Original Paper

Application of oxygen sensors in industrial glass melting tanks

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A comparative study of electrochemical oxygen sensors for glass melts employing zirconia solid electrolytes developed by Schott Glaswerke and by the HVG is reported. The sensors applied in a feeder channel of a melting tank producing green glass yielded slightly different but reproducible results despite different constructions. The zirconia reference electrodes achieved more than one year active lifetime at 1200 °C. Their potentials directly compared over extended periods agreed within less than 3 mV. The potential differences of the platinum measuring electrodes were traced to temperature gradients. Newly installed platinum electrodes show "induction periods" caused by convectional and diffusional equilibration of adhering surface with bulk melt. Unexpected sudden oxygen inhomogeneities of the melt were detected and explained.

Einsatz von Sauerstoffsensoren in industriellen Glasschmelzwannen

Es wird über eine vergleichende Untersuchung von elektrochemischen Sauerstoffsensoren mit Zirkondioxid-Festelektrolyten für Glasschmelzen, die von den Schott Glaswerken und von der HVG entwickelt wurden, berichtet. Trotz ihrer unterschiedlichen Konstruktion ergaben die verschiedenen Sensoren, die in einem Feeder einer Grünglaswanne eingesetzt wurden, geringfügig unterschiedliche, aber reproduzierbare Ergebnisse. Für die Zirkondioxid-Elektroden ergab sich eine Lebenszeit von über einem Jahr bei 1200 °C. Ihre in ausgedehnten Meßzeiten direkt verglichenen Potentiale stimmen innerhalb von 3 mV überein. Der Grund für Potentialdifferenzen der Platin-Meßelektroden waren Temperaturgradienten. Neu installierte Platin-Elektroden zeigen eine „Induktionsperiode", die durch die Equilibrierung von anhängender Oberflächenschmelze und Schmelze am Meßort durch Konvektion und Diffusion verursacht wird. Unerwartete, plötzliche Sauerstoffinhomogenitäten der Schmelzen wurden entdeckt und ihre Ursache aufgeklärt.

1. Introduction

The redox state of oxidic glass melts is significant for several properties of the melts, e.g. refining behaviour, stability of silver- and lead-containing melts, platinum corrosion, and formation of platinum particles, as well as of the glasses produced, e.g. colour, cutting behaviour and brittleness. Its characterization, measurement and control during glass melting are thus of high interest. Since all redox components contained in a melt are in equilibrium with its intrinsic redox system oxygen–oxide [1], the oxygen fugacity[1] can be used to characterize it as long as the "oxygen ion activity" or basicity, is constant, which is approximately the case with most industrial glass melts. The oxygen fugacity can be measured continuously on-line during glass melting. Schott Glaswerke [1 and 2] and the Hüttentechnische Vereinigung der Deutschen Glasindustrie (HVG) [3 and 4] developed p_{O_2}-measuring cells, which have been applied in the laboratory and in industrial glass melting units. The industrial versions of these cells differ according to the different demands of their application. Thus, for optical and special glasses high accuracy of the measured data is mainly emphasized, while for the HVG cells applied in container and flat glass production, where the use of recycled cullet and filter dust with considerably varying redox state must be controlled, easy handling and low cost are of primary concern. The different sensors have been applied in parallel in the feeder channel of a green glass melting unit for several months in order to test their relative performance and accuracy. The main results of this comparative study are reported in this paper.

2. Principle of electrochemical p_{O_2} measurement

2.1 Isothermal measurements

The oxygen fugacity is measured by means of an electrochemical cell consisting of a measuring platinum electrode, Pt(m), immersed in the glass melt and a platinum

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[1] In the literature "oxygen activity" is often used instead of "oxygen fugacity" to indicate that the oxygen content of a condensed phase is detected. According to Henry's Law, which is valid for physically dissolved oxygen in glass melts, the oxygen fugacity is proportional to the oxygen activity.

