

Solid-state reference electrodes for potentiometric sensors

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Received: 7 March 2008 / Revised: 22 April 2008 / Accepted: 25 April 2008 / Published online: 4 June 2008
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Abstract The availability and application of solid-state reference electrodes for potentiometric electrochemical sensors are briefly reviewed. For a long time, considerable efforts have been made to combine solid-state indicator electrodes with equivalent reference electrodes to take advantage of the absence of liquid system components to full capacity. In spite of various suggestions to solve the problem, no type of solid-state reference electrode is so far available with properties completely identical to conventional ones.

Keywords Reference electrode · Reference electrolyte · Gel electrolyte · Filled polymer · Transition metal oxide bronze · REFET

Introduction

It is generally accepted that long-term stability of an electrochemical cell used for potentiometric determinations of dissolved ions is significantly determined by the potential stability of the reference electrode. Although scientific interest is primarily devoted to ion-sensitive electrodes e.g. the indicator electrode, progress with regard to the reference electrode can also be ascertained.

For measurements at which it is only important to maintain a reasonably constant comparative potential value for a defined measuring period, sometimes inert noble metals or metals covered with hardly soluble metal salts or metal oxides are used, where mixed potentials are generated [1]. Probes of

that kind are called quasi-reference electrodes [2]. From the point of electrochemistry, the thermodynamically defined classical real reference electrode is a special electrode (also called half-cell) featuring a reversible cell electrode reaction and a stable electrolytic contact to the analyte, which result in a defined and stable electrode potential. For that reason, a very small flow of electrolyte has to be established. The reference electrolyte must not necessarily react with components in the solution to be analysed. Consequently, the composition in the reference electrode itself and in its vicinity may remain widely unchanged. A diaphragm, a grinding, a ceramic fibre or instead of these a fine porous membrane limits the flow of electrolyte through the liquid–liquid junction [3]. Summarised, the mentioned facts are schematically shown in Fig. 1.

Mostly electrodes of the second kind are used as reference electrodes. On account of its environmental compatibility, the Ag/AgCl, Cl⁻ electrode is preferably used. The Hg/Hg₂Cl₂, Cl⁻ (calomel) electrode, introduced by Ostwald as early as 1894 [4], has advantages with regard to potential stability and the influence of light, but it is only applicable up to temperatures of about 80 °C. This electrode is commercially available, while, in contrast, the Tl(Hg)/TlCl, Cl⁻ system, the Thalamid™ electrode, has been banned because of its toxicity. An overview of the classical reference electrode was given by Ives and Janz [5] and Galster [6]. Kaden and Vonau [7] reported on electrochemical reference electrodes especially for pH measurements and discussed advantages and drawbacks of single reference electrodes.

A general imperfection of the classical reference electrode is closely connected with the use of aqueous solutions. The activity of potential determining ions can vary due to an outflow of inner electrolyte via the liquid–liquid connection. To avoid the contamination of the analyte by the reference electrolyte, a bridge electrolyte is sometimes used. On the

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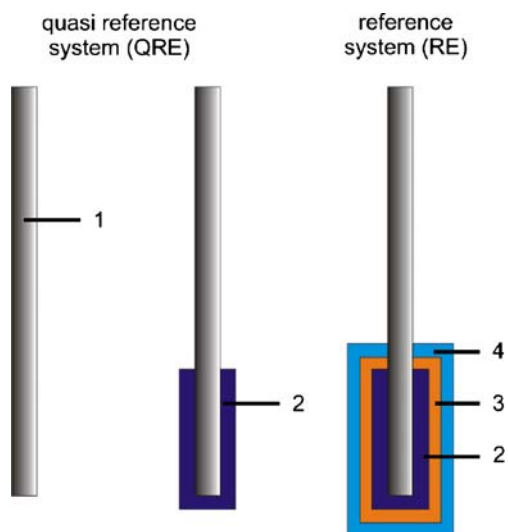


Fig. 1 Main components of a quasi-reference electrode (*QRE*) and a real reference electrode (*RE*). 1 Metal lead, 2 hardly soluble metal salt or metal oxide, 3 reservoir containing the related anion, 4 liquid-tight coating with diaphragm or optional fine porous membrane

other hand, the outlet can be blocked by materials in real analytes such as in biological systems. Reference electrodes have to meet several requirements. Their potential should be stable and reproducible even after a small electric current flow. Their potentials must be independent of the composition of other ions in the analyte, that means not influenced by pH value, concentration of redox species and dissolved oxygen, etc.

The tendency to develop miniaturised electrochemical systems such as lab-on-chip arrangements and to make use of mass production led to reference electrodes in planar embodiment. This is supported by new technological approaches such as the thick film and thin film techniques. Although a lot of scientific approaches were reported, the classical rod-shaped reference electrode is still commercially very dominating.

In this paper, a review will be given on the efforts to improve both well-known electrodes of the second kind,

based on solidified reference electrolyte and solid-state reference systems.

Concepts for reference electrodes

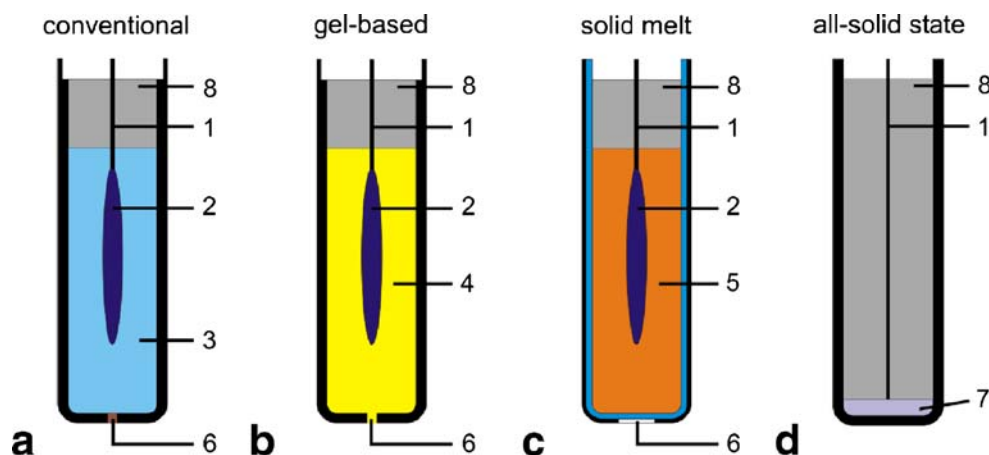
Although the term “solid-state reference” is widely used in the literature, it is differently interpreted by different authors. For this paper, we summarise the activities in the improvement of solid-like reference electrodes into four main groups:

1. Improvement of the classical rod-shaped reference electrode
2. Realisation of a planar conventional reference electrode
3. Implementation of reference systems for ISFETs
4. Establishing of an all-solid-state reference

The basic principles of all reference electrodes discussed in this paper are illustrated schematically in Fig. 2.

