ION-SELECTIVE ELECTRODES | Glass Electrodes☆

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Introduction

Glass electrodes sensitive to hydrogen ions are the most commonly used sensors in chemistry and related disciplines. They belong to potentiometric membrane sensors and are constructed in various configurations depending on the application. Their basic design and properties are described and discussed in this article. Among their important properties is the selectivity, which depends on the composition of the glass. Glass electrodes are used mainly for pH measurements, but they may compose a part of more sophisticated systems in gas sensors or enzymatic sensors. Recently glasses, based on nonsilica structure, have been used in potentiometric measurements.

The complexity of processes responsible for functioning of glass electrodes resulted in several attempts to elaborate an adequate theoretical basis. The four fundamental have been discussed, namely: the adsorption potential theory, the membrane potential theory, the statistical-mechanical theory, and the phase boundary potential theory. Actually as a most adequate explanation is connected with the last theory. It assumes that the measurable analytical signal is a consequence of the thermodynamic balance between the glass phase and the electrolytic solution. The principal role in the potential formation plays the glass layer being in direct contact with the solution, however, such processes as adsorption, ion penetration and chemical attraction help to explain some facts of the electrode behavior and should also be taken into consideration. This indicates the complexity of processes responsible for the functioning of the glass electrodes.

Origin of Glass Electrodes

Glass electrodes are ion-selective electrodes, that belong to the group of electrodes with a noncrystalline solid membrane. Typical glasses are supercooled liquids with a network composed most commonly of silicon oxide; however other compositions may have similar properties and can be used as sensors.

The formation of an electric potential difference on a thin glass membrane in contact with solutions was observed by Cramer in 1906, and used for construction of a device for measuring the acidity of solutions by Haber and Klemensiewicz in 1909. Due to the high resistance of the glass membrane, practical application in routine measurements of acidity, and of course solution pH, was postponed until the invention of the vacuum tube amplifiers, and later semiconductors. One of the first types of glass used in manufacturing electrodes was introduced in 1928–1929 by Corning under the designation 015. The research devoted to the mechanism of this electrode action was a stimulus that helped to develop and introduce other types of ion-selective electrodes.

Electrode Design

A typical glass electrode (Figure 1) consists of a thin glass membrane (thickness 50–300 μm) at the end of a glass tube acting as (a) an insulator and (b) as a container of the internal solution in which the internal (reference) electrode is immersed. This internal electrode is usually a silver/silver chloride electrode and therefore the internal solution should contain a fixed concentration of chloride ions. Thus the glass electrode is in fact a half cell with a membrane forming a contact to the other half-cell:

$$\text{Ag}|\text{AgCl}, \text{KCl}|\ \text{glass membrane}$$

The resistance of the whole electrode, depending on its composition and dimensions, is in a broad range of 1–1000 MΩ. Due to the high resistance the cable connecting it to the measuring device (voltmeter, pH-meter) must be protected from electrostatic

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interferences. The potential difference between the two sides of the glass membrane is proportional to the difference of the pH values on both sides, according to the Nernst equation

$$\Delta E = 2.303\ RT/F(pH_1 - pH_2) \quad [1]$$

if the electrode for hydrogen ions is considered. To measure an unknown pH value it is therefore necessary to know the pH on one side of the membrane and measure ΔE. In practice, for determination of the unknown pH value there is no need to know the exact pH of the internal solution but only to keep it constant. The cell with glass and reference electrodes is calibrated with buffer solutions used as hydrogen activity standards. The same principle is the basis of measurements with cation selective electrodes that measure pM rather than pH.

Various applications of glass electrodes resulted in production of such electrodes in various dimensions and different shapes. Sensors compatible with contemporary miniaturized instruments have been constructed as micro-devices with sensitive area below 1 mm^2 or usable in flow systems.

