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Electrochemical Sensors for the Analysis of Gases

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1 INTRODUCTION

The demand for clean air and surface water and the legal regulations to this end call for devices for testing and supervising the composition of these media. In such work, the analysis of gaseous components is particularly important. In the past, such demands have led to the development of sensors for determining the concentration of a gaseous component in a gaseous mixture or in a solution in a liquid. Apart from this, however, sensors for gases find many applications in science and technology. One type of such sensors operates on electrochemical principles. In consequence, many electrochemical processes for the determination of gaseous components have been described. The present paper presents a summary of this work.

The term "sensor" denotes a device with which the concentration of certain gaseous components can be measured. In the broad sense of the term, it includes the electronic transducer, to which usually an electronic evaluating device is connected. In our description, the emphasis is on the transducer. Peripheral devices necessary to ensure proper functioning of the measuring system, such as regulating devices for maintaining constancy of temperature and velocity of flow, are only mentioned in passing.

Indirect processes, in which the electrochemical reaction is only used to indicate the endpoint of a chemical titration or the like, are not considered.

A sensor must meet the following requirements:

High accuracy,
Wide range of measurement,
Good reproducibility and constancy of the indicated value,
Low sensitivity to external disturbances,

High selectivity for the components to be determined,
Rapid response, particularly when the sensor is to initiate a control function.

The preceding requirements differ in relative importance according to the purpose of the application.

A further important point to be borne in mind in considering the applications of sensors is the costs, which are principally determined by the peripheral devices. These costs are usually difficult to estimate, for which reason they are not considered here.

2 THERMODYNAMIC TREATMENT OF ELECTRODES INVOLVING A GAS PHASE

Electrochemical reactions are characterized by the passage of electric charges (ions or electrons) through a metal-electrolyte phase boundary (or in some cases semiconductor-electrolyte). This produces electrical potential differences between the conducting phases. The same holds when a gas phase participates in the electrode reaction: electrons are exchanged between the electrode material and the gas molecules, and an oxidation or reduction reaction product of the gas passes into the electrolyte. It is characteristic for the electrode reactions of gases that the electrode material is not attacked, but only effects the electron exchange. Such electrodes are termed redox electrodes. The electrode reaction with a gas phase can proceed either at a metal liquid boundary, e.g.

$$\frac{1}{2}H_2 \text{ (gas)} \rightleftharpoons H^+\text{(aq)} + e^-\text{(metal)} \tag{1}$$

or at a metal-solid electrolyte boundary, e.g.

$$\frac{1}{2}O_2 \text{ (gas)} + 2e^-\text{(metal)} \rightleftharpoons O^{--}\text{(ZrO}_2\text{)} \tag{2}$$

For the thermodynamic treatment of gas electrodes, the individual intermediate stages of the overall reactions play no part, because in equilibrium a definite concentration of a gas in the dissolved and adsorbed states corresponds to its partial pressure in the gaseous phase. The potential of the electrode at the metal-electrolyte interface measured as cell voltage E against a definite reference electrode depends on the concentrations (activities) a_i and partial pressures p_i of the components i of the overall equation. This is expressed in the Nernst equation,

$$E = E^o + \frac{RT}{zF} (\Sigma\nu_i \ln a_i + \Sigma\nu_i \ln p_i) \tag{3}$$

In this equation E^o is the standard equilibrium potential, ν_i are the stoichiometric coefficients of the substances involved in the overall reaction, and z is the number of the positive charges moved through the interphase in the chosen direction of the electrode reaction.