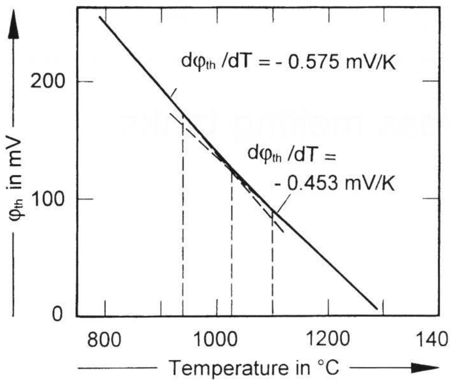


Figure 1. Dependence of relative potentials of a ZrO_2 electrode, with 1 bar oxygen partial pressure, in the nonisothermal green glass melt on temperature showing that the melt exhibits different temperature-independent standard Seebeck coefficients $d\varphi_{th}/dT$ below 940 and above 1100 °C. Reference potential: $\varphi_{th} = 0$ mV at 1300 °C

electrode Pt(r) in an atmosphere with a reference oxygen partial pressure separated from the melt by a solid electrolyte, e.g. yttria-stabilized zirconia, $ZrO_2(Y_2O_3)_n$. The cell is represented by

cell scheme I:

$Pt(r), O_2(r)/ZrO_2/melt, O^{2-}(m), O_2(m)/Pt(m)$

where $O_2(r)$ and $O_2(m)$ are oxygen in the reference electrode compartment and in the melt, respectively, and O^{2-} means free oxygen ion or its equivalent [1] of the melt. The isothermal electromotive force (emf), E, at the temperature T of the cell is given by equation (1)

$$E(T) = \frac{RT}{4F} \ln \frac{p^*_{O_2}(m)}{p_{O_2}(r)} \qquad (1)$$

with $p^*_{O_2}(m)$ = oxygen fugacity of the melt and $p_{O_2}(r)$ = = oxygen partial pressure of the reference gas. Rearrangement of equation (1) yields equation (2) giving the oxygen fugacity of interest,

$$p^*_{O_2}(m) = \exp\left(\frac{4FE(T)}{RT} + \ln p_{O_2}(r)\right) \qquad (2)$$

where R is the gas constant and F the Faraday constant.

2.2 Nonisothermal measurements

Sensors for industrial measurements generally have a reference electrode which is separated from the melt by a zirconia rod merely touching the melt surface [5]. These so-called „dissolving electrodes" are lowered as their lower end is dissolved away by the melt. They have thus a considerably extended lifetime, compared to reference electrodes contained in a zirconia tube with a relatively thin wall, but they yield nonisothermal E values since the reference electrode and glass melt have different temperatures. Such cells with a nonisothermal solid electrolyte are represented by

cell scheme II:

$Pt(r), O_2(r)(T_r)/ZrO_2/(T_r)\,melt, O^{2-}(m), O_2(m)(T_m)/Pt(m)$

and the oxygen fugacity of the melt obtained from these cells at temperature T_m is given by equation (3)

$$p^*_{O_2}(m) = \exp\left(\frac{4F}{RT_m}(E - E_{th,ZrO_2}) + \frac{T_r}{T_m} \ln p_{O_2}(r)\right) \qquad (3)$$

where E_{th,ZrO_2} is the thermoelectric voltage of the zirconia bridge between the reference electrode and the melt. It is obtained from equation (4)

$$E_{th,ZrO_2} = \int_{T_r}^{T_m} \frac{\partial \varphi_{th,ZrO_2}}{\partial T}\,dT = \frac{\partial \varphi_{th,ZrO_2}}{\partial T}(T_m - T_r) \qquad (4)$$

where $(\partial\varphi_{th,ZrO_2}/\partial T)$ is the standard Seebeck coefficient of the zirconia, which is $-(0.4739 \pm 0.0015)$ mV/K for partially stabilized ZrO_2 with 4.53 mol% Y_2O_3 [6] and -0.4505 mV/K for fully stabilized ZrO_2 containing 9.57 mol% Y_2O_3 [1]. An equation for the standard Seebeck coefficient as a function of the yttria content of the ceramic has been given in [1].