Composition of the Glass Membranes

A glass membrane is composed of oxides such as SiO_2, B_2O_3, P_2O_3, As_2O_3 and GeO_2, and oxides of monovalent or divalent metals for example, Na_2O, K_2O, Li_2O, CaO. The most common glass membranes are, however, based on the silicon skeleton, containing oxygen atoms around the silicon tetrahedrons. The oxygen may form bridges between the silicon atoms or be nonbridging. The latter can be associated with single charged cations. The alkali metal cations may be exchanged with ions in solution and generate the potential response of the glass electrode. The analyte ions on the surface sites tend to diffuse inside the hydrated gel layer. Such diffusion probably takes place by means of a defect and jump mechanism, in which the interstitial cations play a major role. The tendency to interact more selectively with a given ion depends on the composition of the glass. The typical glass composition for a hydrogen ion sensitive electrode (Corning 015) contains 22% Na_2O, 6% CaO and 72% SiO_2 and responds according to Nernst equation (eqn. [1]) up to pH 11–12. Replacement of sodium for lithium extends this range up to pH 13. The partial replacement of silicon dioxide by trivalent element oxides favors the selectivity for alkali metal cations as the excess of negative charge must be neutralized by the alkali metal cations. An appropriate composition of the glass membrane enables us to use them as sensors for several metal cations. The preferred composition of some glasses used in ion sensors is presented in Table 1.

Major changes in the composition of glasses cannot be made arbitrarily because excessive amounts of alkali metal oxides lower the membrane durability in solutions. On the other hand, too high a proportion of silica decreases the hydrophilicity of the membrane which is indispensable of the membrane for proper functioning of the membrane. The optimum water uptake by the hydrated layer of the electrode membrane varies from 50 to 100 mg cm^{-3}. The thickness of the hydrated layer on both sides of

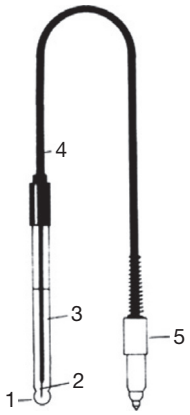

Figure 1 Typical commercial glass membrane electrode. (1) sensitive glass membrane; (2) Ag/AgCl internal reference electrode; (3) internal solution with constant pH; (4) cable; (5) plug.

Table 1 Composition of some typical glasses used as membranes.

Increased selectivity for	*Membrane type*	*Chemical composition mole (%)*
H^+	Corning 015	22% Na_2O, 6% CaO, 72% SiO_2
Na^+	NAS 11–18	11% Na_2O, 18% Al_2O_3, 71% SiO_2
K^+	NAS 27–04	27% Na_2O, 4% Al_2O_3, 69% SiO_2
Li^+	LAS 15–25	15% Li_2O, 25% Al_2O_3, 60% SiO_2
$NH4^+$	NAS 27–03	27% Na_2O, 3% Al_2O_3, 67% SiO_2, 3% ZnO

the membrane, which is responsible for the electrode response, varies from 5 to 100 nm (Figure 2). Therefore drying out of the membrane is destructive to the electrode performance. The lifetime of glass electrodes depends on the glass composition, aggressivity of solutions, and temperature. An alkaline solution affect the silicon-oxygen network, and acid attack causes the replacement of metal ions by hydrogen ions, in the hydrated silica layer. Special electrodes can work up to 80°C, but an increase of temperature promotes solution attack on the membrane and changes the parameters of the electrode. Changes of the temperature influence not only the prelogarithmic term of the Nernst-Nikolsky equation, but also the equilibria in the solution and at the phase boundaries. A glass electrode with the internal redox system: Pt | I_2/I^- |, replacing the usual silver/silver chloride system, is much less dependent on the temperature changes (Ross electrode).

Selectivity

The Nernstian response, that is, range of the linear dependence of potential versus pH, in the absence of interfering ions extends usually from pH 1 up to pH 11; however, many contemporary electrodes, depending on the glass composition, have made possible pH measurements up to pH 13. The response of the glass electrodes to metal cations extends down to 10^{-5} mol l^{-1}, and this is caused mainly by the presence of interferents (hydrogen ions for cation electrodes).