The classical reference electrode of the second kind with liquid electrolyte depicted in Fig. 2a consists of a combination of a metal, one of its hardly soluble salts and an electrolyte with a defined anion activity, which determines the activity of the metal ion via the law of mass action e.g. in the Ag/AgCl, Cl^- system. The electrolytic connection between the reference system and the analyte is made via a stick diaphragm. Any application of liquid system components leads to numerous drawbacks, such as position dependence when the electrodes are stored or used, limited possibility for miniaturisation, mechanical fragility and limitations in applications under high pressure and temperature. Therefore, an important research and development objective is to replace liquid functional components. Figure 2b shows the conventional electrode with a gel-like electrolyte in which KCl is dissolved. In this version, the electrolytic contact between the inner electrolyte and the analyte is made by a small hole. In Fig. 2c, an electrode is shown with a solid KCl, which can be prepared by melting KCl. At the bottom of this electrode, a small part of the ceramic electrode body is not covered and

Fig. 2 a–d Basic principles of reference electrodes (e.g. Ag/AgCl reference element). 1 Metal lead (Ag), 2 hardly soluble metal salt (AgCl), 3 aqueous solution containing the related anion (KCl), 4 hydrogel-trapped KCl solution, 5 solid melt of the metal salt (KCl), 6 junction (diaphragm, porous ceramic or opening), 7 all-solid reference element, 8 insulating encapsulation material



acts as diaphragm. An all-solid reference electrode illustrated in Fig. 2d is composed of a metallic wire in close contact with a mixed ionic electronic conductor. This type of all-solid electrode does not need any diaphragm.

Improved conventional reference electrodes

Electrodes with gel-solidified reference electrolytes

Concerning pressure resistance and temperature range, the field of application for the liquid reference electrolyte is considerably limited. In case of high temperature, the electrolyte boils or reacts with the reference system; at low temperature it freezes. To overcome these phenomena, admixtures of suitable solvents are added, which increase the boiling point and decrease the freezing temperature. If the electrodes are to be used under pressure, great effort for pressure compensation is sometimes made to avoid electrolyte contamination by the analyte solution and resulting measurement errors. That is the reason why pressure compensation by solidification of the electrolyte was recommended [8]. By this method, the electrode will be virtually closed above the diaphragm, so that an outer overpressure does not effect permeation of measuring solution into the system. The electrolyte should be thixotropic and of high viscosity.

Sealers such as agar–agar or gelatine, which were formerly used, are nowadays replaced by substances like aerosil™, methyl and hydroxyethyl cellulose, polyvinyl alcohol or polyvinyl acrylamide. These sealers form a relatively raw network, in which the ions of the electrolyte can move largely unhindered. A medium effect does not have to be considered and decrease of conductivity can generally not be observed. Apart from pressure resistance, the gel solidification of the electrolyte provides the advantage of position independence of the electrode during storage and use. There is no electrolyte outflow, so that the electrodes are service reduced. Important properties of gels and gel-like stiffened systems are thixotropy, rheopexy, syneresis and sorption. The thixotropic behaviour of the gels can be observed with the naked eye. Under mechanical stress viscosity decreases, otherwise a strengthening occurs. This can take seconds but also days or weeks.

Rheopexy characterises a non-Newton flow behaviour in terms of a fluid solidification at increasing shearing stress. However, solidification mostly happens only until a certain shear force is achieved, which is indicated by the flow limit. Below this point, the gel is elastic and when the force effect ends, it can return to the initial state. However, when the force increases above this limit, the gel starts to flow.

Syneresis can be observed particularly for inorganic gels or under long-running thermal and/or mechanical stress in organic gels. After a while, the gel begins to shrink and to secrete the dispersant; the gel decomposes [9].

A gel property of particular importance for its use as electrolyte is the sorption ability. If pores and meshes of the gel network in which the dispersant is located are large enough, ions and also molecular-dissolved compounds can swing within them. The ions can reach every point within the gel framework relatively easily and can interact there. First of all, these interactions are influenced by the gel structure. However, the structure is not influenced by the sorption process.

Advanced gel electrolytes show high temperature stability (up to 130 °C, no flowing should occur) and good pressure resistance. Because of the thixotropic behaviour of most of the gels, possible compromises have to be made. A sufficient quantity of electrolyte salt has to be dissolved into the gel by dispersion. Alkaline salts can influence gel formation and gel structure in a negative as well in a positive manner. By substances such as ethylene glycol or glycerol, which serve as flexibiliser for the gels, the amount of solvable electrolyte salt (mostly KCl) in the dispersant is limited. As is generally known, the Nernst equation does not consider concentration but activity of chloride ions. Therefore, with a low KCl content in the gel, potentials can be achieved comparable to those of conventional saturated silver chloride electrodes, provided that the gel solution is saturated with KCl.

A distinction can be made between auxiliary and principal valent gelling agents. In the first case, a prefabricated polymer is subsequently welled in a dispersion medium. The structural elements are held together by intermolecular forces. At these points, intermolecular bonding mechanisms act. Additionally, an entanglement of the macromolecules can be observed. Inherently, these gels are less pressure-resistant than principal valent ones. If pressure is applied to the gels, in a first step stiffening occurs, and when a critical value is exceeded the gels begin to flow. As long as the macromolecules have not been destroyed by force effect, the liquefaction is reversible. Upon completion of the force effect, the intermolecular bonds rebuild again. For the application of these gels, it is inconvenient that they are swellable nearly without limit. When exposed to a solvent, the gel often incorporates solvent molecules, while returning into the sol state. Behaviour like this can be observed with polyvinyl alcohol, polyvinyl pyrrolidone or XanthanGum™.

However, principal valent gels, such as polyacrylamide, tetraethylene orthosilicate or acrylic acid co-polymers, cross-link with real chemical bonds. Here the polymerisation of the monomers takes place directly in the dispersant. Chain length and mesh width can mostly be controlled by dosing catalysers and crosslinkers. Later, these gels are not or only marginally swellable because the meshwork is stiff. Principal valent gels are often more pressure resistant than auxiliary valent ones. However, when these chemical bondings are destroyed by force effects or temperature influences, this is irreversible. In both gel groups, the hollow spaces of the meshwork are filled with a liquid. Ions can move unhindered into the entire gel. In

general, electrode reactions are not influenced by the gels used. Particulars of cylindrical reference electrodes with gelatinous electrolyte, according to the German Standard for Reference Electrodes DIN 19 264 are described in [10, 11].

