

Chapter 8

ISE Constructions

8.1 Conventional ISEs with Internal Filling Solution

The schematic sketch of a conventional ISE (an ISE with internal aqueous solution) is presented in Fig. 8.1, left. The main sensing element—the electrode membrane—is fixed in the end of a tubular body. The material of the body depends on the type of the membrane. For glass membrane electrodes, the body constitutes a glass tubing, and the membrane is formed in the end of the body by glass-blowing technique.

There to, the body tubing is immersed for a short while into the electrode glass melt, and then, the drop of the melt is blown into the typical spherical glass membrane. ISEs with crystalline and polymeric membranes, normally, have plastic bodies. Membranes are fixed in the end of the body with a suitable glue or with a clamping nut. In the latter case also, an O-ring made of an inert material (e.g., silicon rubber) is used for a hermetic seal. Typical constructions of the conventional ISEs are shown in Fig. 8.2.

Micro-ISEs for cellular studies (see Sect. 8.4) and electrodes in flow-through cells, in particular in clinical analyzers (see Sect. 8.5), are often of the conventional type, although solid-contact setup (see Sect. 8.2) appears more promising for these miniature devices.

Conventional ISEs contain an internal solution. This can be an ordinary liquid solution or a gel. For stable and reproducible electrical potential at the interface between the membrane and the internal solution, the latter must contain the ion to which the membrane is selective. For instance, for a glass pH electrode, this must be H^+ ; for a Pb^{2+} crystalline electrode, this is Pb^{2+} ; for a K^+ and NO_3^- polymeric electrodes, these are K^+ and NO_3^- , etc.

The membrane and the internal solution are ionic conductors, while the wire is electronic conductor. For a reversible transduction from the ionic conductivity in the internal solution to the electronic conductivity in the wire, an internal electrode is needed. To this end, one can use well-known classical first- and second-kind electrodes, as well as RedOx electrodes. Most often, a second-kind electrode, in particular—Ag/AgCl, is used as the internal electrode in the conventional ISEs. Then, the internal solution must also contain Cl^- ions. For the above listed

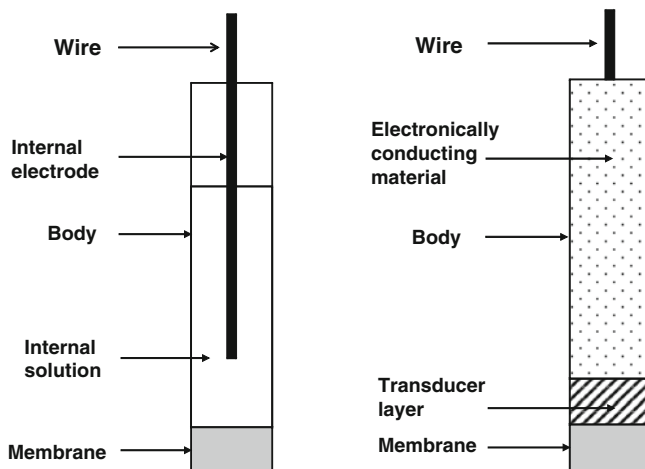


Fig. 8.1 Schematic sketch of a conventional ISE (*left*) and a solid-contact ISE (*right*)

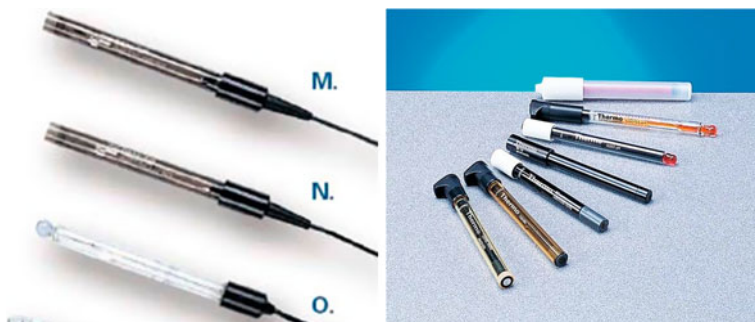


Fig. 8.2 *Left* the Denver Instruments ISEs with crystalline membrane (M), PVC membrane (N), and glass membrane (O). *Right* the Thermo Fisher ISEs

examples, the most typical internal solutions are as follows: 0.01 M HCl, 0.0001 M PbCl_2 , 0.01 M KCl, and 0.01 M NaNO_3 + 0.01 M NaCl, respectively. Potassium ion is controlled mostly in clinical and agricultural samples where the concentration of the target ion is relatively high (about 4.5 mM in blood and up to 0.1 M in carrot juice). Nitrate is measured predominantly in agriculture (e.g., in fertilized soils) and in some polymer production. The target ion concentrations in the samples are rather high. Therefore, the internal solutions in the respective ISEs contain high concentrations of the analyte ions. Lead-selective ISEs are mostly used in environmental control where lead must be measured at trace levels; therefore, the internal solution should not contain high concentrations of the target ions (see also Sect. 7.2). Furthermore, complexing agents can be added for further decrease in the analyte ion activity in the internal solutions in ISEs for trace analysis.

