32] integrates a water reservoir directly into the sensor structure, feeding water to the Nafion membrane through microholes. However, this is only a partial solution to the problem. The water content within the polymer is satisfactorily maintained in this way, but the local water content at the three-phase boundary, that is, within the surface layer where the polymer electrolyte, the working electrode, and the test gas meet, and where the electrochemical reactions occur, remains uncontrolled. Ref. 32 suggests that the RH effect might be corrected for electronically, employing the signal from an independent RH sensor. It has, however, been shown[33] that the rates of water exchange between Nafion and the surrounding gas on an increase and a decrease in the gas RH greatly differ, and this makes the correction difficult.

The lifetime of Nafion containing sensors can be substantially prolonged by covering the Nafion film with a protective perfluorocycloether polymer film, as has been demonstrated on a planar CO sensor.[34,35]

Other polymers with ionic conductivity are only used rarely in amperometric gas sensors. In an attempt at minimizing the response dependence on the RH, a hydrophobic polymer, plasticized poly(vinyl chloride) containing tetrabutylammonium hexafluorophosphate, has been used in an NO_2 sensor;[36,37] the dependence on the RH was suppressed significantly, but not eliminated. Furthermore, a poly(dimethyldiallylammonium chloride) polymer electrolyte has been employed in a planar oxygen sensor[38,39] and the poly(ethylene oxide) complex with $MeCF_3SO_3$ in a galvanic NO_2 sensor; Me is either Ag,[40,41] or Zn, Cu, or Ni.[42] A polymer electrolyte consisting of a composite of low-density poly(ethylene) and tetrathiofulvalinium-tetracyanoquinodimethane has been tested in a sensor for CO_2, NO_2 and O_2.[43]

C. Hydrogels

Instead of employing a solid electrolyte, some sensor structures test hydrogels immobilizing a liquid electrolyte; silica gels obtained by the sol-gel chemistry bear promise for the future.[44] They can simply be prepared by hydrolysis of, for example, tetramethoxy- or tetraethoxysilanes and their properties, primarily the resultant structure, the pore size, shape and distribution, the surface area, the contents of various substances, for example water, within the pores, etc., can be readily affected by the selection of the precursors and additives to the gelatination mixture. The gelatination mixture can be spin-coated over the surface of an inert substrate with the electrodes. In this manner, a gel film immobilizing and electrolyte (sulfuric and perchloric acids) has been prepared in a planar CO sensor with interdigitated electrodes.[45] Compared with an analogous sensor with a Nafion electrolyte, the sensor containing silica-gel is insensitive to variations in the test gas humidity, as its rigid backbone and constant pore size and distribution keep the transport conditions for CO stable, whereas the soft structure of Nafion responds to changes in the RH (see above). An analogous sensor has also been tested for NH_3, CO_2, H_2O_2, and O_2.[46]

A sensor for gaseous hydrogen peroxide[47] employs a silica-gel film simultaneously for immobilization of the electrolyte and as an *in situ* extractor of H_2O_2 from the gaseous phase into the liquid immobilized in the pores of the gel, thus permitting preconcentration of the analyte (a similar preconcentration principle has also been used with Nafion[48,49]). A hydrogel prepared by photopolymerization of hydroxyethyl methacrylate (polyHEMA) also performs two functions in an oxygen planar sensor,[50] by immobilizing the electrolyte and acting as a diffusion-limiting membrane between the test bulk and the working electrode; the use of hydrogel has led to development of a technology for reproducible preparation of sensors with well-defined membrane thickness.

Other materials have been used for immobilization of liquid electrolytes, for example, agarose in a sensor for H_2S and thiols,[51-53] porous SiC saturated with phosphoric acid in an SO_2 planar sensor,[54] or even filter paper in a CO_2 sensor[55] in which the nonaqueous electrolyte penetrated to the electrodes through microholes made in the substrate on the surface of which the Pt microelectrodes were created lithographically.