As compared with aqueous reference systems, electrodes with gel electrolytes feature nearly identical and highly reproducible potentials, even with a lower content of KCl dissolved in the gel. The temperature range and pressure range of electrodes with gel electrolytes can be enlarged considerably. Such electrodes can be sterilised by steam treatment at 130 °C without any degradation. It has been found that gel reference electrodes have a lower lifetime than common ones. This is due to a limited and not reclaimable KCl reservoir. The concentration of KCl decreases continuously by diffusion and electrolyte flow. This in turn leads to a slow drift of the potential. Significant differences between a hole diaphragm and a ceramic diaphragm were observed. Generally, electrodes with ceramic diaphragm have a considerably longer lifetime (see Fig. 3).

Nevertheless, gel electrodes are not suitable for all kinds of potentiometric determinations. Pros and cons are summarised in Table 1. In some cases (Table 2), alternative solutions were found to overcome extreme measuring conditions. Depending on the specific application, the best method has to be found.

In the literature, it was frequently reported that by using gel electrolytes an infiltration of measuring solution into the electrode is prevented. Several experiments with coloured analytes demonstrated however that an intrusion of the measuring solution into the electrode cannot be completely prevented by the application of gel electrolytes. It is only significantly delayed. Under normal pressure, missing electrolyte flow can even promote diffusion into the gel. For electrodes with a hole diaphragm, this process happens naturally by preference. Colour experiments showed that measuring solution slowly diffuses into the gel electrolyte and gradually rises upwards. As a consequence, also the electrode potential changes over time. Potential characteristics based on diffusion effects after changing the analytes were discussed in detail by Gabel et al. [12]. Meanwhile, the gel-based re-

ference electrodes are commercially important and offered by the most of electrochemically orientated companies.

Compared with gelation, a still higher degree of solidification of the reference electrolyte can be achieved by insertion of the salts into strong hardening polymers, such as polyvinyl chloride, polyethylene, epoxy resins and vinyl esters [13–15]. While in this case the so-called extrinsic conducting polymers (CP) are existent, there are also conceptions to use intrinsic conductible ones e.g. polypyrrole or poly(3,4-ethylenedioxythiophene), for the fabrication of solid-state reference electrodes [16, 17]. Here, two different arrangements have been tested: only consisting of CP and those where the CP phase is covered with a poly(vinyl chloride)-based outer membrane of tailored composition. The first mentioned arrangement was designed to suppress or compensate cation and anion exchange, using mobile perchlorate ions and poly(4-styrenesulfonate) or dodecylbenzenesulfonate anions as immobilised dopants. Sufficient stability of potentials has been obtained for poly(3,4-ethylenedioxythiophene) or polypyrrole doped with poly(4-styrenesulfonate) anions and covered by a poly(vinyl chloride)-based membrane, containing both anion and cation exchangers as well as solid potassium chloride and silver chloride with metallic silver.

Electrodes with solidified reference electrolyte

Figure 2c shows the basic design of a highly innovative all-solid reference electrode with solidified reference electrolyte [18]. The reference system consists essentially of a sintered Ag/AgCl mixture, which is embedded in a solid melt of KCl. It is arranged inside a cylindrical hollow body from porous alumina oxide ceramics, the outer surface of which is coated with a chemical-resistant stoved insulation layer. At the closed bottom of the hollow body, a circular area is held free from the coating. In this area, the ceramics with a pore size of about 2 µm acts as a diaphragm, which provides for the necessary electrolytic contact to the measuring medium. The upper third of the hollow cylinder is poured with hot curing epoxy resin. In a somewhat modified configuration, the lower part of the hollow cylinder is filled with an additional solid melt of a salt mixture with a higher melting point, which fulfils the function of a bridge electrolyte. Also in this case, the Ag/AgCl compound is only in direct contact with the KCl melt.

A photograph of the reference electrodes according to Fig. 2c is given in Fig. 4. The two samples differ only in the diameter of the circular free diaphragm surface. By varying the contact area, it is possible to optimise the interaction between the measuring medium and the inner system of the reference electrode. Apart from other advantages like the solid molten KCl electrolyte, it is especially noteworthy that at this type of reference electrode the diaphragm is an integral material fraction of the sensor body. Due to this

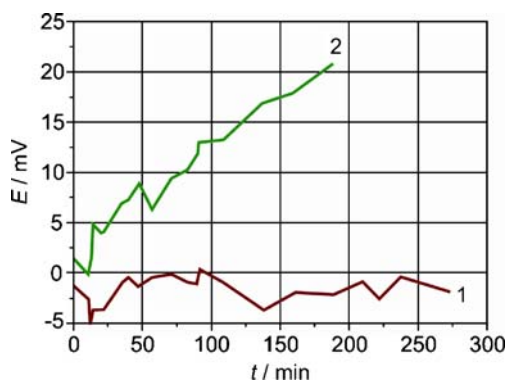


Fig. 3 Long-term stability of gel-solidified reference electrodes with ceramic diaphragm (curve 1) and hole diaphragm (curve 2)

Table 1 Subsumption of pros and cons of gel reference electrodes

Advantages	Drawbacks
Electrode potentials comparable with those of conventional electrodes with liquid electrolytes	Increased diffusion potentials when changing solutions
Increased ability to work under high temperature (depending on gel type, up to 121 °C)	Irreversible bleeding
Applicable with hole diaphragm	Biofouling (for several gels)
Pressure resistant	Electrolyte not renewable
Sterilisable in steam	Gel aging
Retarded diffusion of solutions into the electrolyte	Decolourisation
Position independent usage is possible	Cumbersome preparation
	Some gels contain toxic/carcinogenic substances

feature, the well-known technological problems are avoided, which arise when the diaphragm must be fitted into other materials by gluing or smelting.

As shown in Fig. 5, the potential of the all-solid reference electrode is, as is necessary, largely unaffected by the pH value of the measuring medium. In spite of considerable differences in the pH value and the composition of the test solutions, the potential of the electrode in each case remains within a range of hardly more than 1 mV after a response time of a few minutes. This behaviour is similar to that of reference electrodes using gel-strengthening electrolytes.

The potential of these all-solid reference electrodes also proved to be very stable even over longer periods of time. In a 3-month long-term test in the laboratory with changing temperatures, potential fluctuations of less than 2 mV have been observed, which can be estimated as quite satisfying. The drift of test specimen according to Fig. 5 with greater free surface area of the diaphragm is lower than the drift of specimen with the smaller diaphragm. This suggests the possibility to optimise this parameter in diverse practical operating conditions.

Since it is intended to use the reference electrodes preferably in the food industry or biotechnology, they must be sterilisable. In sterilisation tests, the electrodes have been exposed in laboratory autoclaves to steam sterilisations of 15 min at 121 °C and 2 bar pressure, as generally recommended.