Internal solutions often contain some other additives, for example, to prevent freezing during electrode transportation in winter.

As example of the charge transfer in a conventional ISE, let us consider a K^+ ISE filled with KCl solution and equipped with Ag/AgCl internal electrode, see Fig. 8.3, top. Across the membrane/solution interface, charge is transferred by K^+ ions. The respective exchange currents are high, securing the electrochemical equilibrium at the interface [1, 2]. Within the internal solution, charge is carried by K^+ and Cl^- ions. At the interface between the internal solution and Ag/AgCl electrode, Ag atoms reversibly oxidize to Ag^+ cations, producing electrons: $Ag^{Ag} \leftrightarrow Ag^{+,aq} + e^-$. The silver cations with the chloride anions produce low-soluble salt: $Ag^{+,aq} + Cl^{-,aq} \leftrightarrow AgCl \downarrow$. Due to these reversible processes, the activity of silver ions in solution is determined by the chloride activity:

$$a_{Ag^+,aq} = SP_{AgCl} / a_{Cl^{-,aq}} \tag{8.1}$$

The internal Ag/AgCl electrode potential can be expressed as follows:

$$\begin{aligned} \varphi_{Ag/AgCl} &= -\frac{\mu_{Ag^+}^{0,Ag} - \mu_{Ag^+}^{0,aq}}{F} - \frac{RT}{F} \ln \frac{a_{Ag^+}^{Ag}}{a_{Ag^+}^{aq}} \\ &= -\frac{\mu_{Ag^+}^{0,Ag} - \mu_{Ag^+}^{0,aq}}{F} - \frac{RT}{F} \ln \frac{a_{Ag^+}^{Ag} a_{Cl^{-,aq}}}{SP_{AgCl}} \end{aligned} \tag{8.2}$$

If the chloride activity is well above $\sqrt{SP_{AgCl}}$, the electrode potential is very stable. This is why the concentration of Cl^- ions in the internal solution must be 10^{-4} M or higher.

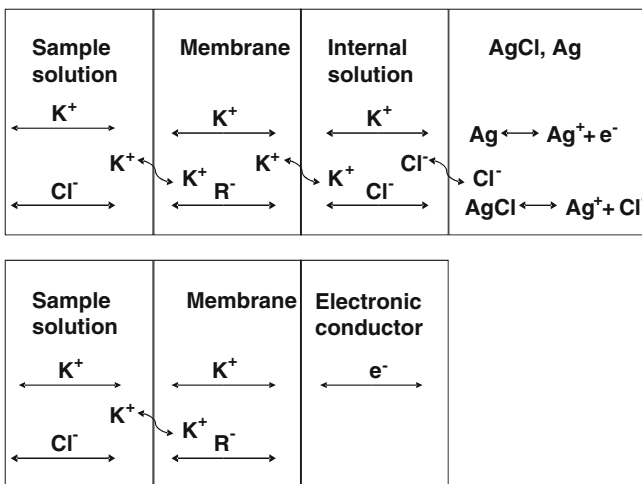


Fig. 8.3 Charge transportation in a conventional K^+ ISE (top) and a coated-wire K^+ ISE (bottom)

In this way, in the conventional ISEs, the reversible charge transfer is arranged, including the interface between ionically and electronically conducting phases. When all reactions involved are fast, the electrode behaves as ideally non-polarizable. This is why the conventional ISEs, if properly maintained, show excellent stability and reproducibility of the potentials. However, if electrode is not sealed hermetically, the internal solution must be from time to time replaced with a fresh portion.

8.2 Solid-Contact ISEs

8.2.1 Why Solid Contact?

It is difficult to make small-size conventional ISEs with internal solution and internal electrode. This hinders the ISE application in small volumes which would be especially advantageous for the analysis of clinical and biological samples. Furthermore, the conventional construction is non-compatible with the modern planar technologies. Therefore, for decades, researchers strived for the elimination of the internal solution and the internal electrode and for the replacement thereof with the so-called “solid contact”.

The solid-contact ISEs (see Fig. 8.1, right) comprise of an electronically conducting substrate covered with a transducer layer (see below) and a sensor layer (still called membrane) on the top of the transducer layer. The substrate may be a metal wire. In this way, it is possible to decrease the diameter of the ISE down to 0.6 mm and less. One can use a relatively large conducting plate as the substrate and cover it with the transducer layer and then with the sensor layer. After that, the three-layer construct can be cut into a number of pieces each being an individual solid-contact ISE. The latter approach utilizes the advantages of the planar technology and promises mass production of low-cost sensors.

