Chapter 8
Reference Electrodes in Oxidic Glass Melts

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8.1 General

Reference electrodes to be used in oxidic glass melts are either based on the redox system oxygen/oxide or—in more rare cases—on systems metal/metal oxide [1]. Either of them must be constructed so that it yields a constant potential difference between the oxidic melt of interest and the metal parts of the electrode, i.e., it must represent a constant potential, the “reference potential (difference)” between the glass melt of interest and the metal contact of the electrode. In this chapter the first electrode type treated is the oxygen/oxide reference electrode, which is more often applied than the second type, the metal/metal oxide electrode, whose application is more complicated and thus usually less often applied than the oxygen/oxide reference electrode.

8.1.1 Oxygen/Oxide-Based Electrodes

The reference electrode of these oxygen sensors consists of a platinum electrode in a reference gas with defined oxygen partial pressure, which is separated from the melt by a wall of doped zirconia solid electrolyte with unit oxide transport number. Yttria (Y_2O_3) is used as the second oxide (dopant), which renders the doped oxide solid electrolyte more stable than calcium oxide (CaO) and magnesium oxide (MgO), which have also been tried as the second component of the doped ceramic but were found rather unsatisfactory. Practical units applied in laboratory and industrial glass melts consist of a combination of the essential (platinum) electrode and the zirconia electrolyte, which are constructed for easy handling. These units are called

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"reference electrodes," "zirconia reference electrodes," or briefly "zirconia electrodes," although the solid electrolyte is only part of the unit. The latter term, however, can quite generally be used as long as the underlying mechanism is clear to the user. This terminology will thus also be applied in this chapter.

It is emphasized, however, that the expression given to the electrodes is not merely a matter of semantics but concerns also the potential differences within the electrodes due to the different materials (e.g., zirconia, platinum, gas with certain oxygen contents) and their arrangements. Thus, the "potential" of a "zirconia electrode" $\varphi_{\text{zirconia electrode}}$, i.e., the Galvani potential difference between the oxygen-bathed platinum electrode and the glass melt, is actually the sum of two Galvani potential differences, i.e., the Galvani potential difference between inner electric potentials (ϕ) of the platinum and the zirconia (wall) and that between the zirconia (wall) and the oxidic melt, as demonstrated by Eq. (8.1),

$$\varphi_{\text{zirconia electrode}} = \left(\phi_{\text{Pt}} - \phi_{\text{ZrO}_2}\right) + \left(\phi_{\text{ZrO}_2} - \phi_{\text{m}}\right) = \left(\varphi_{\text{Pt}} - \varphi_{\text{m}}\right) \qquad (8.1)$$

which, under isothermal conditions, reduces to the potential difference between platinum and melt because of the uniform potential of the solid electrolyte (ZrO_2) (Y_2O_3). This, however, is not the case if the zirconia within the electrode is subject to temperature gradients (see below). Also, Eq. (8.1) demonstrates that a zirconia electrode can be understood to be a platinum electrode within a glass melt whose oxygen partial pressure can be arbitrarily changed by outside means.

8.1.2 Construction of Zirconia Electrodes

The basic composition of zirconia electrodes allows (and necessitates) the construction of several different types of electrodes.

The simplest form is the *zirconia tube reference electrode*, whose prototype was already tested by *Besson* [2] and applied in laboratory glass melts by *Plumat* [3]. The cross section of this type presented in Fig. 8.1 shows that the zirconia is arranged as a closed-end tube, which contains a four-bore alumina tube in which three platinum wires are contained: one wire connecting the outside contact in the electrode head to the platinum electrode at the lower end of the tube, and two wires connecting the outside to a thermocouple, which is buried in the zirconia grit at the lower end of the tube so that the temperature of the zirconia grit, which contacts the zirconia tube, is measured at the lower end of the electrode. The reference gas is supplied through the fourth bore (or, alternatively, through one of the other three bores of the alumina tube) to the zirconia grit. The reference gas leaves the grit at the interior of the zirconia tube through the space between the Al_2O_3 and the ZrO_2 tubes and the insulated metal head of the arrangement, which also serves to stabilize the electrode mechanically. The electrochemically active part of zirconia tube electrodes is thus the bottom part of the arrangement and is strictly isothermal. Zirconia tube electrodes thus yield the most accurate results of all constructions developed.