A glass pH electrode exhibits the so-called alkaline error, which means that in the alkaline pH range the potential response is influenced by the presence of sodium ions. The study of this behavior gave rise to the Nikolsky equation

$$E = E_0 + \frac{RT}{z_i F} \ln \left(a_i + \Sigma K_{ij}^{pot} a_{ij}^{z_i/z_j} \right) \qquad [2]$$

which is an expanded form of the Nernst equation valid in cases when beside the main ion, a_i, with charge z_i, also other ions, a_j, with charge z_j, influence the response. In the case of the sodium ion error $a_j = a_{Na}$. The Nikolsky equation indicates the importance of electrode selectivity, which is quantitatively expressed by the selectivity coefficient, K_{ij}^{pot}. The values of selectivity coefficients are important when characterizing the behavior of electrodes sensitive to metal ions. However, these values are not real constants characteristic for a given type of electrode as they depend on the method of measurements and the history of the electrode. Their limiting values are expressed by the product of the constant for the exchange reaction, for example, Na(glass) $+H^+ \rightleftarrows$ H (glass) $+$ Na^+ and the ratio of the ion mobilities:

$$K_{Na,H}^{pot} = K_{exch} \frac{U_{Na}}{U_H} \qquad [3]$$

The values of the selectivity coefficients for some glass electrodes are given in Table 2.

The response times (95% of the equilibrium potential change) given in the literature often correspond to the response time of the whole cell. They are in the order of a few seconds, but also depend on the glass composition, the presence of interferents, the concentration, the temperature and the electrode aging.

The measured potential may also be influenced by the so-called asymmetry potential. This is a residual potential between the two glass membrane surfaces when solution on both sides are identical. The asymmetry potential is due to differences in structural

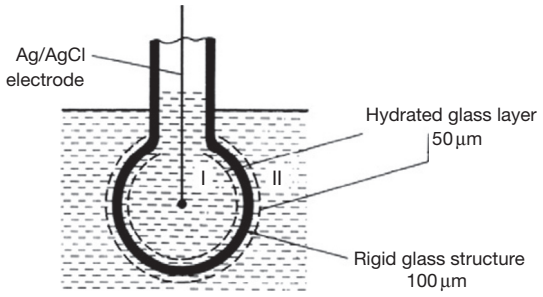

Figure 2 Schematic representation of the hydrated layer of a pH sensitive glass membrane electrode. (I) Internal reference solution; (II) external (sample) solution of unknown pH.

Table 2 Selectivity coefficients, K_{ij}^{pot}, for some glass membrane electrodes.

Membrane type	*Selectivity coefficients for interfering ions*				
	H^+	Na^+	K^+	NH_4^+	Ag^+
NAS 11–18	10^3	1	10^{-3}	3×10^{-5}	4×10^2
NAS 27–04		10^{-1}	1	3×10^{-1}	

stresses at the two surfaces, differences in the surface history (aging), and interaction with different solutions. The asymmetry potential may change with time.

Applications

The need of pH measurements in numerous fields of human activity, such as medicine, pharmacy, biology, environmental control, but also chemical industry, food chemistry, corrosion protection etc. resulted in numerous functions and in consequence of different sizes and shapes of glass electrodes.

Commercial glass electrodes, mostly for pH measurements, differ in construction because they have to serve different purposes. The electrode tips may have different shapes including tubular flow-through electrodes (Figure 3). Special electrodes are used under conditions of high pressure or high temperature or in shock conditions. Electrodes for medical applications in particular for measurements *in vivo* and control of biotechnological processes should not be destroyed during sterilization at 120°C. Special construction is necessary for microelectrodes for biochemical purposes. They can be as small as 0.5 μm in diameter to enable measurements within single cells. Nanoscale liquid glass electrode is used under flow conditions. Such electrode can be integrated into nanodevices and fluidic systems.

In many cases it is convenient to use combination electrodes which contain the indicator glass membrane electrode and the reference electrode in one rigid body (Figure 4(a)).

Glass membrane electrodes, mainly used for pH measurements but also for the NH_4^+ ion determination and used for construction of gas sensors (Figure 4(b)). Such sensors, based on a principle presented by Severinghaus (1958), consists of glass electrodes covered by a thin film made of porous hydrophobic plastic, so that the solution cannot penetrate into the pores. A thin layer of an electrolyte solution is located between the surface of the film and the glass surface. The pH value of that solution changes under the influence of a gas (e.g., NH_3, CO_2, SO_2), diffusing through the film, and is the measure of the gas concentration in the sample solution.