Elimination of the internal reference system and replacement thereof with a solid contact appears a purely technical task. However, solving this task encounters fundamental problems. So far, these problems are solved for glass and crystalline electrodes and remain largely unsolved for polymeric membranes with ionophores. From the practical point of view, these problems result in insufficient long-term stability of the ISE potentials and in poor piece-to-piece reproducibility.

Since the interpretation of the measured signal—the EMF—relies on the calibration, the stability of the calibration parameters (E^0 and S) over time directly translates into the accuracy and the reliability of the analysis. Normally, the slope value is stable whatever the ISE construction: conventional or with a solid contact. However, the standard potentials of the solid-contact ISEs often change from day to day in a chaotic way. This causes unpredictable parallel shifts of the calibration curve, which, in turn, worsens the accuracy of the measurements. The low piece-to-piece reproducibility within a series of replica electrodes, from the practical

point of view, hinders the interchangeability of the ISEs. From the academic viewpoint, it indicates the insufficient knowledge of the regularities governing the electrode potential formation.

The ISE membrane is an ionic conductor, and the boundary potential at the membrane/solution interface is a well-defined value determined by the equilibrium distribution of ions between the phases. The substrate (a metal or a carbon-based material) is an electronic conductor connected (via a wire) to the measuring device. Therefore, the stability and reproducibility of the readings require a stable electrical potential at the interface between the ionically conducting membrane and electronically conducting substrate. This potential must be defined by a RedOx reaction at the interface between these phases (like the oxidation and reduction of silver in Ag/AgCl electrode). Furthermore, this RedOx reaction must be fast, and the two phases must be buffered with respect to the reactant: to re-establish the equilibrium in the case of some external perturbations [3]. Without a suitable RedOx reaction, the interface is blocked: Ions are confined to the membrane, and electrons cannot leave the substrate. Consequently, the interface between the membrane and the substrate constitutes a capacitor and behaves as an ideally polarizable electrode.¹ A fortuitous tiny charge causes a significant change in the potential of such an electrode.

8.2.2 Solid-Contact ISEs with Glass and Crystalline Membranes

The problem of the stabilization of the potentials of the solid-contact ISEs with glass and crystalline membranes has been solved successfully. The internal surface of the glass membrane is covered by a metal alloy, containing small amount of the respective alkali metal. The wire directly contacts the alloy. For instance, pH solid-contact electrodes with membranes containing Li₂O and a Sn alloy doped with Li show excellent stability over time [4, 5]. The potential at the interface between the membrane glass and the alloy is determined by the equilibrium of the oxidation/reduction in Li: $\text{Li}^{\text{Alloy}} \leftrightarrow \text{Li}^{+\text{,glass}} + e^{-\text{,alloy}}$. Thus, for these solid-contact ISEs, the concept of the classical first-kind electrode is exploited. The piece-to-piece reproducibility of these electrodes allows for factory calibration: The user gets the calibration parameters from the manual, and these parameters retain their values for years [4, 5].

¹ Ideally polarizable electrode is an electrode characterized by the absence of net current between the electrode surface and the electrolyte. Even tiny electric charge causes large change in the potential (large polarization) of such an electrode. On the contrary, the potential of an ideally non-polarizable electrode is virtually non-sensitive to any charge passed. The classical examples of the ideally polarizable and ideally non-polarizable electrodes are, respectively, mercury and platinum electrodes in a solution containing a RedOx couple.

The concept of the second-kind electrode is used as a basis for solid-contact ISEs with crystalline membranes [6]. These membranes contain Ag_2S or other low-soluble salt AgX with $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{J}^-, \text{SCN}^-$ —in ISEs selective to the respective anions. Electrodes selective to Cu^{2+} , Pb^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} contain Ag_2S and a sulfide of the respective metal. The internal side of the membrane is covered with a thin layer (film) of vacuum-sputtered silver, and the wire is then soldered to this silver layer. The RedOx equilibrium is established between Ag^+ ions in the crystalline membrane and Ag atoms in the silver metal film. The solid-contact ISEs with chalcogenide glass membranes are arranged in an analogous way [7].

Detailed description of various solid-contact ISEs is presented in review papers [8–10].

8.2.3 *Ionophore-Based Solid-Contact ISEs Without Transducer Layer*

First attempts of making solid-contact ISEs with ionophore-based membranes were undertaken in 1970s. These were Selectrodes [11, 12] and the so-called coated-wire electrodes [13–15]. Selectrodes constitute porous graphite rods impregnated with a liquid membrane cocktail (without polymer). In the coated-wire electrodes, the membrane is deposited on the surface of a noble metal wire: Pt, Au, Ag—by dipping wire into membrane cocktail. The electrodes of both these types show practically the same working ranges and selectivities as conventional electrodes with the same membrane compositions. However, the potentials of these ISEs drift chaotically and relatively fast—up to 10 mV/h. The potentials of replica electrodes prepared in exactly the same way sometimes differ in the range of 20–100 mV.