Table 2 Alternatives for gel electrodes

Problem	Solution
High external pressure	Continuous pressurisation Double junction (direct contact between electrolyte and measuring solution is prevented) Big reservoir container (utilisation of gravitation, at low overpressure) Frequent electrolyte change
High temperature	Glycerine/ethylene glycol addition to aqueous electrolyte (increasing of boiling temperature)
Paste-like samples	Usage of electrodes with large electrolyte flow instead of hole diaphragm

The test specimens have been proven as fully functional after sterilisation. Their potentials had shifted only slightly by less than 1 mV.

In industrial measuring technology, combination electrodes are often preferred, at which the indicator electrode and the reference electrode are joined together to form a constructive unit. As an example, in Fig. 6 a pH combination electrode is presented consisting essentially of a solid Sb indicator electrode and an internal reference electrode according to Fig. 2c.

A number of pH combination electrodes according to Fig. 6 have been manufactured, successfully tested in the laboratory and also practically applied. Within the pH range 2 to 9, the mV/pH characteristics are linear with the slope >55 mV/pH at 25 °C with small deviations of about 2 mV. The pH probes are completely steam-sterilisable. As a result of the sterilisation procedure, the sensitivity is somewhat reduced, whilst the zero point remains nearly unaffected. Application tests with the all-solid pH combination electrode were performed in a brewery. In the food industry, chemical sensors are needed for process monitoring and quality control of meat, dairy products, beverages and a variety of other foods [19].

Conventional reference electrodes in planar design

The need for reliable, simple and cost-saving sensors especially in environmental and medical fields of application led to the introduction of mass production technologies for their

**Fig. 4** Photo of all-solid reference electrodes according to Fig. 2c with different sizes of the free surface of the diaphragm

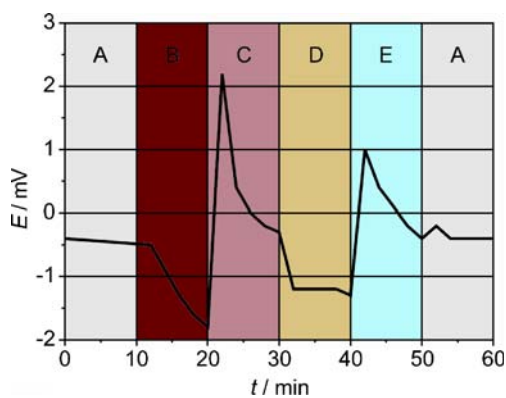


Fig. 5 Potential of an all-solid reference electrode according to Fig. 4 in different test solutions, measured against a conventional Ag/AgCl, Cl^- reference electrode at room temperature. A sat. KCl, B pH=1.68, C pH=4.01, D pH=6.86, E pH=9.18

manufacture. This involves the use of materials capable for large-scale production as well as the utilisation of appropriate manufacturing technologies. The increasing demand was accompanied with the effort to miniaturise the sensors for use in hand-held instruments or small automatic analysers. An advantage was especially the production with methods of microsystem technology. Two different strategies for the use of sensors have been pursued. On the one hand, low-cost disposables with simple designs and cheap component parts have been produced—especially in the field of medical sensors. On the other hand, sensor systems have been developed with sophisticated technologies to increase the lifetime of the devices without reduction of the sensor performances. In particular, the design of a planar reference electrode for amperometric and potentiometric analysers is still an ambitious challenge to scientists.

Generally both quasi-reference systems (QRE) [20, 21] and reference systems (RE) according to Fig. 1 are used for planar electrochemical sensors. QRE are preferably used for

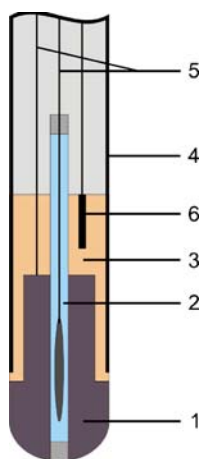


Fig. 6 pH combination electrode with a solid Sb indicator electrode, containing an internal all-solid reference electrode according to Fig. 2c. 1 Sb indicator electrode, 2 reference electrode, 3 sealing compound, 4 sensor shaft (stainless steel), 5 connecting leads, 6 temperature probe

miniaturised lab-on-chip systems with defined and specific operational conditions. An example of a planar sieve-printed Ag/AgCl quasi-reference electrode on an electrochemical multi-parameter lab-on-chip configuration is presented in Fig. 7. Apart from the reference electrode, an oxygen sensor, a pH sensor and an impedance structure are prepared on the aluminium oxide ceramic substrate [22].

For the realisation of miniaturised planar reference electrodes with methods of microsystem technology, the well-known Ag/AgCl, Cl^- system has mostly been chosen as the basic structure. This consists of a silver electrode, in general chemically or electrochemically chloridised or covered with a sieve-printed AgCl layer. For the manufacturing of the silver layer, thick film or thin film technologies can be applied. If the required constant chloride concentration could not be achieved by fixation in the analyte solution itself, the main interests of the developers focussed on the maintenance of a stable chloride concentration in the reference element. Different, in part contradictory, assumptions have to be considered for a miniaturised Ag/AgCl, Cl^- reference electrode. For a long lifetime, a large quantity of e.g. KCl solution has to be placed in a very limited volume. An appropriate exchange of charge carriers between the inner solution of the planar device and the analyte has to be established to guarantee low resistance of the electrode—best achieved without loss of KCl and AgCl and without contamination of the reference element with substances present in the solution. Last but not least, the reference electrode should be storable for a long time without aging and immediately ready for use.

To overcome all these problems, different strategies have been pursued. The loss of KCl and contamination of the reference element can be reduced by a restriction of the contact area to the solution. However, this causes higher resistance and slower response of the system. A similar effect can be obtained by the employment of a gel electrolyte to reduce the diffusion of the enclosed chloride. For the fixation of the electrolyte salts e.g. hydrogels like

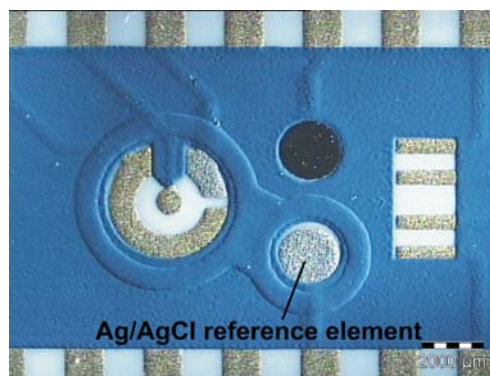


Fig. 7 Ag/AgCl quasi-reference electrode on a sieve-printed planar lab-on-chip system

agarose [23] have been used. Tymecki et al. [24] establish a KCl reservoir by grinding the protective paste with finely powdered potassium chloride. The small holes and channels of the cured paste filled with KCl crystals facilitate the contact to the Ag/AgCl reference element.