For nonaqueous solid electrolytes with oxygen-ion conduction, the usual reference electrode is an oxygen electrode with a pressure of 1 atm. In this case the pressure dependence of the potential of the oxygen electrode (2) is given by

$$E = - 4.96 \cdot 10^{-5} \text{ T} \log p_{O_2} \tag{4}$$

3 INFLUENCE OF MASS TRANSPORT ON ELECTRODE PROCESSES INVOLVING A GAS PHASE

As in many other electrochemical reactions, polarization effects play an important part also in electrochemical sensors. One effect, namely the influence of transport processes on the electrode kinetics, is used in the diffusion limiting current sensors and has to be discussed therefore in detail. If the transport is impeded in any way, so that the velocity of the transfer reaction can be greater than that of the material transport, the latter determines the velocity of the electrochemical reaction. The transfer reaction produces concentration changes at the electrode, until in the stationary state a sufficient force for the transport to and from the reaction site of the particles taking part is built up. There are particularly simple conditions, if the effects of migration and convection are largely eliminated. This may be realized by selection of proper experimental conditions, which are described later on. In this case, a convection-free liquid layer exists immediately adjoining the electrode surface, so that, when a current flows, material transport is effected solely by diffusion as a result of the built-up concentration gradient.

The stationary diffusion current determined by the concentration gradient is given by Fick's first law of diffusion as

$$i_{diff} = D_i \cdot zF \cdot \frac{C_i - C_o}{\delta} \qquad (5)$$

Here, i_{diff} is the diffusion current per unit surface area and D_i is the diffusion coefficient of the reacting substance. δ is the thickness of the diffusion layer, C_i and C_o are the concentrations of the reacting substance remote from the electrode and immediately adjoining its surface, respectively.

If a substance is removed from the system by the electrode reaction, then, if the polarization is strong enough, the concentration C_o at the electrode surface can become zero, so that every particle reaching the electrode reacts at once. The diffusion current of Eq. (5) then attains the limiting value:

$$i_L = D_i \cdot zF \frac{C_i}{\delta} \tag{6}$$

which is termed the limiting current density. This is proportional to the concentration of the diffusing reacting substance in the bulk of the solution, a fact widely used for analytical purposes, for example, for the polarographic analysis from the gas phase.

If the electrode consists of the three-phase system: solid electronic conductor-liquid electrolyte-gas phase, the electrode reaction can proceed by solution of gas molecules in the liquid electrolyte and diffusion to the electrode surface, where the electrochemical reaction proper, namely, charge transfer, occurs. The conditions are then the same as for dissolved solid substances. For the gas concentration in the electrolyte, Henry's law can be applied, according to which the solubility is proportional to the partial pressure.

The problem becomes more complicated when additional diffusion impedance in the gas phase or by a membrane occurs. In this case, various diffusion and permeation resistances may additively determine the velocity of the overall reaction. For example, partial pressure gradients can occur in the gas phase, if the gas involved in the electrode reaction is mixed with an excess of an unreactive gas. This is termed gas-side concentration polarization (1). Above all, when material transport takes place through the pores of a solid, which is the case with all porous electrodes and in particular with gas-diffusion electrodes, such effects play an important part. The theory of these phenomena has been developed chiefly in connection with work on fuel cells (2,3). Equally important is diffusion through interposed membranes, as in membrane-covered polarographic gas detectors. In such cases, the material transport to the electrode can be treated as linear diffusion through a two-layer system (4).

For practical use, the so-called gas diffusion electrode, in which a porous matrix of solid electron-conducting material (metal, carbon) is partly penetrated by electrolyte and partly filled with gas, is important. Partial hydrophobization or slight excess pressure of the gas fixes the three-phase boundary in the electrode, the gas standing in capillary equilibrium with the electrolyte and the solid electrode material. According to the thin-film model, a thin wetting film of the electrolyte covers the walls of the pores in the neighborhood of the meniscus, and the electrochemical reaction can occur only in a restricted zone in which the diffusion path through this wetting film is short and the electrolyte resistance low (see Fig. 1).

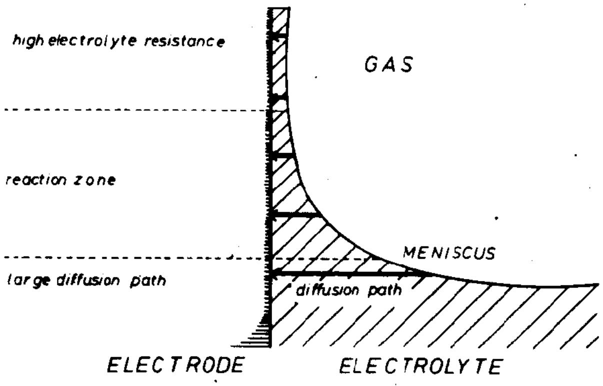

Fig. 1. Schematic representation of the gas/electrolyte interface on a partially immersed electrode.