The reason is that the membrane/graphite and membrane/wire interfaces are blocked (see above), and the respective potential is sensitive to even small accidental charges. This sensitivity is inversely dependent on the capacity of the interface:

$$d\varphi = C^{-1}dQ \quad (8.3)$$

Here, C is the capacitance and dQ is the accidental charge. This simple equation shows that increasing the capacitance, that is, by increasing the area of the contact, allows for some stabilization of the potential.

In reality, the membrane/graphite and membrane/metal interfaces are partly unblocked by oxygen and other RedOx agents penetrating through the membrane. The oxygen-induced RedOx processes provide for some stabilization of the potential so that the calibration parameters retain their values for some time (about one hour) [16, 17]. It was reported on the dependence of the coated-wire electrode potentials on the oxygen partial pressure in the ambient air [17].

The first-kind electrode concept is not promising for ISEs with the ionophore-based membranes. These membranes sorb water from solutions. Furthermore, water penetrates through the membrane and forms a thin layer on the metal surface. The metal ion concentration in this aqueous layer is not stable, causing instability of the electrode potential.

Grekovich suggested using the second-kind electrode concept. It was reported on solid-contact ISEs for Cl^- , Br^- , and SCN^- anions with high stability and reproducibility of the potentials [18]. Membranes containing PVC, plasticizer (dibutyl phthalate), and ion exchanger, TDAX tetradecyl ammonium salt ($\text{X}^- = \text{Cl}^-$, Br^- , SCN^-), were deposited on the respective second-kind electrode: Ag/AgCl , Ag/AgBr , or Ag/AgSCN . This approach is limited to anions producing low-soluble silver salts.

8.2.4 Solid-Contact ISEs with Electron–Ion-Exchanger Resins in the Transducer Layer

Doping the membrane with suitable RedOx agents may stabilize the solid-contact ISE potentials. Then, however, the RedOx agents must be confined to the vicinity of the electronic conductor. Otherwise, the ISE is sensitive to RedOx components in samples. Stefanova therefore suggested the use of electron–ion-exchanger resins EO-7 and EI-21 [19, 20]. The EO-7 resin constitutes a polymer with quinone–hydroquinone functional groups. The EI-21 resin is a polymeric cation exchanger with $-\text{SO}_3^-$ groups, containing Cu^{2+} counter-ions. Part of Cu^{2+} is electrochemically reduced to Cu which forms tiny copper metal particles. The electrodes are prepared by depositing the membrane cocktail containing also the resin and carbon black on graphite substrate. After the evaporation of the cocktail solvent (THF), a mixed-conducting layer forms on the top of the graphite rod. The ionic conductivity in this transducer layer is due to the presence of mobile ion-exchanger sites (e.g., ClTPB^-), ions, and charged ion–ionophore complexes. The electronic conductivity is due to electrons in Cu metal particles and in carbon black. The sensor membrane (without resin particles and carbon black) is deposited on the top of this transducer layer. The scheme of a potassium-selective solid-contact ISE of this type is shown in Fig. 8.4.

Ions K^+ and R^- move freely within the transducer layer, in the same way as in the membrane. Between the membrane proper and the resin, ion-exchange equilibrium is established: $2\text{M}^{+, \text{membrane}} + \text{Cu}^{2+, \text{resin}} \leftrightarrow 2\text{M}^{+, \text{resin}} + \text{Cu}^{2+, \text{membrane}}$. Together with RedOx equilibrium in the resin, $\text{Cu}^{\text{resin}} \leftrightarrow \text{Cu}^{2+, \text{resin}} + 2\text{e}^{-, \text{resin}}$, these processes ensure reversible transduction from ionic to electronic conductivity. Carbon black plays a dualistic role: connecting the resin particles with one another and with the substrate and increasing the capacitance of the interface between ionically conducting and electronically conducting phases. This mixed-conducting layer works as transducer from ionic to electronic conductivity.

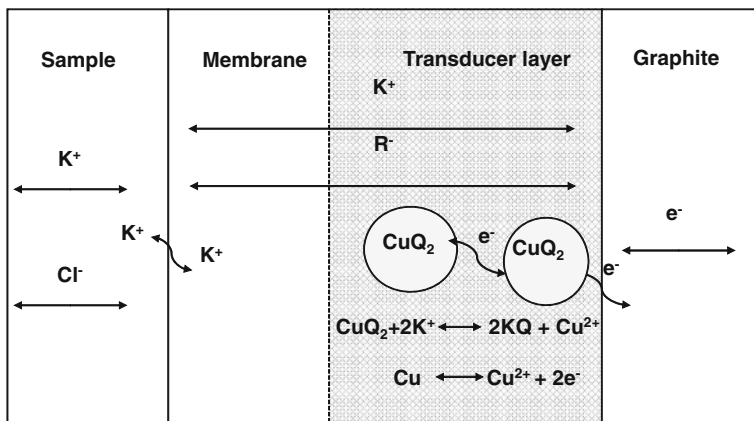


Fig. 8.4 Scheme of solid-contact ISE with EI-21 resin in the transducer layer. Q^- is the anionic functional group in the resin. Carbon black suspension is shown with grey dots