For practical and economic reasons oxygen sensors have often spearated measuring and reference electrodes, which introduces the nonisothermal glass melt, in addition to the nonisothermal zirconia bridge, into the measuring cell. The cell, which is thus further complicated, is represented by

cell scheme III:

$Pt(r), O_2(r)\,(T_r)/ZrO_2/(T_c)\,melt, O^{2-}(m), O_2(m)\,(T_m)/Pt(m)$

where T_c is the temperature at the contact of melt and zirconia bridge. The thermoelectric voltage $E_{th,m}$ of the melt is obtained from equation (5)

$$E_{th,ZrO_2} = \int_{T_c}^{T_m} \frac{\partial \varphi_{th,m}}{\partial T}\,dT \qquad (5)$$

where the derivative $(\partial\varphi_{th,m}/\partial T)$ is the standard Seebeck coefficient of the melt as defined in [6] and the fugacity of the melt at T_m as measured by cell scheme III is finally given by equation (6)

$$p^*_{O_2}(m) = \exp\left(\frac{4F}{RT_m}(E - E_{th,ZrO_2} - E_{th,m}) + \frac{T_r}{T_m} \ln p_{O_2}(r)\right). \qquad (6)$$

The standard Seebeck coefficient is a specific property of the melt and, in many cases, is a function of temperature [7]. It can be determined by means of two zirconia reference electrodes, which exclude any influence of temperature-dependent redox potentials [6]. The green glass melt investigated has two temperature ranges with different standard Seebeck coefficients, which are −0.575 mV/K below 940 °C and −0.453 mV/K above 1100 °C, and a transition region between these temperatures [8] (figure 1).

2.3 Mixed potentials exhibited by measuring electrodes

The platinum measuring electrode is normally dipped into the melt through the melt surface and is often contacted by melt parts with different oxygen fugacities. They can, for example, be caused by slowly flowing melt near the surface, which equilibrates with the atmosphere above the melt [4 and 9], by temperature gradients along the platinum electrode, which, particularly if the melt contains polyvalent ions, cause corresponding gradients of the oxygen fugacity, or by melts which are inhomogeneous with respect to the oxygen concentration because of a high load of the melting unit. The parts of the electrode thus contacted by melt with differing oxygen fugacities represent electrodes which are short-circuited by the electrode metal. The measuring electrode consequently exhibits a mixed potential [5]. This disturbing effect, in principle, cannot completely be prevented but can be minimized by kinetic means [1 and 5]. Figure 2 shows the principle by presenting the current density−potential curves of two platinum electrodes with different surface areas, A_s and A_b, where index s means small or surface and index b big or bulk, which are contacted by melt with different oxygen fugacities. The currents, given by the product of current density, i, and surface area, A, which flow through the electrode surfaces on short-circuiting have an equal absolute magnitude, $|i_s A_s| = |i_b A_b|$. The current densities are thus inversely proportional to the surface areas, $|i_s/i_b| = A_b/A_s$, which, according to figure 2, results in a small polarization, $(\varepsilon_m - \varepsilon_b^0)$, of the electrode with the large surface compared to the polarization, $(\varepsilon_s^0 - \varepsilon_m)$, of the electrode with the small surface. For application to the problem at hand the measuring platinum electrode should therefore have a large surface area in the melt range whose oxygen fugacity is to be measured and a relatively small surface area in the other parts of the melt. For an electrode crossing the surface of a slowly flowing melt, it has been found that a surface ratio from 20 to 60 suffices to neglect the difference between the polarized potential and the equilibrium potential to be measured and that, at these ratios, the measured potential represents the equilibrium potential with good approximation [5]. The same conditions apply to electrodes in temperature gradients, such as those installed in a side wall, the bottom, or within the cooling region of a feeder channel.

3. Construction of the sensors and their location in the glass tank

3.1 Oxygen sensor of Schott Glaswerke

The industrial type of sensor developed by Schott Glaswerke has been described in detail elsewhere [1, 2 and 5]. The measuring platinum electrode was a platinum tube with approximately 15 mm diameter internally supported by an Al_2O_3 tube and carrying a platinum flag with approximately (2×25) cm^2 surface area at its lower end. A thermocouple was located in the supporting alumina tube at about the centre level of the platinum flag. Connecting and thermocouple leads were insulated by thin alumina tubes.