III. ELECTRODES

A. Electrodes of Pure Metals and Carbon

Noble metal (Au, Pt) electrodes are usually either mechanically pressed onto the solid electrolyte, or created at the electrolyte surface by vacuum plating (Au). The sensitivity of the monitoring of gaseous analytes present in a gaseous phase then depends not only on the catalytic activity of the electrode material, but also on the length of the three-phase boundary (electrolyte-electrode-gas), which in principle is determined by the indicator electrode perimeter, P; it has been shown[28,56] that the sensor sensitivity is proportional to the ratio, P^2/A, where A is the geometric surface area of the electrode. The shape of the indicator electrode that is optimal from this point of view is a fine mesh that can be produced readily on the electrolyte surface by vacuum plating. However, if the dimensions of the solid electrolyte vary in time, such as with Nafion in dependence on the gas humidity, then vacuum-plated electrodes may often be damaged[28,56,57] and fine minigrids electro-formed from a metal foil and mechanically pressed onto the polymer surface are much more suitable. A gold minigrids have been used in NO_2 sensors containing Nafion[58] or a polymer electrolyte based on plasticized PVC containing a hydrophobic electrolyte.[36] A stable electrode with a favorable P^2/A ratio can also be prepared by plating or sputtering a metal onto a porous teflon membrane that is then pressed onto Nafion, the metal facing the Nafion electrolyte; this approach has been adopted with platinum electrodes in a CO sensor.[59]

With planar, non-porous electrodes obtained by vacuum plating or by pressing a metal foil[54] onto a Nafion membrane, electrochemical reactions may only occur at the metal/Nafion boundary, and it has been demonstrated[29,60] for an oxygen sensor that this boundary behaves as a microband electrode; analogously, fine grids can be considered as arrays of microband electrodes[58] and thus the sensor sensitivity is enhanced through transport phenomena characteristic of microelectrodes and their arrays.[61]

Vacuum plating/sputtering and screen printing are the principal methods of electrode preparation in planar sensors permitting the creation of electrodes with a wide range of sizes and shapes, for example, fine grids,[28,56] interdigitated arrays,[45,48,49,62,63] and even individually addressable arrays that can be applied to the monitoring of the spatial distribution of a gaseous component in, for example, biological tissues, or as detection elements for the so-called electronic nose; such an array of 1024 microelectrodes has been employed for two-dimensional mapping of oxygen distribution.[64] On the other hand, closely spaced microelectrodes may suffer from the problem of chemical cross-talk, that is, the products of the electrochemical reactions at one electrode may affect the course of the reactions at a neighboring electrode.[55,63]

An important (and patented[65]) method for the creation of metal electrodes on the surface of Nafion membranes is based on a chemical reduction of suitable salts of the metal. A solution of such a salt is in contact with one side of the membrane, or the membrane is impregnated with it. Platinum and gold electrodes are mostly prepared in this way, by the reduction of H_2PtCl_6, $Pt(NH_3)_4Cl_2$ or $HAuCl_4$ with alkaline solutions of $NaBH_4$ or N_2H_4; the mechanism of the formation of the metal layer has been studied in detail in Ref. 66, and the properties of the electrodes obtained have been characterized using a great variety of optical and electrochemical methods (e.g., Refs. 67-69). These electrodes are porous, and the values of their roughness factor, RF (the ratio of the microscopic vs. geometric surface area) are from hundreds to thousands; hence, they exhibit a high catalytic activity and long three-phase boundaries, even if the latter are rather poorly defined

compared with vacuum-plated electrodes. They are mechanically very stable and can be created on either one or both sides of the membrane. Electrodes of metals other than platinum and gold, for example, Cu[70] or Ir, Os, Re, Ag, and Ni,[71] can also be obtained by chemical reduction of metal salts. This electrode type is used not only as indicator electrodes, but also as pseudoreference electrodes, provided that they are in contact with air; their potentials vs. SHE are then ca. 1 V (Pt/air) and 0.8 V (Au/air). A combination of electrodes with different RF values (e.g., a platinum electrode obtained by chemical reduction at one side of a Nafion membrane and a platinum wire pressed onto the other side of the membrane) has been employed in a galvanic sensor monitoring H_2 in air that does not require a reference — pure air,[72] utilizing the fact that the mixed potential of platinum electrodes depends on their RF.[73]