Solid-contact ISEs for K^+ , Na^+ , NH_4^+ , Ca^{2+} , NO_3^- , CO_3^{2-} ions with EI-21 resin in the transducer layer are much more stable than the analogous Selectrode or coated-wire ISEs. The electrode potentials in control solutions retain values within $\pm 1-2$ mV during several days. However, periods of stability alternate with sudden potential jumps in 2–5 mV within a few hours. The most probable reason for these jumps is extraction of some RedOx agents from samples. These agents diffuse across the membrane and reach the transducer layer with RedOx-sensitive components after a few days. At this time, the potential undergoes sharp change [21].

8.2.5 Solid-Contact ISEs with Conducting Polymers in the Transducer Layer

Conducting polymers (CP) appear very promising for the stabilization of the solid-contact ISEs potentials. Most of the conducting polymers are *p*-type semiconductors when oxidized and doped with anions to maintain the macroscopic electroneutrality. There are, however, also *n*-type CPs doped with cations. Thus, the doping/de-doping reaction is coupled with oxidation/reduction of the polymer. In this way, CPs work as transducers from ionic to electronic conductivity. Most popular CPs used in solid-contact ISEs are polythiophenes: polytrioctylthiophene (POT), polyethylenedioxythiophene (PEDOT), polyaniline (PANI), and polypyrrole (PPy). All these CPs belong to the *p*-type semiconductors.

Thorough discussion of the advantages and limitations of various CPs for the solid-contact ISE purposes is presented in Bobacka et al. [8]. The oxidation potential of POT is too high, and therefore, its oxidation degree is too low under normal conditions. Therefore, its conductivity and RedOx capacity are also low.

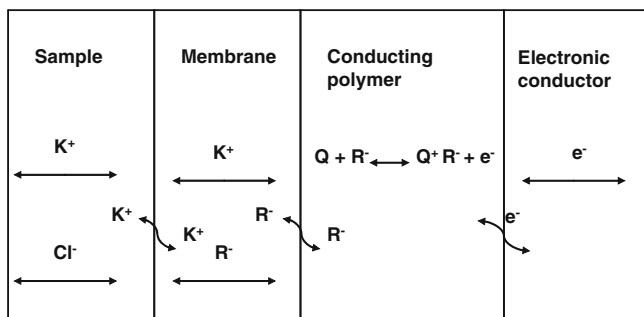


Fig. 8.5 Scheme of solid-contact ISE with a *p*-type conducting polymer in the transducer layer

Oxidized PEDOT, PANI, and PPy are stable under normal conditions; these CPs have high RedOX capacity and, consequently, less sensitive to external RedOX agents. However, CPs, especially PANI, are sensitive to pH. Therefore, oxygen, CO_2 , and even water may cause changes in the oxidation state of CPs. This is one of the reasons why the potentials of solid-contact ISEs are not as stable as one could expect. Lindfors [22] studied the light sensitivity of the solid-contact ISEs potentials with PPy, POT, PEDOT, and PANI in the transducer layer. ISEs with POT showed highest and those with PPy, the lowest sensitivity to light [22].

Scheme of a potassium-selective solid-contact ISE with a *p*-type conducting polymer in the transducer layer is shown in Fig. 8.5.

Many inorganic ions [8, 23, 24], ionic surfactants [25], and polyions [26] are measured with solid-contact ISEs containing CPs in the transducer layer. Using CPs, it is possible to make very small ISEs, for example, within a syringe needle [27] or even microelectrodes for measurements within a living cell [28]. It is also possible to avoid metal or carbon substrate: Full-plastic ISEs for K^+ and Ca^{2+} ions were described by Michalska and Maksymiuk [29].

8.2.6 Influence of Water Uptake on the Stability of Solid-Contact ISEs

Although conducting polymers and ion-to-electron-exchanger resins provide for reversible transduction from ionic to electronic conductivity, solid-contact ISEs with ionophore-based membranes are not as stable as electrodes with glass and crystalline membranes. A significant difference between these types of ISEs is the ability of polymeric membranes to sorb water. Water in membranes is present in significant quantities and forms aggregates with different sizes and diffusion coefficients [30–34]. Water uptake is strongly dependent on the nature of the polymer; POT sorbs much less water than plasticized PVC [34]. Furthermore,

water forms a continuous layer with the thickness of about 10 nm in between the membrane and the transducer layer [34–37]. Thus, an internal aqueous solution spontaneously forms in solid-contact ISEs with polymeric membranes. The volume of this solution does not exceed 0.05 μl , and therefore, its composition, although with some delay, strongly depends on the ambient conditions due to diffusion of electrolytes across the membrane. Therefore, the presence of the water layer worsens the stability of solid-contact ISEs.