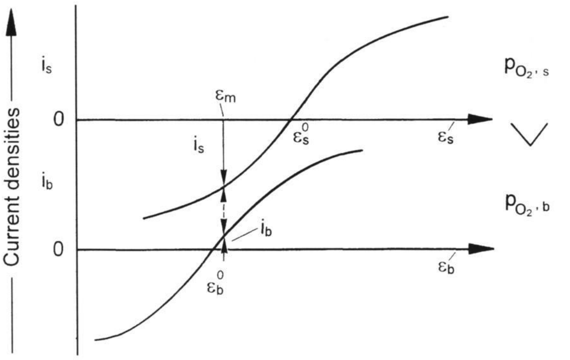


Figure 2. Current density−potential curves of two parts of a platinum measuring electrode immersed in a glass melt, one part near the melt surface, $i_s = f(\varepsilon_s)$, and the other in the bulk of the melt, $i_b = f(\varepsilon_b)$, with different oxygen fugacities, $p_{O_2,s} > p_{O_2,b}$. ε_s^0 and ε_b^0 are respective equilibrium potentials. Short-circuiting results in current densities whose ratio is inversely proportional to the ratio of the surface areas of the electrode parts $|i_s/i_b| = A_b/A_s$, which thus determines the mixed potential ε_m of the electrode relative to the equilibrium potentials of the electrode parts, e.g. $(\varepsilon_s^0 - \varepsilon_m) > (\varepsilon_m - \varepsilon_b^0)$ and $\varepsilon_b^0 \approx \varepsilon_m$ if $A_s/A_b \ll 1$, since the currents through the electrode parts have equal absolute magnitudes. Adjustment of the appropriate relative surface areas of a platinum measuring electrode thus allows to nearly exclude polarization of the measuring electrode part by electrode parts contacting melt volumina which are not of interest.

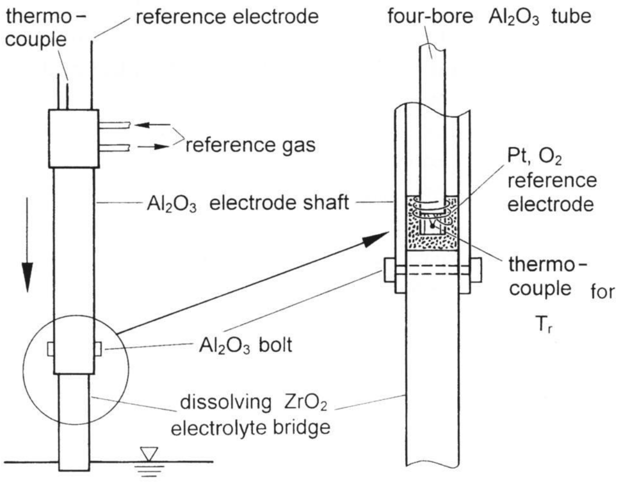


Figure 3. Long lifetime, dissolving zirconia electrode characterized by a ZrO_2 electrolyte bridge between the Pt, O_2 reference electrode and the melt as developed by Schott Glaswerke.

The dissolving zirconia reference electrode is sketched in figure 3. It consisted of a 3 cm outer diameter alumina shaft, which carried the dissolving ZrO_2 electrolyte bridge,

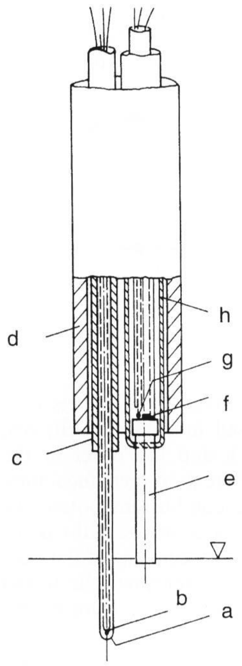


Figure 4. Oxygen sensor based on a dissolving ZrO_2 electrolyte developed by HVG for the use in the forehearth. The sensor consists of: platinum measuring electrode (a), thermocouples (b and g), alumina tubes (c, d and h), yttrium-stabilized zirconia (e), platinum reference electrode flushed with air (f).

the platinum reference electrode, inlet and outlet tubes for the reference gas, and a thermocouple that measured the temperature at the reference electrode. As with the measuring electrode, the unit was closed at the upper end by a specially designed electrode head fabricated from stainless steel. The reference electrode could be lowered according to the dissolution of the zirconia bridge, which, however, was not necessary due to the long lifetime of the material in the green glass melt. Reference gases were 100 % oxygen and "synthetic air", i.e. 20 % oxygen and 80 % argon, which could be chosen according to the experimental requirements. Gases were transported to the Schott reference electrode by means of stainless steel tubing (Swagelock).