Even at gas electrodes with two solid phases (metal and solid electrolyte), in which there is naturally no wetting film, it is often the case that transport processes determine the reaction velocity. So, for the oxygen reduction at porous noble metal films on a zirconia electrolyte, diffusion limiting currents have been found under particular conditions (5-7).

4 PRECEDING REACTIONS IN THE GAS PHASE

In the cases of electrode reactions of a gas hitherto considered, it was assumed that the gas acts directly as reaction partner. This means that the Nernst equation for the overall reaction contains the partial pressure directly present in the gas phase, which is not produced by a chemical reaction. Such an electrode is termed an electrode of the first kind, in contrast to an electrode of the second kind, in which a preceding chemical equilibrium determines the activity of the components affecting the potential.

The participation of the gas phase in preceding chemical reactions is particularly important for electrochemical gas sensors. Above all, when no equilibrium with the gas phase exists, potential deviations occur. The two possibilities, of equilibrium and nonequilibrium with the gas phase, are discussed in the following sections.

4.1 Electrode Reaction with Gases under Equilibrium Conditions

If the partial pressure of a gas that determines the potential is determined by a chemical equilibrium, an electrode of the second kind exists. The equilibrium can be homogeneous, for example,

$$CO_2 \rightleftharpoons CO + \frac{1}{2} O_2 \qquad (7)$$

or heterogeneous, for example,

$$NiO \rightleftharpoons Ni + \frac{1}{2} O_2 \qquad (8)$$

Such equilibria - particularly involving oxygen - are particularly important for gas chains with solid electrolytes (8) at high temperatures, because equilibrium at such temperatures is readily attained. These equilibria can be used to produce extremely small partial pressures very exactly at an electrode. Thus, for example, oxygen partial pressures from 10^{-5} to 10^{-21} atm. can easily be produced through the CO_2-CO equilibrium, and H_2-H_2O mixtures give oxygen partial pressures in the range 10^{-20} to 10^{-23} atm. (9). For reference potentials in oxygen measuring cells, heterogeneous equilibria involving a metal/metal-oxide mixture are commonly used, for example, Cu-Cu_2O, Ni-NiO, Co-CoO, Fe-FeO, Mo-MoO_2, and others (10).

Occasionally, a gas mixture contains a number of components, all involved in the attainment of equilibrium. An important example is the exhaust gases of a motor vehicle, in which the reaction of hydrocarbons with air may be expected to produce a wide variety of products. At thermodynamic equilibrium, an oxygen partial pressure dependent on the air/fuel ratio is attained, which determines the potential of the oxygen electrode. This potential can be measured and used for the control of an optimal air/fuel ratio (see Chapter 9).

4.2 Nonequilibrium with the Gas Phase

If the system gas-phase/electrode is not in thermodynamic equilibrium and if a chemical reaction involving the gas phase proceeds at the electrode surface, a reaction-dependent potential is attained, differing from the single electrode potential of the individual components. In considering this, it must be assumed that the reaction at the electrode surface proceeds by adsorbed species, occurring as intermediate products and effectively determining the potential.

Basically, two different mechanisms for the heterogeneous chemical reaction are possible (11). On the one hand, there is an electrochemical mechanism, in which the components react with one another in consecutive anodic and cathodic reactions with zero net current at the phase boundary, and on the other hand there is a nonelectrochemical mechanism, in which a purely chemical transfer reaction proceeds in the adsorbed state. In the case of the electrochemical mechanism, a mixed potential is formed at the electrode.

The nonelectrochemical mechanism (12) which is valid for many catalytic processes, proceeds through a purely chemical transfer reaction. The reactants are adsorbed and dissociate at the electrode surface, where a transfer of atomic species occurs. In stationary reaction conditions, the velocities of surrendering and accepting the transmitted particles are equal, and a definite activity of the species determining the potential is attained at the surface and is different from the equilibrium activity.