Test for the presence of water layer was proposed in Fibbioli et al. [38]. The idea of the test is as follows. Let us have an ISE for I^+ ions in contact with IX electrolyte solution for some time. Then, we replace the IX solution with a JX solution, and J^+ ion is discriminated by the membrane. The potential of an electrode without water layer drops fast into the negative direction and maintains a stable value. When this electrode is removed from JX solution and placed back into IX solution, the potential returns to its initial value, like shown in Fig. 8.6, solid line. If a water layer is present, J^+ ions diffuse through the membrane to the water film, and I^+ ions diffuse from the film to solution. This results in depletion of the water layer in I^+ ions, while the solution in the utmost vicinity of the membrane also contains I^+ ions. Therefore, when such an ISE is immersed into JX solution, the potential drifts to more positive direction. When the ISE is placed back into IX electrolyte, the potential shows an overshoot because the water layer is depleted in I^+ ions, and then, the potential drifts to the initial value, see Fig. 8.6, dotted line.

In order to avoid the formation of the water layer, the water uptake must be reduced by decrease in the plasticizer content in membrane [39] or by replacement PVC with another polymer. It is also advisable to increase the hydrophobicity of the transducer layer and the substrate. To this end, very useful are dispersed carbon materials like carbon nanotubes [40, 41] and porous graphite [42, 43].

Fig. 8.6 Scheme of the water layer test. *Solid line* refers to an ISE without water layer, *dotted line*—with water layer

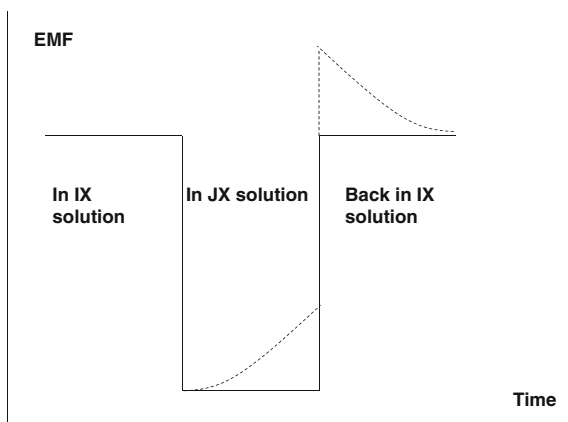
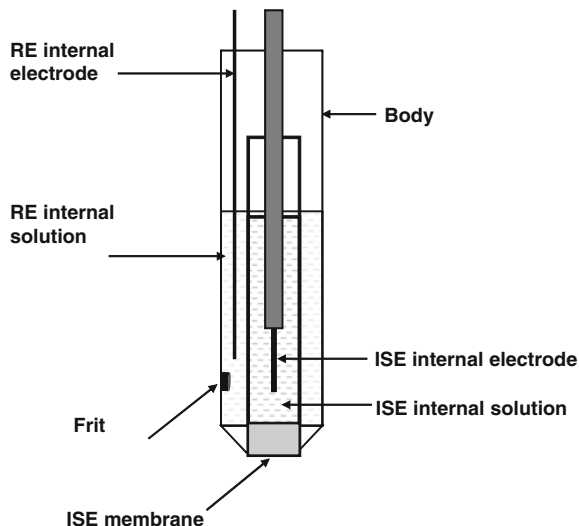


Fig. 8.7 Scheme of a combination electrode



8.3 Combination Electrodes

Combination electrodes constitute an ISE and a reference electrode (RE) combined in one body. The constructions of REs are discussed in detail in Sect. 9.1. A schematic sketch of a combination electrode is shown in Fig. 8.7. The body contains two compartments: for the ISE and for the RE; often, these are two coaxial cylinders: inner cylinder for the ISE and the room between the cylinders—for the RE. The ISE is in contact with the sample or calibrator solution through the membrane. The role of the liquid junction plays a frit made of a porous ceramics or glass.

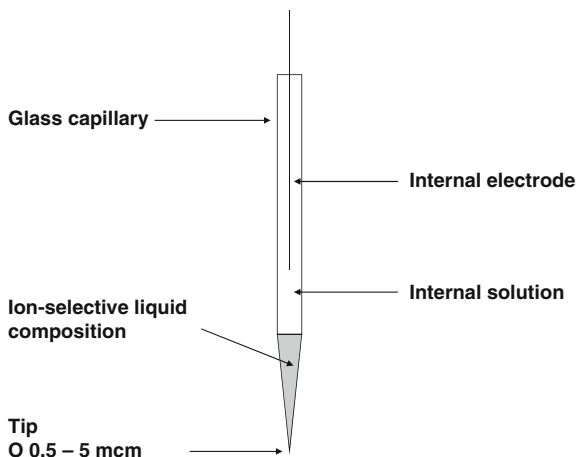
Combination electrodes are convenient in use, especially if only one ion must be controlled. It is not advisable to have several combination electrodes in one sample beaker because of the increased contamination of the sample with electrolytes from the REs. Therefore, if a number of ions must be measured in the same sample, it is better to use ordinary ISEs and an ordinary RE.