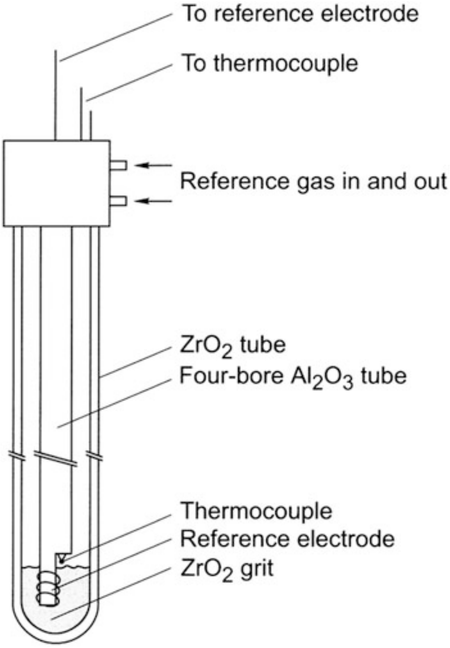

Fig. 8.1 Cross section of zirconia reference tube electrode. Only the bottom part of the zirconia tube contains the platinum contact and the thermocouple both buried in zirconia grit and in intimate contact with the zirconia tube. The reference potential is thus strictly isothermal. Because it is easily broken, the use of the zirconia tube is restricted to laboratory measurements

A basically similar construction is given by the *zirconia disk electrode*. Its inner parts are the same as those of the zirconia tube electrode. The zirconia tube is merely replaced by a platinum tube, which is closed at its lower end by a zirconia disk sintered onto the lower open end of and thus closing the platinum tube. Different from zirconia tube electrodes, this arrangement is rather insensitive to thermal shock. However, it exhibits the phenomenon of “bubble boring” or “bubble drilling” through the horizontal zirconia disk [4] that “captures” gas bubbles at its lower horizontal surface, which, due to their strong movements at the contacting plane of zirconia and melt, dissolve part of the ceramic disk and thus “drill” holes through the zirconia. Bubble drilling through perpendicular ceramic walls is thus less often observed than that through horizontal walls. Perpendicular ceramic walls, however, are not or less often given by zirconia disk electrodes.

8.1.2.1 Zirconia Electrodes with Longer Lifetime

One of the disadvantages of more or less all zirconia electrodes is the rather strong corrosion (or “solubility”) of the zirconia ceramics in oxidic melts. This fact prompted us to construct electrode units especially for application in industrial glass melting tanks, which are distinguished by rather long lifetimes despite the relatively high corrosion of the zirconia.

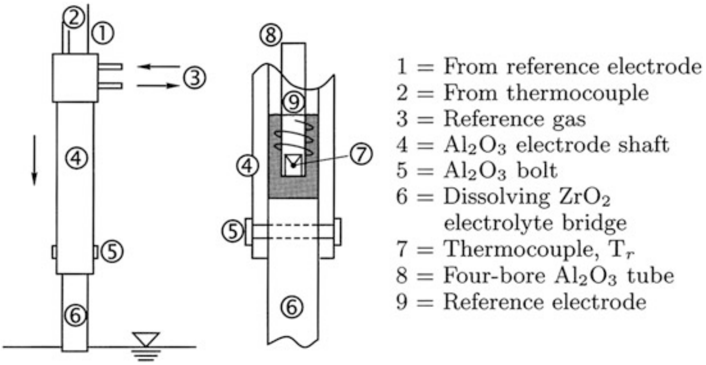

Fig. 8.2 Essential upper part (*left*) and cross section (*right*) of the upper part of a dissolving zirconia reference electrode. The upper part is contained in an alumina tube, which is similar to that shown on the *left side* and closed by the upper end (*right*) of a zirconia rod. The zirconia electrolyte bridge is kept in place by an alumina bolt. The zirconia rod serves as an electrolyte bridge between the upper zirconia and the melt. Its slow dissolution in the melt determines the lifetime of the unit