The contact between the reference element and the solution can also be achieved by a heterogeneous membrane—the hydrophilic part facing the inner electrolyte [25]. The hydrophobic outer part oriented towards the analyte solution can be passed by gas and water molecules. A comparable way has been chosen by Shim and Kwon [26]. In this study, silicon polymer is oriented towards the potassium chloride side while a Nafion™ film and a polyurethane polymer are placed upon the analyte side. Polystyrene-based quaritanised ammonium salts used as chloride source for the Ag/AgCl reference element have been presented by Kinlen et al. [27]. A Nafion™ coating was further used as a protection layer against the analyte solution. In the patent [28], a porous film is described with a laminated hydrophilic polymer on this structure facing the conductor electrode. Other authors [29, 30] introduce a polymer mixture of porous and hydrophilic polymers based on e.g. cellulose acetate and polyurethane to protect the KCl-bearing electrolyte. To increase lifetime, the loss of silver halide and electrolyte salts can also be reduced by repeated alternating laminated layers of silver halide thin films and hydrophobic films [31]. Kwon et al. [32] have coated a Ag/AgCl electrode with a silicone rubber membrane, Nafion™ as cation exchanger membrane and a polyurethane-based membrane. This outmost layer was containing a H⁺-ion-selective ionophor for an improved cation transport to the Nafion™ membrane, which led to a remarkable decrease of the potential drift of the reference electrode.

Further minimisation of leaching of the potential determining salts can be achieved by the integration of a longer channel between the reference element and the contact zone towards the analyte matrix. This enhances the lifetime while accepting a small drift during the operating time. Microsystem technologies and even flex circuit technology [33] have been applied to construct reference electrodes with channel-type structures. Diffusion channels integrated in a planar substrate for a prolonged ion transport way have been described by Gumbrecht et al. [34]. The diffusion could be additionally influenced by the use of hydrogels. In [35], polyvinylpyrrolidone is used as inner KCl solution carrier. Additionally, this reference element is combined with an ion-selective membrane for a self-diagnosis of the electrode system. Even on planar structures [36] e.g. cotton threads, glass fibres or filter materials can be integrated to establish the contact to the solution. Furthermore, the liquid junction is not placed on the flat surface of the structure—the channel, enclosed by a protective membrane, ends on the top edge of the structure. pHEMA was used by Högg et al. [37] as KCl-bearing inner electrolyte to fill a channel between junction and Ag/AgCl

reference element. Alternatively [38], a filter paper soaked with the electrolyte was laminated on the sensor structure. Suzuki et al. [39–41] increase the lifetime of the reference electrode by two ways. On the one hand, the surface of the silver chloride film is protected with a water-repellent layer—a loss of silver halide is only possible at the small edges of the silver layer. On the other hand, the planar electrolyte layer has to be filled with KCl solution only before the measurement—no activity loss during storage is possible. The injection ports are integrated in the planar substrate.

Another solution for the problem of prolonged lifetime is the integration of a KCl reservoir, which compensates the loss of the salt during the lifetime of the reference electrode. But unfortunately the basic planar structure offers only a small volume for the reservoir. This reservoir principle has been utilised by Birch et al. [42]. The Ag/AgCl, Cl[−] electrode is covered by a polymeric layer containing silver halide and potassium chloride to establish the contact zone. The enhanced lifetime is limited by the KCl enclosed in the polymer. In [43], a disposable thick film reference electrode is described with an immobilisation of silver halide in the thick film paste printed on the connecting pad. The swelling of this layer while the sensor is in operation is supported by a hydrophilic silicate-based filler. A comparable way has been found by Cranny and Atkinson [44]. They have included potassium chloride into a low firing glass or into a silicone polymer paste. Polyvinyl ester resins for the enclosure of KCl have been investigated by Desmond et al. [45]. A similar design has been chosen by Gerlach et al. [46] and Vonau et al. [47] for a smart card application. The thickness of the Ag/AgCl layer and a resin comprising the KCl crystals does not exceed 350 μm at all. The excellent long-time response of the smart card reference electrode in different solutions is shown in Fig. 8.

A further enhancement of this configuration is an integration of a salt reservoir within the supporting substrate [48, 49]. The reservoir for e.g. KCl is placed on the back of the sieve-printed Ag/AgCl electrode. A cavity is filled with the solid electrolyte enclosed in a polymer, and the conductor electrode is printed on the planar reservoir. A second, smaller layer with the salt is placed in front of the electrode

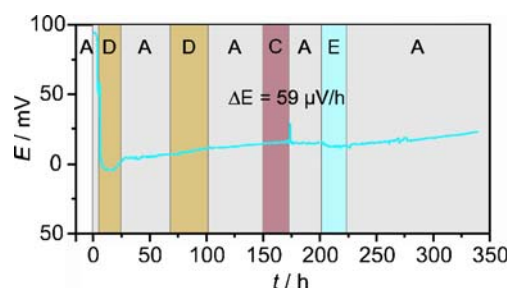


Fig. 8 Long-time response of a planar reference electrode (Ag/AgCl covered with a KCl-bearing epoxy resin) stored in different solutions. A 0.1 M KCl, C NBS buffer 4.01, D NBS buffer 6.86, E NBS buffer 9.18

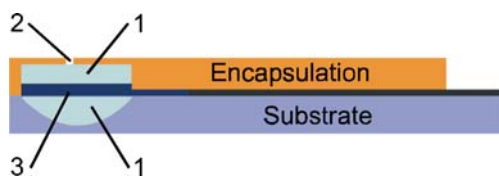


Fig. 9 Planar reference electrode system with additional reverse side KCl reservoir. 1 Outer and inner KCl solution, 2 junction, 3 measuring electrode (Ag/AgCl) with metallic lead

contacting the solution. The KCl passes from the back through the silver chloride layer to establish a constant potential. This design allows a thicker volume for the storage of salts to prolong the lifetime and for other interesting ingredients. The design of the planar reference electrode system with reverse side reservoir is shown in Fig. 9.

For a short time hydrophobic ionic liquids are introduced for the protection of the Ag/AgCl layer and for the establishment of the electrolytic contact to the analyte solution. The new developments are based on investigations of Kakiuchi et al. [50] describing a classical reference electrode design with a gelled ionic liquid separating the inner electrolyte from the sample solution. This design reduces the variations of electrical potentials at the liquid junction and the contamination of the inner reservoir. The same author [51] presents an advancement in which no inner electrolyte is still necessary because the potential determining AgCl is slightly soluble in the covering ionic liquid itself. The reference electrode is designed as a coated wire electrode comprising a chloridised silver wire enclosed by a thick membrane of the AgCl-saturated ionic liquid 1-methyl-3-octylimidazolium bis-(trifluoromethylsulfonyl)imide. A publication of Maminska et al. [52] presents the design of all-solid-state miniaturised reference electrodes suitable for flow-through analysis, which were applied as reference electrodes in flow cell measurements with potassium-selective planar microelectrodes. The electrodes exhibit good potential stability, reproducibility and long-term stability. They are based on Ag/AgCl planar microelectrodes covered with PVC membranes containing the ionic liquid 1-dodecyl-3-methylimidazolium chloride. The membrane with this additive provides an internal solid electrolyte, maintaining constant chloride concentration in the layer and thus constant potential of the Ag/AgCl, Cl^- electrode in a solution of different concentrations of chloride and other interfering anions. A disadvantage of ionic liquid-based reference electrodes is at the moment their loss of ionic components in the sample solutions and the influence of hydrophobic and multivalent ions on their performance.