8.4 Micro-ISEs for Cellular Studies

Microelectrodes are used for measurements of ion concentrations in living cells. Obviously, these electrodes must be very small and therefore constitute glass capillaries, containing liquid membrane compositions in tip. Scheme of a microelectrode is shown in Fig. 8.8.

The tip diameter is about 0.5–5 μm . Because of high resistivity, polymeric membranes are not suitable for microelectrodes. Furthermore, in order to increase

Fig. 8.8 Scheme of a microelectrode



the dissociation degree of electrolytes in membrane, polar solvent oNPOE (see Sect. 4.3) predominates among other solvents used with ionophore-based membranes. From the manufacturing point of view, it is also necessary to use liquid membranes in microelectrodes because these are prepared by sucking the membrane composition into the capillary. Capillaries must be hydrophobic to avoid water leak between the membrane phase and glass. Thereto, the tip is silanized. Microelectrodes fundamentals and practice are thoroughly described by Ammann [44].

8.5 Flow-Through ISE Cells

Many applications of ISEs suggest measurements in flow. For instance, electrodes may be placed into a bypass in an industrial process. Application of ISEs for clinical analysis also requires flow-cells to decrease consumption of samples and also enhances the reliability of the measurements. This is often achieved by alternating samples and calibrators, and for this task, measurements in flow-cells are superior to those in beakers. A typical example of flow-through ISEs and assembled flow-cell for clinical analyzer is shown in Fig. 8.9, left.

In the electrode bodies are two channels: vertical channel for the membrane and internal reference system and horizontal channel for samples and calibrators. Once the cell is assembled, sample/calibrator channels of individual electrodes make a channel across the whole cell like shown in Fig. 8.9, right. Normally, 30–100 μl of sample or calibrator is enough to measure concentrations of several ions using a flow-through cell like shown in Fig. 8.9.

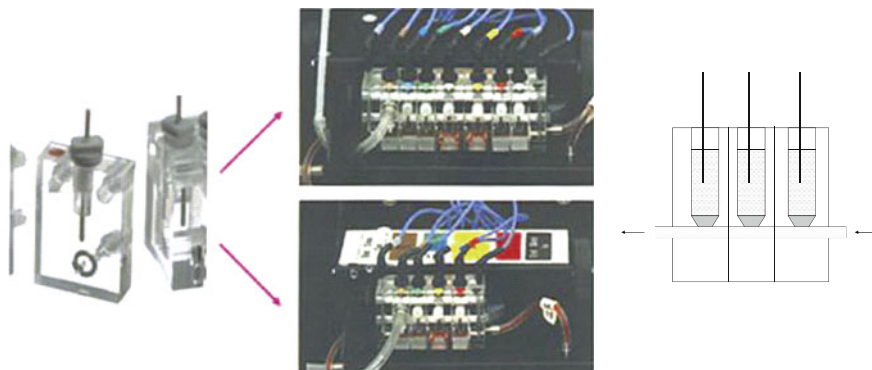


Fig. 8.9 *Left* flow-through cell with ISEs for clinical analyzer Konelab (Thermo Fisher). Electrodes (*left*) and assembled flow-through cells with five ISEs and a RE (*right, top*) and with three ISEs and a RE (*right, bottom*). Terminal electrodes are for conductivity measurements—to control whether the channel contains sample or is empty. Next to *left* terminal electrode, the RE is located. *Right* scheme of a flow-through cell