8.1.2.2 Dissolving Zirconia Electrodes

A dissolving zirconia reference electrode is schematically depicted in Fig. 8.2. It is specifically designed for application in technical (industrial) melting tanks [5–8]. Its considerably longer lifetime compared to, e.g., zirconia tube electrodes is achieved by an ~10–12 cm long electrolyte bridge consisting of a doped zirconia rod, which provides the ionic contact between the upper reference electrode and the surface of the melt and slowly dissolves away at its lower end. The upper end of the rod-shaped electrolyte bridge is inserted into an inert alumina tube where it is kept in place by a horizontal alumina bolt because alumina and zirconia (and doped zirconia) cannot be joined by sintering due to their slightly different coefficients of thermal expansion. However, the mechanical construction necessitates a slight overpressure of the reference gas within the alumina shaft in order to avoid diffusion of gases above the melt through the slits between zirconia rod and alumina electrode shaft and thus a contamination of reference gas and platinum electrode. The perpendicular electrode is continuously or stepwise lowered according to the dissolution rate of the zirconia rod in order to maintain the contact of zirconia rod and melt. Dissolving zirconia electrodes are thus also particularly suited for streaming glass melts which remove traces of dissolved zirconia from the melt near the lower end of the corroding rod and thus eliminate even slight changes of the melt composition near the surface.

8.1.2.3 Temperature Influence

Because, however, the temperatures of glass melt and upper reference electrode at the alumina electrode shaft differ considerably, measuring cells employing dissolving zirconia electrodes are nonisothermal electrochemical cells as indicated by the electrode scheme, cell (I),

$$\mathrm{Pt}, \mathrm{O}_2(\mathrm{r})(T_\mathrm{r})|\mathrm{ZrO}_2|(T_\mathrm{m})\mathrm{melt}, \mathrm{O}^{2-}, \mathrm{O}_2(T_\mathrm{m})|\mathrm{Pt} \tag{8.I}$$

where T_r and T_m are reference and melt temperature, respectively, and ZrO_2 is the nonisothermal dissolving ZrO_2 electrolyte bridge. As demonstrated by Eq. (8.2), the standard thermoelectric emf, $E_{\mathrm{Th,ZrO_2}}(T_\mathrm{r}, T_\mathrm{m})$, of the zirconia electrolyte must be known for correcting the thermoelectric emf, $E_{\Delta T}(T_\mathrm{r}, T_\mathrm{m})$, along the zirconia bridge in order to obtain the oxygen partial pressure of the melt [5, 6],

$$p_{\mathrm{O_2,m}}(T_\mathrm{m}) = \exp\left\{\frac{4F}{RT_\mathrm{m}}\left[E_{\Delta T}(T_\mathrm{r}, T_\mathrm{m}) - E_{\mathrm{Th,ZrO_2}}(T_\mathrm{r}, T_\mathrm{m})\right] + \frac{T_\mathrm{r}}{T_\mathrm{m}} \ln p_{\mathrm{O_2,r}}\right\}, \tag{8.2}$$

which is assumed isothermal in this equation. This quantity had been measured before when thermoelectric data of molten glasses were thoroughly studied [9, 10].

8.1.2.4 Measurement of the Thermoelectric Power (emf) of Yttria-Doped Zirconias

The thermoelectric emf, $E_{\Delta T}(T_\mathrm{r}, T_\mathrm{m})$, of yttria-doped zirconia, which is applied in Eq. (8.2), must be known with extremely high accuracy if sufficiently correct oxygen partial pressures are to be determined. The accuracy of most literature data, however, turned out to be less accurate to guarantee the degree of accuracy needed for the calculations. In addition, the exact magnitude of the thermoelectric power depends on the exact yttria concentration of the ceramics and on the properties of the individual zirconia charges, such as possible trace impurities and special sintering conditions [9]. It was thus unavoidable to measure and compare the thermoelectric data of all individual zirconia specimens, $ZrO_2(Y_2O_3)$, applied to the construction of the reference electrodes. For this reason we devised a reproducible method of checking each individual zirconia material before its application as electrode material [11].