Many catalytic hydrogen and oxygen transport reactions proceed according to this mechanism. For example, in the water-gas reaction at a Wüstite surface (13) adsorbed oxygen is produced as intermediate product, and in the stationary state of the reaction,

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad (9)$$

the velocity of oxygen transport to the catalyst,

$$CO_2 \longrightarrow CO + O_{ad} \qquad (10)$$

is equal to the velocity of withdrawal of oxygen from the catalyst

$$O_{ad} + H_2 \longrightarrow H_2O. \qquad (11)$$

The same effect arises in high-temperature oxygen sensors with solid electrolyte when they are exposed to a reactible gas mixture not in equilibrium. The oxygen activity attained at the electrode during the course of the reaction then does not correspond to the thermodynamic equilibrium, so that false results can be obtained.

5 IONIC AND ELECTRONIC CONDUCTIVITY IN SOLIDS

The interaction between a gas and a solid, involving heterogeneous chemical or electrochemical reactions, has been used in many different ways for sensors. In particular, the conductivity properties of a solid play an important part and must be considered if the phenomena are to be fully understood. Thus, for example, a number of gas sensors are solid electrolyte systems with electrode reactions at solids of predominantly ionic conductivity. In such cases, the utility of a given substance as electrolyte requires practically pure ionic conductivity, with only a slight electronic conductivity.

In ionic conduction, not only are electric charges transported, but also chemical species. In solid materials this proceeds through disorders in the crystal lattice. Basically, three sorts of charged atomic defects responsible for ionic conduction in solids are distinguished, namely,

1. Charged defects, when individual particles are lacking in the lattice;
2. Ions in interstitial positions, when individual particles are present in excess;
3. Foreign ions, when lattice positions are occupied by ions of other substances. These can cause, under suitable conditions, an ionic conduction.

The charge condition is always related to the undisturbed lattice.

In electronic conduction, the mobile particles are quasifree electrons or positive holes. The concentrations of defect order centers in solids depend on the partial pressure of a component in the gas phase.

In recent work, doped zirconium dioxide and doped thorium dioxide have become particularly important as solid electrolytes with predominantly oxygen-ion conduction. On adding a few percent of CaO, MgO, or Y_2O_3 to ZrO_2 or ThO_2, a cubic lattice of the fluorite type is stabilized, in which, furthermore, the ratio of cations to anions is displaced in the direction of metal ions. The lattice contains vacant oxygen sites, which are responsible for the conduction at high temperatures.

This concentration of vacancies produced by doping, and hence the ionic conduction, changes hardly at all on alteration of the oxygen partial pressure:

$$(V_o) \approx \text{const} \qquad (12)$$

although oxygen reacts sparingly with the lattice defects in accordance with the equation

$$\frac{1}{2}O_2\ (\text{gas}) + Vo^{++} + 2e^- = O_o \tag{13}$$

The law of mass action can be applied to this equation as follows:

$$p_{O_2}^{1/2}\ (Vo^{++})(e^-)^2 = K_1 \tag{14}$$

which gives, taking the constant concentration of oxygen defects into account,

$$(e^-) \propto p_{O_2}^{-1/4} \tag{15}$$

That is, the concentration of quasifree electrons is proportional to the inverse of the fourth root of the oxygen partial pressure with which the oxide is in equilibrium.

Analogously, the concentration of holes is given by the equation

$$\frac{1}{2}O_2\ (\text{gas}) + Vo^{++} = O_o + 2h^+ \tag{16}$$

from which the following relationship for the concentration of holes is obtained:

$$(h^+) \propto p_{O_2}^{1/4} \tag{17}$$

The electrical conductivity of ZrO_2 containing 10 mole % Y_2O_3 as a function of the oxygen partial pressure has been studied at various temperatures by Burke, Rickert and Steiner (14) using the Hebb-Wagner technique (15,16) with an inert blocking electrode (Fig. 2).