Reference systems for ISFETs

ISFETs (ion-sensitive field effect transistors) are chemically sensitive sensor devices. The ISFET is based on a metal

oxide semiconductor field effect transistor (MOSFET), the metallic gate contact of which has been replaced by an ion-sensitive layer consisting of Si_3N_4 , Al_2O_3 or, recently preferred, of Ta_2O_5 for a pH ISFET. Like all other potentiometric electrochemical sensors, the ISFET pH indicator electrode must be complemented by a reference electrode, the potential of which should be completely independent of the pH value and the presence of other ions in the measuring solution.

The application of a conventional liquid filled Ag/AgCl, Cl^- reference electrode for this purpose, even if it is drastically miniaturised, would considerably impair the attractive properties of the ISFET as an all-solid, small-sized microelectronic sensor device. For this reason over several decades, considerable efforts have been made to develop adequate all-solid reference electrodes for ISFET sensors, which should be particularly suitable for being prepared on a sensor chip together with the ISFET by using conventional IC fabrication technologies. The first approaches to solving this problem were published already in the early 1980s of the past century. The numerous proposals submitted since then may be roughly classified into three categories as shown in Fig. 10.

The earliest ISFET on-chip reference system according to Fig. 10a was described by Comte and Janata [53]. At this Janata-type configuration, a small closed epoxy compartment EC containing a pH-buffered gel is placed on one of a matched pair of pH ISFETs. The electrolytic connection to the solution is made via a glass capillary. At first sight, this seems a rather reasonable version of a reference ISFET, which shows only low pH sensitivity and can be applied together with the “normal” pH ISFET on the same sensor chip in a differential amplifier circuit. But since it has only restricted lifetime and cannot be produced completely by using IC technology, it did not obtain noticeable acceptance.

In contrast to Fig. 10a, the reference system shown in Fig. 10b is not based on an ISFET structure, but is rather a miniaturised planar version of a conventional Ag/AgCl, Cl^- reference electrode. This Prohaska-type microelectrode, which was primarily developed for application in medical research [54], can be prepared in thin film technology using IC-compatible techniques. The general aim is to eliminate the need of a separate reference electrode and to facilitate the use of ISFET. In the sensor literature, the results of relevant development efforts with regard to on-chip integrated planar Ag/AgCl, Cl^- reference electrodes are regularly published [55]. Huang et al. in [56] report on the improvement of integrated Ag/AgCl thin film electrodes for ISFET applications by KCl gel coating. A novel agarose-stabilised KCl gel membrane was introduced to serve both as a polymer-supported solid reference electrolyte and an ionic bridge for Ti/Pd/Ag/AgCl, Cl^- electrodes. Calibrated against the commercial macro Ag/AgCl, Cl^- reference electrode, this minia-

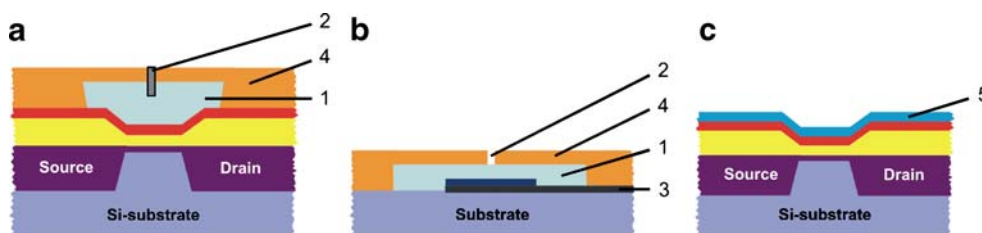


Fig. 10 Different approaches for ISFET reference systems: **a** ISFET with pH buffer compartment, **b** miniaturised Ag/AgCl, Cl^- reference electrode, **c** ISFET with modified pH-insensitive membrane. 1 pH buffer solution (**a**) or KCl solution (**b**); 2 junction, glass capillary (**a**)

or hole (**b**); 3 measuring electrode with metallic lead; 4 cover layer, epoxy compartment (**a**) or thin film cover (**b**); 5 chemically modified surface layer (**c**)

turised system proved to be stable and almost insensitive to changes in Cl^- ion concentration (about 0.02–0.25 mV/pKCl).

A lot of development activities to create a REFET, that means an ISFET-based reference electrode, have been directed to a design as shown schematically in Fig. 10c, where the ion-sensitive membrane of an ISFET is covered with a more or less pH-insensitive membrane or is itself somehow modified to become pH insensitive. This version was initiated by Matsuo et al. [57, 58], who deposited an ion-blocking parylene film on the Si_3N_4 layer on the gate of an ISFET. Errachid et al. [59] described a simple REFET for pH detection in differential mode measurements. The device is based on a pH-insensitive polymeric PVC membrane cast on the gate insulator of an ISFET device that has been previously silylated by chemical grafting of a silane compound. The REFET shows low pH sensitivity (1.8 mV/pH) and is only slightly affected by the concentration of Na^+ and K^+ . The pH response of a combined solid-state device according to Fig. 10b consisting of a pH ISFET, the REFET and a Pt quasi-reference electrode (QRE) was 43.7 mV/pH in the range pH 2 to 9. In [60], the preparation and application of a reference pH sensor is claimed. This reference sensor is based on an extended gate field effect transistor structure and comprises a metal oxide semiconductor field effect transistor on a semiconductor substrate, a sensing unit comprising a substrate, a solid-state conductive sensing layer on the substrate and a polypyrrole layer on the solid-state conductive sensing layer. To obtain a REFET, Chudy et al. [61] applied a membrane containing a highly lipophilic cation complex as an ion-unblocking layer on an ISFET. Lisdat and Moritz [62] suggested a reference element based on a multilayer solid-state structure consisting of a fluoride-sensitive LaF_3 layer, a porous CaF_2 layer and a cellulose-2,4-acetate polymer. More recently, Lee and Sohn [63] reported on the development of a REFET that was produced by applying a polymeric double layer on the Ta_2O_5 surface layer of an ISFET. The REFET itself showed a drastically decreased pH sensitivity of no more than 0.7 mV/pH. Possibilities of modulating the sensitivity of the membrane of an ISFET in the direction to a REFET by ion-implantation techniques [64, 65] and chemical grafting [66] have also been examined. Concerning the functioning of the REFET membranes, Bergveld et al. [67]

studied intensively how electrical and chemical requirements for REFETs may coincide. Two types of REFET structures can be distinguished with respect to the penetration of ions into the polymeric layer, resulting in two different mechanisms of the REFET operation. In a non-ion-blocking REFET structure, ion exchange occurs between the solution and the polymer, whereas in an ion-blocking REFET structure ion exchange is negligible. In the first case, the electrical potential is a membrane potential; in the second, however, it is a surface potential resulting from reversible ion-complexation reactions at the surface of the polymer [60].