In addition to the electrodes, the sensor unit contained a thermocouple, protected from melt and atmosphere by a platinum tube which measured the temperature at the contact of melt and zirconia bridge. The appropriate thermoelectric voltages of the glass melt and of the partially stabilized zirconia were taken into account and had been fed into the evaluating computer programme.

3.2 Oxygen sensor of the HVG

The HVG sensor is presented in figure 4. It is based on the sensors described in [9 and 10] and was developed particularly for the application in container and flat glass factories. Easy handling and reliability of the sensor unit were emphasized. Since the sensor was planned for wide use in the glass industry, the assembly was as simple as possible without affecting its measuring performance. Besides, the sensor was designed for an application in feeder channels, which is the optimum location for measuring the redox state since the melt produced by the melting unit has reached its final state before arriving at the forming machines.

As seen in figure 4, the measuring platinum electrode consists of a rod-like platinum socket which dips into the melt for only several centimetres. As experienced earlier [11] and concluded from the reported application, this does not significantly influence the measured data in flowing glass melts as in feeder channels. This simple shape of the measuring electrode is thus preferred for its better mechanical stability.

As already reported, the particular green glass melt, in which the sensors were applied, has two temperature ranges with different standard Seebeck coefficients, both of which have to be taken into account in order to obtain most accurate measurements. For an application of the HVG oxygen sensor, however, an average of the values for the stabilized zirconia applied and the melt was used; the value was −0.46 mV/K.

3.3 Location of the oxygen sensors in the furnace

The sensors were installed in the feeder channel of the melting tank. Measuring and reference electrodes were positioned in flux direction, and the different sensor units had a distance of approximately 20 cm at the same level with respect to the flux. During most of the time, Schott and HVG sensors were used, and during several more weeks, comparative measurements were carried out on two identical HVG sensors. The temperatures of the measuring and the reference electrodes as well as the electromotive forces of each of the sensors were measured. The temperature of the melt/zirconia contact was measured by the Schott sensor. In addition, contacts to the reference and measuring electrodes of each of the sensors were available and allowed cross measurements and the measurement of the values of E between the different measuring and reference electrodes, respectively.

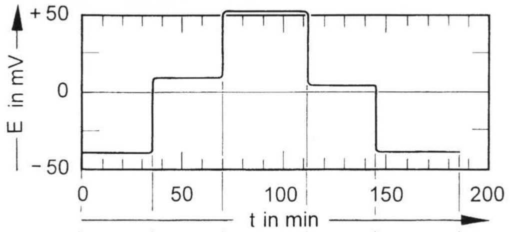
4. Results

4.1 Lifetime of the zirconia reference electrodes

The zirconia reference electrodes of both Schott and HVG sensors were kept in the melt for three months. At the end of this time, only minor corrosion of the fully and the partially stabilized zirconia ceramic which had been in contact with the flowing melt was detectable. In addition, no time-dependent adverse influence of the extended measuring time on the measured E values could be detected, which was shown by installing new sensors at the end of the test. A lifetime of the dissolving zirconia reference electrodes of at least one year can thus be expected at temperatures between 1100 and 1200 °C. However, it is noted that, according to experience with different types of melt at Schott Glaswerke, the lifetime of zirconia bridges can be considerably shorter. Melts with high lead content are typical examples. The short lifetime of the ceramic can, at least in part, be compensated by the initial length of the zirconia bridges.