Carbon electrodes are prepared by pressing the material onto a Nafion membrane; glassy carbon has been used in a sensor for gaseous WF_6[74] and reticulated vitreous carbon (RVC) in an NO_2 sensor.[37] RVC seems to bear promise for working electrodes of gas sensors, as it is chemically resistant, its structure is favorable for the creation of long three-phase boundaries, and it is substantially cheaper than platinum and gold. Graphite electrodes have been prepared by painting a suspension of a graphite colloid solution in methylisobutyl ketone over the Nafion membrane surface.[57]

B. Electrodes Covered by Catalyst Films

Various catalysts have been used to improve the selectivity of sensors, by covering metal electrodes with catalyst films, forming catalyst composites with the electrode material, or adding a catalyst to the solid electrolyte. For example, platinum interdigitated electrodes with a film of mixed-valent ruthenium oxide have been employed in a sensor for vapors of methanol and *N*-nitrosamines;[48,49] the catalyst acts as a redox mediator, thus permitting monitoring of electroinactive gases. In this case, the catalytic electrodes were covered with a layer of the Nafion electrolyte. An analogous catalyst, a colloidal mixture of ruthenium oxide/cyanoruthenate complex (a ruthenium analogue of the Prussian blue), acts simultaneously as a catalyst and as the electrolyte; the mixture has been applied onto the gold electrodes of a planar sensor for methanol vapors.[75] The hydration by the atmospheric humidity suffices for the obtaining of a satisfactory ionic conductivity of the material; a modified design in which an anion exchange membrane is impregnated with the catalyst has also been tested.

A gold microelectrode covered with a polyaniline film that decreases the overpotential for the reduction of carbon dioxide has been applied for the detection of CO_2 in DMSO,[76] a carbon electrode with a film containing Co-porphyrine has been used in an O_2 sensor.[77] A disposable sensor for formic acid in air[78] employs as a catalyst a mixture of formate dehydrogenase, NAD^+, and the Medola blue, immobilizing the catalyst on a screen-printed carbon electrode by sol-gel, alginate gel, or glycerol solution techniques.

C. Composite Materials

Classic composites with pronounced catalytic properties are Teflon®-bonded noble metal electrodes prepared by mixing a finely dispersed metal with PTFE powder and pressing the composite onto a solid electrolyte. A composite with platinum black has, for example, been used to detect CO[31] or O_2,[79] and a composite with colloidal gold for detection of ozone.[80] Composite electrodes of gold or graphite dispersed in zirconium hydrogenphosphate have been applied to NO and NO_2 sensors with inorganic proton conductors.[15]

Mixtures of various metals with a graphite emulsion have been employed in sensors for diverse gases (the metal is given in the parentheses):[30] H_2 (Pd), O_2 (Pt), CO_2, and NH_3 (Cu). Screen-printed electrodes of a mixture of the Co-porphyrin catalyst with carbon powder have been contained in a planar sensor for H_2S, gaseous thiols, and dimethylsulfide.[51-53] The sensor response results from the cobalt-catalyzed chemical oxidation of thiols (RSH) followed by electrochemical regeneration of the catalyst,

$$2Co(II) + RSH \Leftrightarrow 2Co(I) + RSSR + 2H^+$$

$$2Co(I) \Leftrightarrow 2Co(II) + 2e^-.$$

A solid-state galvanic sensor for O_2[81] contains a composite electrode of a mixture of Fe(II), Fe-phthalocyanine, Pt-black, and $PbSnF_4$. A highly specialized composite, Fe-phthalocyanine+$PbSnF_4$+conductive whiskers $9Al_2O_3.2B_2O_3$, has replaced the classic platinum electrode in an oxygen sensor yielding a stable reponse even under pressures of the order of MPa.[24] A composite electrode, consisting of a mixture of silica gel, carbon or graphite powder and a Co-porphyrin catalyst, has been used for detection of O_2, CO_2, and SO_2.[82,83]

IV. CONCLUSIONS

The development and testing of new materials have principal importance for the further progress of chemical sensors.[84] More specifically, the practical use of amperometric sensors is often hampered by a general problem of electroanalytical methods, namely, instability of the sensor output signal in time, resulting from direct contact of the electrodes with the components of the test bulk and with the products of their electrochemical reactions. Therefore, the search for new materials for electrochemical sensors is even more desirable in this field. This will not only improve the static and dynamic properties of a wide range of sensors, but also contribute to minimization of the problems associated with electrochemical sensors and electroanalytical techniques in general.

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