References

1. K.N. Mikhelson, J. Bobacka, A. Lewenstam, A. Ivaska, *Electroanalysis*, 2001, 13, 876.
2. K.N. Mikhelson, J. Bobacka, A. Ivaska, A. Lewenstam, M. Bochenska, *Anal. Chem.*, 2002, 74, 518.
3. B.P. Nikolskii, E.A. Materova, *Ion-Selective Electrode Rev.* 1985, 7, 3.
4. M.M. Shultz, O.S. Ershov, G.P. Lepnev, T.M. Grekovich, A.S. Sergeev, *Russ. J. Appl. Chem.*, 1979, 52, 2487 (Russ.).
5. A.A. Belyustin, A.M. Pisarevskii, G.P. Lepnev, A.S. Sergeev, M.M. Schultz, *Sens. Actuators B*, 1992, 10, 61.
6. Yu. G. Vlasov, Y. E. Ermolenko, O. A. Iskhakova, *J. Anal. Chem. USSR*, 1979, 34, 1175.
7. Yu.G. Vlasov, E.A. Bychkov, *Ion-Selective Electrode Rev.* 1987, 9, 3.
8. J. Bobacka, A. Ivaska, A. Lewenstam, *Chem. Rev.* 2008, 108, 329.
9. A. Michalska, *Electroanalysis*, 2012, 24, 1253.
10. N.M. Ivanova, M.B. Levin, K.N. Mikhelson, *Russ. Chem. Bull.*, 2012 (full reference will be provided).
11. J. Ruzicka, C.G. Lamm, *Anal. Chim. Acta*, 1971, 54, 1.
12. J. Ruzicka, E.H. Hansen, J.C. Tjell, *Anal. Chim. Acta*, 1973, 67, 155.
13. R. W. Cattrall, H. Freiser, *Anal. Chem.*, 1971, 43, 1905.
14. R.W. Cattrall, D.M. Drew, *Analyt. Chim. Acta.*, 1975, 77, 9.
15. R. W. Cattrall, I. C. Hamilton, *Ion-Selective Electrode Rev.*, 1984, 6, 125.
16. R.P. Buck, V.R. Shepard, *Anal. Chem.*, 1974, 46, 2097.
17. A. Hulanicki, M. Trojanovicz, *Anal. Chim. Acta*, 1976, 87, 411.
18. A.L. Grekovich, K.N. Mikhelson, S.E. Didina, N.V. Garbuzova, E.A. Materova, *Ion Exchange and Ionometry*, 1982, 3, 130 (Russ.).
19. O.K. Stefanova, N.V. Rozhdestvenskaya, V.F. Gorshkova, *Sov. Electrochem*, 1983, 19, 1225.
20. O.K. Stefanova, N.V. Rozhdestvenskaya, B.A. Mukhitdinova, E.E. Ergozhin, O.V. Sofronova, T.E. Barinova, *Sov. Electrochem.*, 1990, 26, 976.
21. G. A. Khripoun, E. A. Volkova, A.V. Liseenkov, K.N. Mikhelson, *Electroanalysis*, 2006, 18, 1322.
22. T. Lindfors, *J Solid State Electrochem*, 2009, 13, 77.

23. T. Lindfors, H. Aarnio, A. Ivaska, *Anal. Chem.*, 2007, 79, 8571.
24. A. Michalska, A. Ivaska, A. Lewenstam, *Anal. Chem.*, 1997, 69, 4060.
25. A. Kovacs, B. Csoka, G. Nagy, A. Ivaska, *Anal. Chim. Acta*, 2001, 437, 67.
26. K. Fordyce, A. Shvarev, *Anal. Chem.*, 2008, 80, 827.
27. S.V. Lamaka, M.G. Taryba, M.L. Zheludkevich, M.G.S. Ferreira, *Electroanalysis*, 2009, 21, 2447.
28. N. Rubinova, K. Chumbimuni-Torres, E. Bakker, *Sens. & Actuat. B*, 2007, 121, 135.
29. A. Michalska, K. Maksymiuk, *Anal. Chim. Acta*, 2004, 523, 97.
30. N.V. Rozhdestvenskaya, O.K. Stefanova, *Sov. Electrochem.*, 1982, 18, 1379.
31. J.D. Harrison, X. Li, *Anal. Chem.*, 1991, 63, 2168.
32. Z. Li, X. Li, S. Petrovic, J.D. Harrison, *Anal. Chem.*, 1996, 68, 1717.
33. Z. Li, X. Li, M. Rothmaier, J.D. Harrison, *Anal. Chem.*, 1996, 68, 1726.
34. T. Lindfors, F. Sundfors, L. Höfler, R.E. Gyurcsanyi, *Electroanalysis*, 2009, 21, 1914.
35. F. Sundfors, L. Höfler, R.E. Gyurcsanyi, T. Lindfors, *Electroanalysis*, 2011, 23, 1769.
36. L. Gorski, A. Matusevich, M. Pietrzak, L. Wang, M. E. Meyerhoff, E. Malinowska, *J Solid State Electrochem*, 2009, 13, 157.
37. R. De Marco, J.P. Veder, G. Clarke, A. Nelson, K. Prince, E. Pretsch, E. Bakker, *Phys. Chem. Chem. Phys.*, 2008, 10, 73.
38. M. Fibbioli, W.E. Morf, M. Badertscher, N.F. de Rooij, E. Pretsch, *Electroanalysis*, 2000, 12, 1286.
39. M. Puntener, M. Fibbioli, E. Bakker, E. Pretsch, *Electroanalysis*, 2002, 14, 1329.
40. G.A. Crespo, S. Macho, F.X. Rius, *Anal. Chem.* 2008, 80, 1316.
41. G.A. Crespo, S. Macho, J. Bobacka, F.X. Rius, *Anal. Chem.* 2009, 81, 676.
42. C.Z. Lai, M.A. Fierke, A. Stein, P. Bühlmann, *Anal. Chem.*, 2007, 79, 4621.
43. M.A. Fierke, C.Z. Lai, P. Bühlmann, A. Stein, *Anal. Chem.*, 2010, 82, 680.
44. D. Ammann, *Ion-selective Microelectrodes*, Springer, Berlin-Heidelberg-New York-Tokyo, 1986.