The principle of these measurements is sketched in Fig. 8.3. The arrangement consists of two zirconia electrodes with 1 bar oxygen partial pressure at different temperatures, which are snugly pressed against the ends of the 10–12 cm long nonisothermal zirconia rod under investigation [9, 10]. Variable temperature profiles of the rod are provided by a specially designed temperature furnace [11], the heating alumina tube of which contains the actual measuring arrangement according to

$$\mathrm{Pt}, \mathrm{O}_2(T_1)|\mathrm{ZrO}_2\ \text{specimen}|(T_2)\mathrm{Pt}, \mathrm{O}_2 \tag{8.II}$$

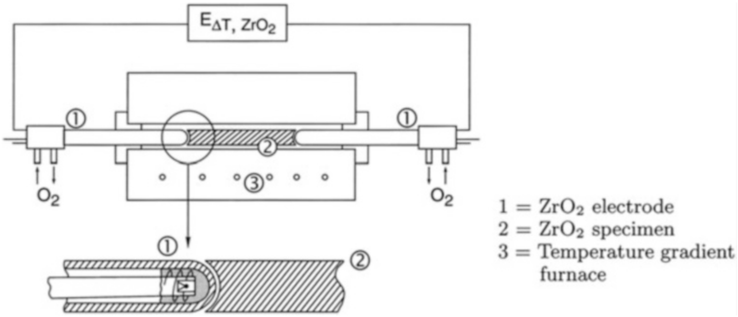

Fig. 8.3 Arrangement for measuring thermoelectric emfs of doped zirconia rods used as zirconia electrolyte bridges. The specimen is clamped between two zirconia electrodes with equal oxygen partial pressure. The zirconia rod is kept in a temperature field due to the specially designed temperature gradient furnace

and thus yields the emf of the ZrO_2 specimen as a function of the temperature difference. Additionally, the temperature gradients can be subdivided and reversed, which increases the accuracy of the measured data by eliminating any asymmetries of the arrangement.

8.1.2.5 Properties of Doped Zirconia Materials

In agreement with the literature, standard Seebeck coefficients of yttria-doped zirconias are independent of temperature and proportional to the molar yttria concentration of the ceramics [10, 12]. For the material most frequently applied during this investigation they can be represented by the linear relationship [11]:

$$\frac{\mathrm{d}E_{\mathrm{Th,ZrO_2}}(T)}{\mathrm{d}T} = ac_{\mathrm{Y_2O_3}} + b, \tag{8.3}$$

where the constants are $a = 4.643 \times 10^{-3}\,\mathrm{mV/(K\,mol\%)}$ and $b = -0.4949\,\mathrm{mV\,K^{-1}}$. For example, the standard Seebeck coefficient of the most frequently applied zirconia composition in this study, i.e., $(ZrO_2)_{0.9547}$ $(Y_2O_3)_{0.0453}$, is (-0.4793 ± 0.0015) $\mathrm{mV\,K^{-1}}$ within the temperature range 700–1,550 °C.

8.1.2.6 Zirconia Reference Electrodes with Special Protection Devices

In addition to the electrode specimens described so far, we have constructed four more electrode types.

1. *The corrosion-protected zirconia electrode* is protected from corrosion by a platinum tube around the alumina shaft, which protects the ceramics from condensing vapors of melt components with high vapor pressure. An additional

gutter at the lower end of the Pt tube ensures that condensed liquid compounds of the melt trickle down from the Pt tube to the zirconia and corrode the zirconia electrolyte bridge [13].

2. *The isothermal zirconia electrode* involves a heating device, which keeps the temperature of the reference electrode automatically equal to that of the measuring electrode by means of an additional electronic control unit and thus eliminates thermoelectric voltages in the first place [14].
3. *The contamination-protected zirconia electrode* incorporates a second closed-end zirconia tube within the alumina shaft which is ionically contacted by the electrolyte bridge through zirconia grit and contains the platinum reference electrode, which is thus protected from melt vapors when the overpressure of the reference gas accidentally drops to the pressure of the tank atmosphere [15].
4. *Various designs of a hook-shaped zirconia electrode* with horizontal electrode shaft and perpendicular zirconia electrolyte bridge allow the sensors to be applied through windows in the side walls of glass melting tanks. “Top application” through the melt surface is thus unnecessary by these considerably more practicable constructions [16].

All zirconia reference electrodes described above can be checked for correct functioning by defined changes of the oxygen reference partial pressure, which must be “answered” by the theoretical emf change if the electrode functions correctly. This check can even be accomplished during the application of the electrodes due to the short response times of the Pt, O_2 electrode on changing the oxygen partial pressure.