4.2 Electrochemical performance of the zirconia reference electrodes

The potential differences of the zirconia reference electrodes of Schott Glaswerke and HVG were directly measured, while the reference gases were repeatedly changed from oxygen to synthetic air and back with the Schott sensor and from oxygen to air and back with the HVG sensor. Figure 5 gives a typical example. The thermoelectric voltages due to the slightly different temperatures of the electrodes were calculated by means of the appropriate Seebeck coefficients and were taken into account. As shown by the values in figure 5, the potential difference is below 1.1 mV, except when the HVG reference electrode was operated with 100 % oxygen. This effect was traced back to the reference gas, which was introduced into the sensor unit by means of rather long PVC tubing. This material is not well-suited for this purpose, especially when it gets slightly warm, which is unavoidable under the given circumstances. The permeation of gases through the tube wall results in a final oxygen content of the slowly flowing reference gas of 91 and 97 %, as was found in separate measurements. The HVG sensor should thus be applied with air as the reference gas causing zero oxygen concentration difference, which is the most economic solution of the problem, or the tubing should be changed to stainless steel as used with Schott sensors.



HVG, 1118 °C	air	air	O_2	O_2	air
Schott, 1132 °C	O_2	s.air	s.air	O_2	O_2
$E = (\varphi_{HVG} - \varphi_{Schott})$ in mV	-39	+8	+52	+4	-39
$E_{theoretical}$ in mV	-40.1	+8.6	+55.4	+6.6	-40.1

Figure 5. Plot of the potential difference between the zirconia reference electrodes of HVG and Schott Glaswerke during their concurrent application in the feeder of the glass tank. The reference gases of the electrodes were changed between oxygen and air (21 % O_2, 79 % N_2, HVG) and between oxygen and synthetic air (20 % O_2, 80 % Ar, Schott) and back. The maximum potential difference of 1.1 mV (see text) between the electrodes reflects the agreement of the measured data.

4.3 Comparative measurements with Schott and HVG oxygen sensors

Figure 6 presents the oxygen fugacity of the green glass melt as measured by both the Schott and the HVG sensors over a period of 34 d. As expected from the reducing character of the melt, the values are rather low, i.e. between $4 \cdot 10^{-4}$ and $7 \cdot 10^{-3}$ bar as measured by the Schott sensor and between $2 \cdot 10^{-4}$ and $3.5 \cdot 10^{-3}$ bar according to the HVG sensor. The constant difference of the logarithms of the oxygen fugacities over these ranges (figure 6) indicates that the deviation is caused by different actual temperatures of the measuring electrodes, which could indeed be verified. As sketched in the right section of figure 7, the platinum flag of the Schott sensor mainly measuring the oxygen fugacity is at an average level of 8 cm below the melt surface, while the HVG measuring electrode dips only 3 to 4 cm into the melt, and the left part of figure 7 shows the vertical temperature profiles of the melt at the measuring location in the feeder channel measured on two different days. Due to the cooling of the flowing melt in this feeder section, the temperatures at the two measuring electrodes are rather different, the temperature of the Schott electrode being about 70 K higher than that at the HVG measuring electrode. Adjusting the oxygen fugacities indicated by the HVG sensor to 1250 °C by means of the assumed constant Seebeck coefficient indeed shifts the corresponding logarithmic plot, as seen in figure 8, so that the lg(oxygen fugacity) – time curves are on the same level and show very much the same contours. Incidentally, the temperature profile in the range of the actual measuring part, i.e. the platinum flag, of the Schott measuring electrode shows that it can be nearly impossible to measure the exact mean temperature of an electrode part that extends over several centimetres if the temperature profile deviates significantly from linearity (figure 7). A small extension of this electrode range can considerably reduce, and the measurement of the temperature profile of the melt can nearly eliminate this effect, which, however, is not normally observed since oxygen sensors are not necessarily located in a tank region where the melt is subject to strong cooling.

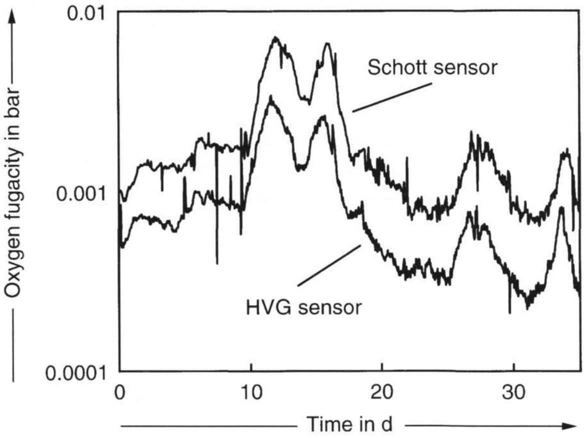


Figure 6. Oxygen fugacity of the green glass melt as measured by the different oxygen sensors during a period of 34 d. The constant difference of the logarithm of the oxygen fugacity was traced back to different temperatures of the platinum measuring electrodes (see figure 7).