Another type of multiple membrane sensor consists of the glass electrode in contact with thin layer of solution, being covered with a immobilized enzyme layer. The enzyme (e.g., urease) catalyzes the reaction of the analyte, e.g., urea in the reaction: $CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$. The resulting change in the pH of the solution in contact with the glass electrode allows quantitative determination of the analyte (in this case urea).

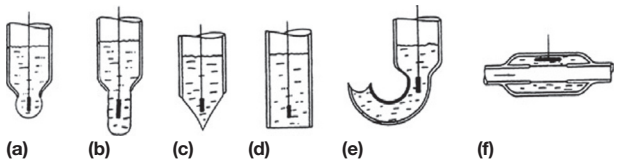

Figure 3 (a–e) Shapes of glass electrode tips and (f) tubular flow-through electrode.

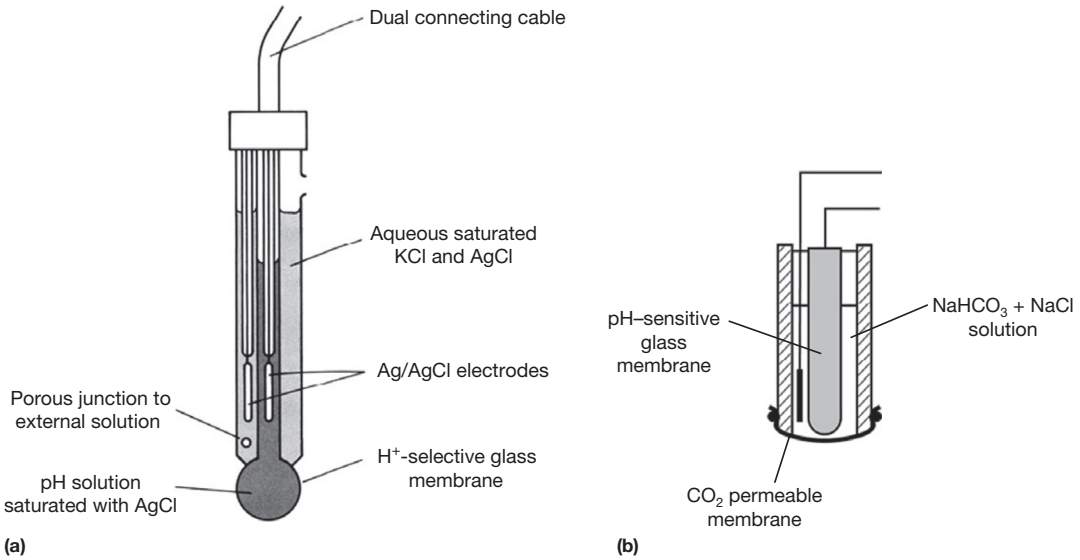

Figure 4 (a) Combination pH sensitive glass electrode with the reference electrode (Ag/AgCl); (b) Carbon dioxide gas electrode based on pH-sensitive glass electrode.

Chalcogenide Glass Electrodes

The general term 'glass electrode' is also used in connection to electrodes which membrane is composed of glasses of different composition and with construction differing from conventional glass electrodes. The glass membrane is composed of amorphous solids which are binary, ternary, or multicomponent compounds of the elements of group III, IV or V (boron, aluminum, gallium, germanium, phosphorus, arsenic, antimony) of the periodic table with sulfur, selenium or tellurium. They can be both stoichiometric (e.g., As_2S_3, GeS_2) and nonstoichiometric (e.g., As_xSe_y). Often the membranes are doped with transition metal compounds. Typical glass membranes are obtained by melting the components and forming the proper membrane from the homogeneous melt. The chalcogenide glass membrane is obtained as a disk cut from the solidified melt, and after polishing is pasted into the plastic body in a similar way as it is done for crystalline ion-selective electrodes.

The chalcogenide glass electrode may be selective, for example, for iron(III) (glass containing $Fe_nSe_{60}Ge_{28}Sb_{12}$), copper(II) ($Cu_6As_4S_9$ – sinnerite), silver(I), lead(II) and cadmium(II). The way it functions is not yet clear: it may be sensitive to powerful redox systems, its characteristics may be influenced by doping and its behavior is often non-Nernstian. Such a glass may exhibit mixed ionic or electronic conductances.

Further Reading

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