8.1.3 Metal/Metal Oxide Electrodes: An Alternative Solution

Although dissolving zirconia reference electrodes as described above provide the maximum lifetime possible and a relatively high mechanical stability because of their construction, a small remaining possibility of breakage and corrosion of the ceramic parts, especially in melts with, e.g., a high lead content, made an alternative reference electrode without these disadvantages highly desirable.

8.1.3.1 Discovery and Development of Metal/Metal Oxide Electrodes

Surprisingly, we observed during experiments with metal rods, which were applied as heating electrodes in industrial melters, that, e.g., molybdenum rods, if not applied for heating, i.e., being nonpolarized, exhibited extremely constant potentials. This observation was the beginning of the development of alternative electrodes, i.e., of metal/metal oxide electrodes, which function similarly as do metal/sparingly soluble metal anion electrodes, for instance, silver/silver halide electrodes, in aqueous solutions, and are known as well-behaving reference electrodes in aqueous solutions. After this discovery, our goal was thus to develop a similar kind of electrode on the basis of our experience, which would be a metal/metal oxide electrode with the favorable properties of molybdenum rods in oxidic melts. This work resulted in an understanding of the stability of the potential of metal/metal oxide systems, as we had observed them in oxidic melts.

8.1.3.2 The Basic Reaction of Metal/Metal Oxide Electrodes in Oxidic Melts

The studied molybdenum rods were actually covered by a thin tight layer of one of their (yellow) oxides, which were in equilibrium with each other during their application for reference purposes. They function thus on the basis of their oxide formation, Eq. (8.III),

$$x\mathrm{M} + y\mathrm{O} \rightleftarrows \mathrm{M}_x\mathrm{O}_y \tag{8.III}$$

and are represented by the electrode scheme $\mathrm{M} \rightleftarrows \mathrm{M}_x\mathrm{O}_y$. If the oxide forms a tight layer at the metal surface, which, after some time, assumes a steady state with relatively small formation and dissolution rates, it represents approximately an equilibrium as indicated by Eq. (8.III), and its equilibrium constant can be written as

$$K(T) = \frac{a_{\mathrm{M}_x\mathrm{O}_y}}{(a_\mathrm{M})^x (a_\mathrm{O})^y}, \tag{8.4}$$

where a is the activity of the species indicated, and a_O is the oxygen activity at the metal/metal oxide phase boundary.

Because both metal and metal oxide are pure condensed phases, and their activities are constant and defined to be unity, the oxygen activity at the phase boundary is fixed by the temperature according to the phase law or, expressed in a different way, its temperature dependence is given by that of the equilibrium constant,

$$a_\mathrm{O}(T) = f(K(T)), \tag{8.5}$$

which can be calculated according to (8.6),

$$\frac{\mathrm{d}\ln p_{\mathrm{O}_2(\mathrm{M}/\mathrm{M}_x\mathrm{O}_y)}}{\mathrm{d}(1/T)} = \frac{2\Delta H^{\ominus}}{yR}, \tag{8.6}$$

where $\Delta H^{\ominus}$ is the standard chemical energy of formation of the pure oxide. Melts contacting the oxide can lead to several interferences, for example, chemical reactions with the oxide, formation of additional solid phases, and alloying the metal with reduced metal from the melt. It is thus unavoidable for practical quantitative applications of the electrodes to conduct measurements which either confirm the absence of interfering reactions or serve as standardizing measurements and yield the "practical $\Delta H^{\ominus\prime}$" for each particular glass melt studied.

Several requirements must thus be met for a satisfactory functioning of metal/metal oxide electrodes. (1) The metal must have a sufficiently high melting point and (2) must not be too inert to allow the oxide to be formed at a sufficient rate; it must, however, (3) be inert enough not to form the oxide at too high a rate so that (4) the lifetime of the electrodes is long enough in the particular melt. (5) The oxide also must have a high melting point, and (6) it must be extremely sparingly soluble in the melt so that, instead of being dissolved after its formation, it forms a steady-state surface layer with a thickness in the range of several atomic dimensions to about 10 nm. For this reason (6) it must be sufficiently tight to ensure that reaction (III) takes place entirely at the phase boundary between metal and oxide after the oxygen has diffused through the layer. Also, (7) it should be a pure oxide ion—or a pure cation conductor for the ideal functioning of the electrode, although the effect of mixed conduction could be taken into account by measurements during the steady state of the electrode.