4.4 Detection of an inhomogeneous oxygen content of the melt

Figure 9 presents the time-dependent electromotive forces measured by two HVG sensors which were located 20 cm

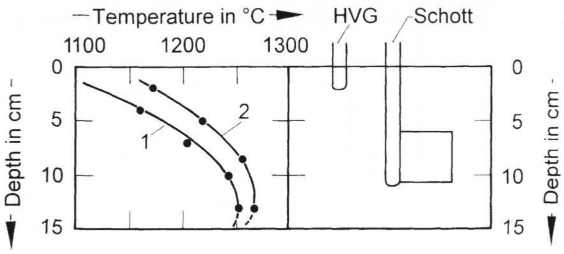


Figure 7. Vertical temperature profiles of the melt at two different days (curve 1 was measured 3 d before curve 2) and shape and location of the platinum measuring electrodes of HVG and Schott Glaswerke in the feeder of the green glass tank explaining the constant difference of the logarithm of the oxygen fugacities measured by the different sensors (see figure 6).

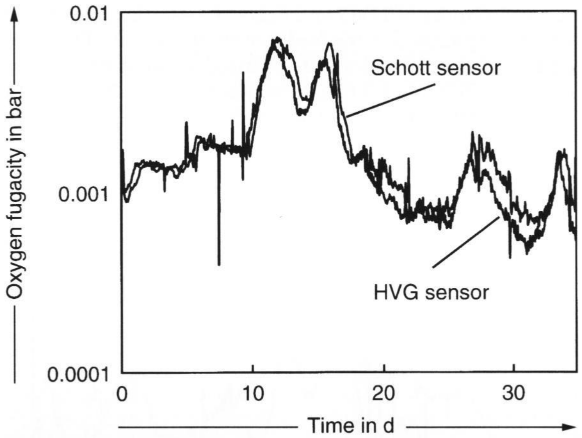


Figure 8. Oxygen fugacity−time plots as presented in figure 6 after adjustment of the data measured by the HVG sensor to 1250 °C (see figure 7), demonstrating equal oxygen fugacities and time dependencies measured by the HVG and Schott sensors.

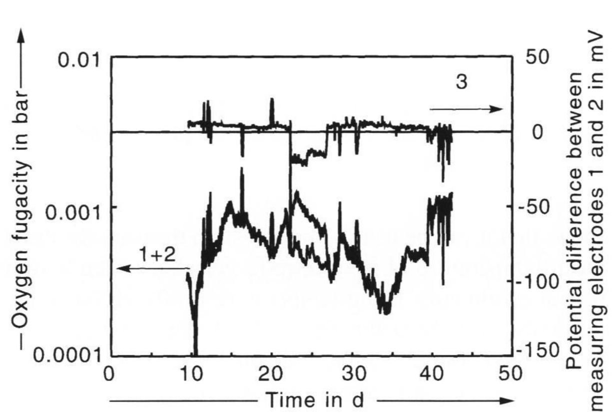


Figure 9. Oxygen fugacities as measured by two HVG sensors 20 cm apart perpendicular to the streaming direction of flow (plots 1 and 2, left ordinate) and potential difference between the platinum electrodes of the sensors (plot 3, right ordinate) during a 34 d measuring period. The different electromotive forces between the 22nd and the 27th day were caused by different local oxygen fugacities of the melt. For further explanation, see text.