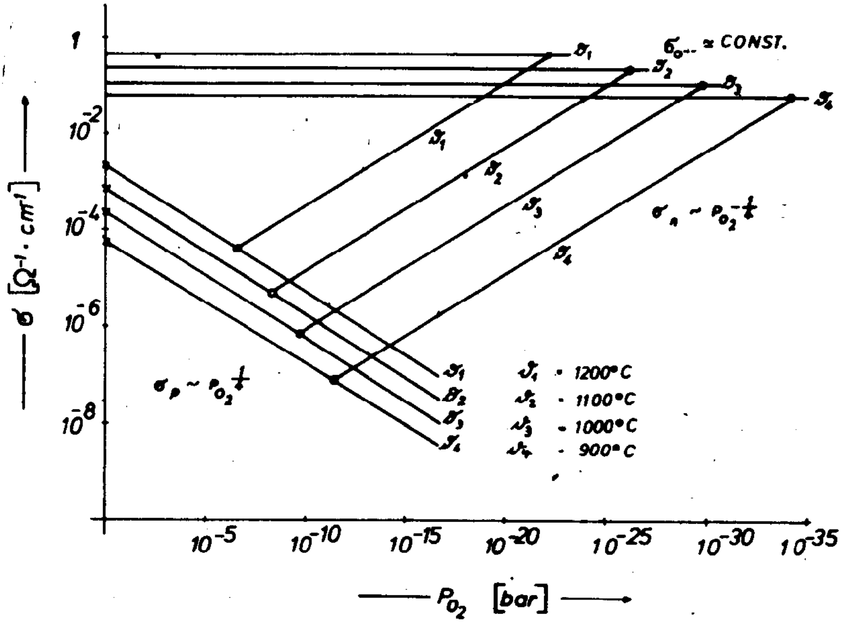

Fig. 2. Partial conductivity in ZrO_2 + 10 mole % Y_2O_3 at various temperatures as a function of the oxygen partial pressure.

It can be seen that at oxygen partial pressures below 10^{-20} bar the electronic conductivity attains the same order of magnitude as the ionic conductivity of the stabilized zirconium dioxide.

The oxygen partial pressure at which the ionic transfer number attains the value 0.5 is a function of the temperature and differs for different materials. If an electrochemical cell is set up using a mixed conductor as solid electrolyte, and if it is operated with various oxygen partial pressures, with chemical potentials of the oxygen μ'_{O_2} and μ''_{O_2}, the emf attained is in any case smaller than the thermodynamic cell voltage. Wagner (16) has calculated the reduction of the cell voltage in the general case and obtained the following relationship:

$$E = \frac{1}{4F} \int_{\mu''_{O_2}}^{\mu'_{O_2}} t_{ion} \cdot d\mu_{O_2} = \frac{RT}{4F} \int_{p''_{O_2}}^{p'_{O_2}} t_{ion} \cdot d \ln p_{O_2} \qquad (18)$$

This relationship between t_{ion} and E makes it possible to calculate the ionic transfer number of a solid electrolyte on a theoretical basis.

Other oxide phases exist, such as TiO_2, CoO, ZnO, or Cu_2O, that are predominantly electron or hole conductors and whose electrical conductivity under equilibrium conditions accordingly depends on the oxygen partial pressure in the surrounding gas phase. In such cases, the oxygen partial pressure determines the metal excess or deficiency in the oxide phase and hence the concentration of the charge carriers. The dependence of conductivity on oxygen partial pressure makes it possible to establish the conduction mechanism in the oxide.

6 METHODS BASED ON VOLTAGE MEASUREMENT

6.1 Systems at Equilibrium Potentials

Nernst's equation (3) gives the potential of an electrode as a function of the concentration or partial pressure of the gas involved. The partial pressure of such a gas, and hence its concentration, can in principle be determined by combining such an electrode, the measuring electrode, with a reference electrode giving a known potential and measuring the equilibrium potential E of the electrochemical cell thus formed. Knowledge and constancy of the other parameters in the Nernst equation are, how-