8.1.3.3 The Main Advantages of Metal/Metal Oxide Electrodes

The main advantage is the absence of ceramic parts so that high corrosion rates and the probability of breakage are excluded. The thermal and mechanical stability enables their introduction and application through the wall and the bottom of technical melters even during the melting process.

A disadvantage, however, is the time-consuming necessity *to standardize the electrodes in each envisaged melt* before their application. This is conducted by means of three different electrodes: a platinum electrode, a zirconia electrode, and the metal/metal oxide electrode to be standardized, which form interconnected electrochemical cells in the oxidic melt of interest.

First, the "standardizing cell" containing the zirconia as the reference electrode has the cell scheme

$$\mathrm{Pt, O_2(r)|ZrO_2|melt, O_2|Pt} \tag{8.IV}$$

exhibits the emf

$$E_1(T) = \varphi_{\mathrm{Pt}}(T) - \varphi_{\mathrm{zirconia\,electrode}}(T), \tag{8.7}$$

and yields the temperature-dependent oxygen partial pressure of the melt according to

$$E(T) = \frac{RT}{4F}\ln\frac{p_{\mathrm{O_2}}(\mathrm{m})}{p_{\mathrm{O_2}}(\mathrm{r})} \tag{8.8}$$

(m: melt; r: reference).

Second, The "reference cell" according to the cell scheme

$$\mathrm{Pt, O_2(r)|ZrO_2|melt, O_2\left|M_xO_y\right|Pt} \tag{8.V}$$

refers the potential of the metal/metal oxide electrode to that of the zirconia electrode,

$$E_2(T) = \varphi_{\mathrm{M/M}_x\mathrm{O}_y}(T) - \varphi_{\text{zirconia electrode}}(T), \tag{8.9}$$

which thus serves as the ultimate reference electrode.

Third, the "measuring cell" containing the metal/metal oxide as the reference electrode and has the cell scheme

$$\mathrm{M\left|M_xO_y\right|melt, O_2|Pt} \tag{8.VI}$$

It is the cell actually to be applied during the practical measurements envisaged and thus yields the emf of interest,

$$E_3(T) = \varphi_{\mathrm{Pt}}(T) - \varphi_{\mathrm{M/M}_x\mathrm{O}_y}(T). \tag{8.10}$$

Combination of Eqs. (8.7)–(8.10) finally yields

$$E_3(T) = E_1(T) - E_2(T), \tag{8.11}$$

which shows that either the directly measured emf $E_3(T)$ of the "measuring cell" and the oxygen partial pressure $p\mathrm{O}_2(T)$ obtained from $E_1(T)$ or the measured emf $E_2(T)$ of the "reference cell," the measured emf $E_1(T)$ of the "standardizing cell," and the oxygen partial pressure $p\mathrm{O}_2(T)$ (from $E_1(T)$) yield the isothermal standardization curve $p\mathrm{O}_2(T_\mathrm{m}) = f(E_3(T_\mathrm{m}))$ at any measuring temperature T_m, which is required for the evaluation of the measurements. For application in nonisothermal melts the temperature of measuring and reference electrode and the possibly temperature-dependent Seebeck coefficient(s) of the glass melts must be known and taken into account.

8.1.3.4 Test Application of Metal/Metal Oxide Electrodes

Various metal/metal oxide electrodes were tested in several glass melts with the result that particularly the systems Mo/$\mathrm{MoO_2}$, W/$\mathrm{WO_2}$, and Ta/$\mathrm{Ta_2O_3}$, the metals and oxides of which exhibit the required sufficiently high melting points (see Table 8.1), show good agreement of practical and theoretical thermodynamic data, i.e., standard chemical energies and standard entropies of oxide formation. These results were obtained in sodium calcium silicate glass melts containing antimony as the fining agent as well as in technical glass melts, for instance, in

Table 8.1 Melting points of some metals and their oxides and temperature-dependent free energies of formation of the oxides, which are of interest for application as alternative reference electrodes in glass-forming melts