For dynamic differential measurements in flow-through cells, simply pair of two ISFETs with identical parameters can be used, one of them being temporarily in contact with a solution of defined pH value. Flow-through systems like this were developed and described by several authors, e.g. [68]. A certain disadvantage of this arrangement consists in the fact that a relatively large distance must exist between the two ISFETs. Therefore, they cannot be integrated in the same sensor chip. Van den Vlekkert et al. [69] covered one of the two pH-sensitive ISFETs with a 200 μm pHEMA hydrogel diffusion barrier to achieve a considerably retarded time response. This pH ISFET, which is modified with regard to the response time, can act as a pseudo-REFET; its field of application, however, is restricted to flow-through systems. In [70], a solid-state reference electrode for an electrochemical system on a microfluidic chip is reported, which is based on electrodeposited anodised nanoporous platinum. The nanoporous platinum oxide with poly-m-PD film shows near Nernstian behaviour, low hysteresis and quick response and is easy to produce and is particularly compatible with microfabrication technologies. Since it responds exclusively to pH, its potential is constant in a buffer solution. An all-solid-state reference electrode based on the layer-by-layer polymer coating was developed for the determination of blood pH and pCO_2 in a flow cell system [71]. It was fabricated by layering a silicone rubber film containing KCl on an AgCl surface, then a perfluorinated ionomer film, and finally a polyurethane-based membrane containing an ionophore, a lipophilic ionic additive and a plasticizer, respectively, were applied. The fabrication of the Ag/AgCl electrode through this layer-by-layer polymer

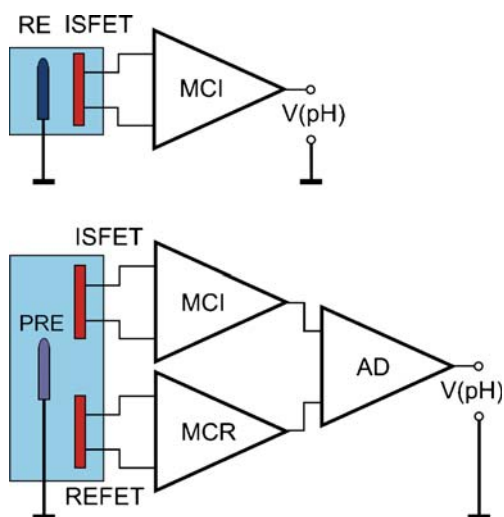


Fig. 11 ISFET measuring circuits with different reference systems. *RE* Reference electrode, *PRE* pseudo-reference electrode, *MCI* (above) ISFET measuring circuit, *MCR* (below) REFET measuring circuit, *AD* differential amplifier, *V(pH)* pH-dependent output signal

coating improved the electrode stability enormously. In addition, the potential drift of the electrode according to the pH of the medium was minimised by introducing a H^+ -ion-selective ionophore (tridodecylamine) into the outmost polymer membrane.

Depending on the kind of the reference electrode, different measuring circuits for ISFETs are recommended. If any really potential-stable reference electrode is available, a simple circuit according to Fig. 11 (above) is suitable. For ISFET/REFET measurements, the differential measuring circuit shown in Fig. 11 (below) must be used. In this case, a pseudo-(PRE) or quasi-(QRE) reference electrode is necessary to provide grounding of the measuring solution. In contrast to a real reference electrode, this electrode must not exhibit a stable potential because its potential fluctuations are eliminated by the common mode rejection of the differential amplifier. An electrode from any chemically resistant material, e.g. a platinum wire or a Pt layer deposited on the ISFET sensor chip, can be applied for this purpose. This arrangement seems to be particularly favourable with regard to the compensation of influences of temperature, light and other disturbance variables. However, the compensating effect must

not be overestimated because it is only noticeable if the ISFET and the MOSFET have identical operating parameters. But this precondition can only be imperfectly realised. In Fig. 11 (below), also a normal reference electrode can be used instead of the REFET. The measuring circuit MCR has to be replaced in this case by a high impedance buffer amplifier. A Wheatstone-Bridge readout interface for ISFET/REFET applications has also been suggested [72]. It allows on-chip integration of ISFET/REFET pairs and will also improve the immunity to noise and interferences.

In summary, it can be ascertained that multiple attempts to create an equivalent long-term stable all-solid reference electrode for ISFET pH sensors have so far not been successful. Neither on-chip preparations of miniaturised planar Ag/AgCl, Cl^- reference systems nor numerous suggestions to modify ISFETs to REFETs have resulted in devices with stability and performance parameters approximately comparable to those of conventional reference electrodes. The miniaturisation of Ag/AgCl, Cl^- electrodes mainly leads to a decrease in lifetime, whereas the surface potentials of pH-insensitive and inert polymeric layers may depend on the general electrolytic constitution of the solution and the adsorption of ions onto the surface [73]. This explains that all ISFET pH probes for industrial process applications commercially available at present are equipped with conventional reference electrodes [74].

Since the reference electrode is an indispensable component of each potentiometric or amperometric electrochemical sensor and is as important as the ISFET indicator electrode itself, the lack of all-solid reference electrodes has till now prevented large-scale introduction of ISFETs into industrial and consumer applications as a substitute for conventional pH sensors. Thus, now as before, the development of an appropriate REFET remains an attractive challenge of innovation [75].

Solid-state reference electrode

Reference electrodes consisting of exclusively solid components without any liquids or solidified liquids are the most attractive solution for reference systems. As the matter of fact, the absence of any liquid system component such as the inner electrolytic solution makes it easy to design planar or miniaturised sensors and allows measurements in broader

Table 3 Sensitivities of transition metal bronze electrodes to dissolved species [83]

	$Na_{0.9}Mo_6O_{17}$	H_xMoO_3	$Ba_{0.12}WO_3$	$Li_{0.4}Mo_{0.95}W_{0.05}O_3$	
				Powder	Monocrystal
pH	+	+/-	-	-	+
pO_2	+	-	-	-	+
Redox	+	+	+	-	?
p cation	+	+	+	+	+

+ Response, - no sensitivity, ? no information up to now

temperature ranges and pressure ranges as well as in non-aqueous solutions with low maintenance.