apart, plots 1 and 2, and also shows the potential difference between the two platinum electrodes, plot 3. Surprisingly, the sensors exhibit different E values during the period from the 22nd until the 27th day, the difference being caused by the measuring electrodes, and thus obviously by different oxygen fugacities of the melt, as indicated by the potential difference of the measuring electrodes during this time, plot 3. The effect is explained by the particular construction of the feeder channel containing the sensors. Since this channel is rather short for spatial reasons, the temperature of the working chamber is held low in order to reach the working temperature of the glass within the channel length. Thus, large temperature differences occur between the main glass flow and near the channel wall. This causes rather high viscosities of some parts of the melt in the working chamber, especially near the entrance of the melt into the feeder channel, and due to the hindered exchange with less viscous melt, and thus creates elements of the melt which do not reach the feeder channel during a low-load period. When the load is increased after this period, these parts of the melt are warmed up due to the increased heat flow and reach the feeder channel as cords, whose oxygen fugacity, which obviously differs from that of the surrounding melt, is measured by one of the electrodes relative to the other. Figure 9 shows that the potentials of the measuring electrodes return to an equal magnitude after this "clearing period". This effect of inhomogeneous oxygen fugacity was always observed after a change of the load. The observation demonstrates a fundamental problem of the application of oxygen sensors in glass tanks, i.e. the choice of an optimum location of the electrodes where the melt is in a representative state. On the other hand, inhomogeneities are a specific property of the particular glass melt, which may also be of interest.

4.5 Effect of the feeder atmosphere

It has often been observed in laboratory and industrial applications that new sensors, when first installed, show considerable drifts of their electromotive force towards smaller values for an initial "induction period". This effect was studied by means of two HVG sensors located in the feeder channel. After some weeks of parallel operation, during which nearly identical E values were measured, one of the sensors was withdrawn from the melt, kept in the feeder atmosphere for 12 h, then reinserted into the melt, where the other sensor had remained during that period. Figure 10 shows the development of the electromotive force of the sensor after its return into the melt, plot 1, and the constant E value of the sensor that had not been removed from the melt, plot 2. The effect is clearly caused by the platinum measuring electrode that had been removed from the melt, which is demonstrated by the difference of the platinum electrode potentials (figure 10), plot 3. The potential shift corresponds to a decreasing oxygen fugacity after the return of the sensor into the melt and is obviously caused by a slow removal of the oxygen which this electrode had gained during its presence in the feeder atmosphere, with which the platinum and the adhering melt had

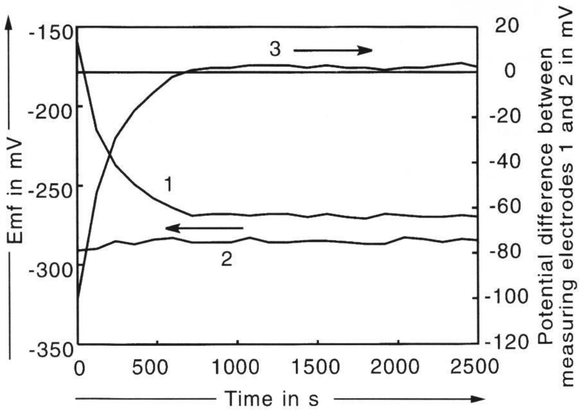


Figure 10. Development with time of the *E* values of (plot 1) a HVG sensor after 12 h of removal from, and subsequent reimmersion into, the melt and (plot 2) of a sensor that had remained in the melt (both left ordinate). The time-dependent potential difference of the platinum electrodes of the sensors (plot 3, right ordinate) indicates that the change of the *E* values (plot 1) caused by the "rinsing" or "equilibration effect" that establishes equilibrium of the melt around and with the platinum electrode of the sensor. The electromotive forces of plots 1 and 2 include also thermally induced voltages within the sensors.

equilibrated. The "rinsing effect" lasted approximately 15 min (figure 10). However, its duration depends on the viscosity of the melt and can be considerably longer in more viscous melts. The effect should, therefore, always be considered as a possible cause when newly installed sensors show inconstant values of *E*.

5. Summary

Electrochemical oxygen sensors employing reference electrodes with solid zirconia electrolytes and developed by Schott Glaswerke and by the HVG, were installed in the feeder channel of a glass tank producing green glass. It is shown that the oxygen fugacity of the melt can be measured reproducibly by both types of sensor despite their different construction. The platinum electrode of such sensors must be specially designed in order to avoid the formation of mixed potentials, which can be caused by temperature gradients and by melt inhomogeneities along the electrode metal contacting the melt. An inital "induction period" of melt- and temperature-dependent duration, during which the platinum measuring electrodes show potential drifts caused by their equilibration with the oxygen content of the melts, must be observed after new sensors have been installed.

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