		$-\Delta G^{\ominus}$ (kJ mol^{-1})			
Melting point (°C)		1,000 K	1,200 K	1,400 K	1,600 K
Ta	2,996				
Ta_2O_5	1,877	1,607	1,523	1,443	1,364
Mo	2,010				
MoO_2	1,927	389			318
W	3,410				
WO_2	1,570	401	367	333	

borosilicate glass melts fined with sodium chloride. Molybdenum showed the least corrosion, which appeared as thin yellow surface layers. The electrodes did not cause any technical problems during several weeks of application. The logarithm of the equilibrium oxygen at the partial pressure at the metal/metal oxide interfaces is a linear function of the reciprocal absolute temperature. It ranges from approximately $\log p_{O_2} = -15$ at 1,000 °C to $\log p_{O_2} = -8$ at 1,600 °C in the cases of molybdenum/molybdenum oxide and tungsten/tungsten oxide and from $\log p_{O_2} = -22$ at 1,000 °C to $\log p_{O_2} = -12$ at 1,600 °C with tantalum/tantalum oxide. These results promise a general application of metal/metal oxide electrodes in technical glass melters in the future in parallel to the well-established use of zirconia electrodes for research purposes in laboratories and for the standardization of the alternative electrodes.

8.1.3.5 The Essential Steps of the Development of Reference Electrodes for Use with Oxygen-Indicating Electrodes

The first electrodes were based on calcia- and magnesia-stabilized zirconia tubes, respectively, and were applied for short-time activity measurements in molten steel and slags in the steelmaking industry. As with the alternative electrodes for glass melts just described, the reference oxygen partial pressure of these electrodes was fixed by a metal/metal oxide system, for instance, iron/iron oxide, nickel/nickel oxide, cobalt/cobalt oxide, chromium/chromium oxide, and others, which were contained in the zirconia tubes. These first electrodes actually represented combinations of zirconia tube electrodes and the alternative metal/metal oxide electrodes contained in the zirconia tubes. Their oxygen partial pressure was fixed by a solid state reaction (metal/metal oxide) but the lack of suitable properties of these oxides, i.e., chemical inertness with respect to glass melts, and tightness and a sufficient ionic conductivity of thin layers of the oxides necessitated an additional protecting and oxide ion-conducting solid electrolyte, for instance, zirconia, between the reference system and the glass melt. Incidentally, at the early stages of our development, zirconia electrodes with nickel/nickel oxide and with cobalt/cobalt oxide reference systems were also tested for applicability in glass melts. However, they were found unsuited for long-term application because of the rather limited lifetime of the metal/metal oxide reference systems, which is caused by the relatively high oxygen partial pressures at high temperatures, and result in a fast decomposition of the fine-grain oxides and the following fast exhaustion and loss of their oxygen content.

8.1.3.6 The Three Preferable Reference Electrodes for Use in Oxidic Melts

As a consequence of these studies, three alternative reference electrodes with particular properties and fields of applicability can be recommended.

First: *zirconia tube electrodes* employ a reference gas (and an outside determined source of oxygen). An advantage is thus a temperature-independent reference oxygen partial pressure and a strictly isothermal functioning. A disadvantage, on the other hand, is their temperature shock sensitivity due to the fragility of the ceramic tube. Zirconia tube electrodes are thus *the choice* in research and development and even *the only choice* if standard Seebeck coefficients of glass melts are to be determined [17].

Second: *dissolving zirconia reference electrodes* also employ a reference gas with temperature-independent oxygen partial pressure. Also, they employ a rather sturdy electrolyte bridge (doped zirconia rod) between upper Pt electrode and melt surface. The electrolyte bridge, however, introduces the additional problem of temperature-dependent measurements of standard Seebeck coefficients and a material check of each zirconia specimen (rod) before its use. Due to the electrolyte bridge, the lifetime of dissolving reference electrodes is much longer than that of zirconia tube electrodes and thus also well suited for industrial melters.

Third: *metal/metal oxide electrodes, particularly molybdenum, tungsten, etc. oxides* offer the advantage of extremely high mechanical stability. They can be inserted into the hot glass melt without any danger of breakage. The number of useful metals, however, is rather limited. Another disadvantage is the cumbersome and time-consuming standardization of the electrodes with respect to other (zirconia) electrodes before application in each envisaged oxidic melt.

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