The main problem to be solved in order to realise such a solid-state reference electrode is to connect the ionic conducting (aqueous) solution with an electronic conductor. From the electrochemical point of view, this contact is an electrode. To maintain a defined potential, the electrochemical reaction with components in the electrolyte has to be avoided or at least diminished. The ion or electron transfer must mainly occur in the solid. For that reason, an electrode material with mixed ionic and electronic conductivity is necessary. Suitable materials are oxides, mixed oxides and salts of oxoanions of the transition elements, which can exist in several valence states. Therefore, an inner redox system can be established, in which electrons delivered by the lower valent cations can be taken of by the higher valent metal cation. Based on former investigations on pH sensitivity of tungsten oxide [76, 77], the electrochemical behaviour of molybdenum and tungsten bronzes were intensively studied [78]. It was reported on sensitivities to dissolved oxygen, alkaline ions and pH [79, 80]. The behaviour of such compounds shows remarkable differences. Depending on the composition, the stoichiometry and the crystal size, different pH, redox, pO_2 and ionic sensitivities can be observed [81, 82]. Summarised, the results are presented in Table 3 [83].

For the illustration of the different electrochemical behaviours of tungsten and molybdenum bronzes, their responses on pH change, dissolved oxygen amount and a varying ratio of a redox couple are shown in Figs. 12, 13 and 14.

Obviously tungsten-doped molybdenum bronze and with a certain limitation $Ba_{0.12}WO_3$ are suited as reference electrode materials. So far, the mechanism of the sensitivity and non-sensitivity, respectively, is not clear. Obviously, the crystal structure and the distribution of different valent ions at the surface and in the bulk play an important role.

To maintain a certain potential, mixtures of conducting polymer and sodium ion conducting Nafion™ were used as

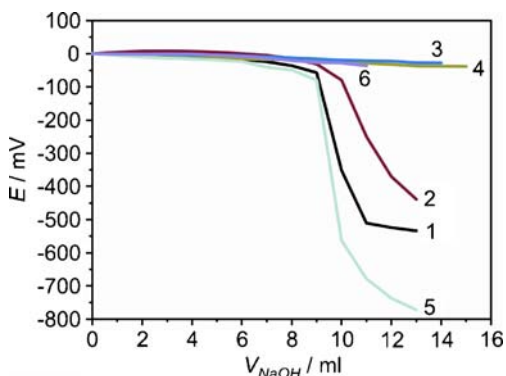


Fig. 12 pH titration curves of different bronze electrodes measured vs. Ag/AgCl, KCl_{sat} electrode. 1 pH glass electrode, 2 $Li_{0.4}Mo_{0.95}W_{0.05}O_3$ (CE), 3 $Li_{0.4}Mo_{0.95}W_{0.05}O_3$ (RE), 4 $Ba_{0.12}WO_3$, 5 $Na_{0.9}Mo_6O_{17}$, 6 H_xMO_3

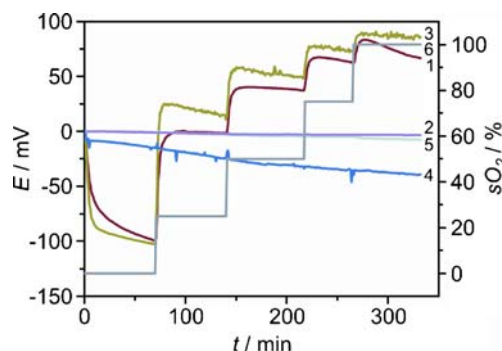


Fig. 13 Oxygen sensitivity of different bronze electrodes. 1 $Li_{0.4}Mo_{0.95}W_{0.05}O_3$ (CE), 2 $Li_{0.4}Mo_{0.95}W_{0.05}O_3$ (RE), 3 $Na_{0.9}Mo_6O_{17}$, 4 H_xMO_3 , 5 $Ba_{0.12}WO_3$

the inner potential lead [84]. For that purpose, also ZnO, which is a semiconductor with a small mobility of Zn^{2+} ions on interstitial sides, is suited [85].

Conclusions and outlook

In many applications in the temperature range $<80\text{ }^\circ\text{C}$, the use of reference electrodes with gel-solidified electrolyte is advantageous concerning practical measurements with the electrodes. Higher temperatures cause an increasing liquefaction of the organic gels and an associated loss of the favourable properties. From $100\text{ }^\circ\text{C}$ and above, substantial changes of the gels occur, which result in a decolouration and in a drift of the electrode potentials. That is the reason why gel-based reference electrodes are only temporary applicable. Particularly with regard to the possibility of steam sterilisation, future developments should focus on the synthesis of heat-sterilisable non-toxic materials.

More favourable in this context are filled resins. However, their preparation is cumbersome and after a few weeks it results in a depletion of reference electrolyte in the areas of the electrode body lying outside. Generally, reference electrodes of this kind rarely achieve the lifetime of gel-solidified ones in

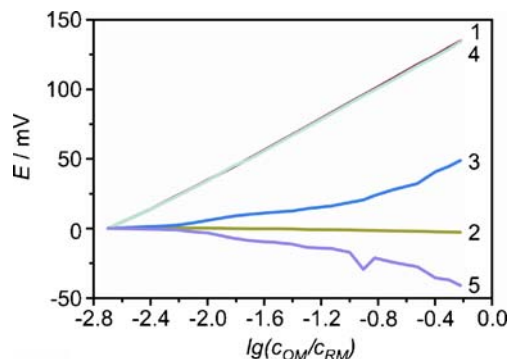


Fig. 14 Potential of different bronze electrodes in dependence on the concentration ratio of the redox couple $[Fe(CN)_6]^{3-/4-}$. 1 Platinum, 2 $Li_{0.4}Mo_{0.95}W_{0.05}O_3$, 3 $Na_{0.9}Mo_6O_{17}$, 4 $Ba_{0.12}WO_3$, 5 H_xMO_3

rough application conditions. Hence, also in this field there is a considerable need for further research to get suitable resins or resin mixtures. Perhaps the use of conducting polymers or ionic liquids may offer new options.

It was demonstrated that the problems regarding the reference systems could not be satisfactorily solved. Nevertheless, improved solidified reference electrodes in conventional as well as in miniaturised designs are developed for practical use. But lifetime, poisoning, the necessity to sterilise and the limited application in extreme temperature ranges restrict the problem-free long-term applicability.

The investigation of all-solid-state references is still in an early state. Although several examples of solid contacts using mixed conductors were reported and the knowledge of solid-state chemistry makes an important contribution, the understanding of electrode processes is insufficient. Basic research on electrochemical kinetics is necessary to clarify the role of charge carriers in the mixed conductor, such as the concentration of ions and electrons, their mobility and the exchange processes between the surface of solids and dissolved ions.

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