

Electrochemical cells for on-line measurements of oxygen fugacities in glass-forming melts¹⁾

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Electrochemical cells for the on-line measurement of oxygen fugacities in oxidic glass-forming melts employing yttria-doped zirconia have been developed for both laboratory and technical application. The basic electrochemistry and the different modes of construction are explained, and two applications are reported, first, the study of redox fining and second, the determination of standard Seebeck coefficients of melts by means of two ZrO₂ reference electrodes.

Elektrochemische Zellen für die kontinuierliche Messung der Sauerstoff-Fugazität in Glasschmelzen

Elektrochemische Zellen für die kontinuierliche Messung von Sauerstoff-Fugazitäten in oxidischen Glasschmelzen auf der Basis von yttriumoxidstabilisiertem Zirkondioxid wurden für die Verwendung im Labor und in technischen Glasschmelzwannen entwickelt. Die zugrunde liegende Elektrochemie und verschiedene Konstruktionen werden erläutert. Außerdem wird über zwei Anwendungen berichtet, erstens über die Untersuchung der Redoxläuterung und zweitens über die Bestimmung des Standard-Seebeck-Koeffizienten von oxidischen Glasschmelzen unter Verwendung von zwei ZrO₂-Bezugselektroden.

1. Introduction

Oxidic glass-forming melts are distinguished by the intrinsic redox system oxygen/"oxide",

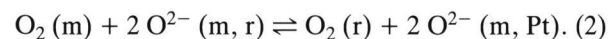


in which "oxide", O²⁻, symbolizes any negatively charged oxygen, e.g. oxide ions (if present) or oxidic anions containing terminals, as ≡Si-O⁻. Being inseparably connected with the melts, this redox system forms equilibria with all other redox systems present and is responsible for the fining process, the melt stability, the optical properties of the glasses produced, and the corrosion of metallic parts of melters and tanks.

Since the "oxide" activity is approximately independent of the oxygen content in most industrially



m and r refer to melt and reference electrode, respectively; | stands for the interface between different phases. Since the ceramic has unit transport number for oxide ions, the arrangement is a cell without transference, and the cell reaction is represented by equation (2),



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produced glass melts due to their small contents of polyvalent ions, equation (1) and the redox state of these melts are characterized by the oxygen fugacity $\bar{p}_{\text{O}_2}^*$, whose knowledge is thus of fundamental interest for glass making. Therefore, electrochemical cells for the on-line measurement of oxygen fugacities in glass-forming melts were developed for both laboratory and technical application [1]. This paper reports on the electrochemistry of the cells and the electrode construction and gives two examples for their application.

2. Electrochemistry of the cells

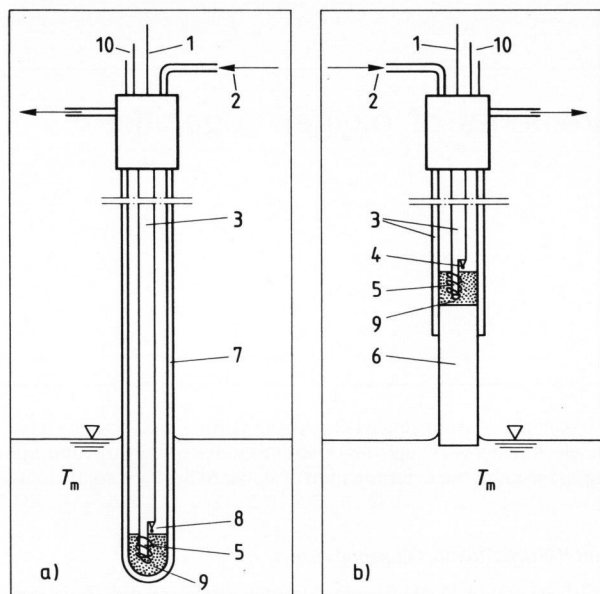
The cells consist of a Pt measuring and a Pt, O₂ reference electrode with defined oxygen partial pressure, which is separated from the melt by yttria-doped zirconia,

The isothermal electromotive force (emf) E of a cell with homogeneous melt is thus given by the oxygen partial pressure of the reference gas, $p_{\text{O}_2(\text{r})}$, and the oxygen fugacity of the melt, $\bar{p}_{\text{O}_2(\text{m})}^*$,

$$E = (R T / 4 F) \ln (\bar{p}_{\text{O}_2(\text{m})}^* / p_{\text{O}_2(\text{r})}), \quad (3)$$

where R = gas constant, F = Faraday constant, and T = temperature, if an identical standard state of oxygen is chosen, and the unknown oxygen fugacity is obtained from equation (4),

$$\bar{p}_{\text{O}_2(\text{m})}^* = \exp (4 F E / R T + \ln p_{\text{O}_2(\text{r})}). \quad (4)$$



Figures 1a and b. Zirconia reference electrodes for glass-forming melts, a) zirconia tube electrode; b) dissolving zirconia electrode. 1: lead wires, 2: reference oxygen, 3: Al_2O_3 tubes, 4: thermocouple T_r , 5: Pt, O_2 electrode, 6: electrolytic ZrO_2 bridge, 7: ZrO_2 tube, 8: thermocouple $T_r = T_m$, 9: ZrO_2 grit, 10: thermocouple.

The cells function reversibly down to at least 10^{-11} bar oxygen.

Equation (3) is also the basis for testing the reference electrodes for proper functioning without removal from the melts since defined alterations of the reference oxygen partial pressure result in corresponding changes of E [1]. Simultaneous slow changes of the measured oxygen fugacity do not interfere because of the fast electrode response (< 20 s).

$$p_{\text{O}_2(m)}^* = \exp \left[4 F E / R T_m + (T_r / T_m) \ln p_{\text{O}_2(r)} - (4 F / R T_m) \int_{T_r}^{T_m} (dE_{\text{Th}} / d(\Delta T)) dT \right], \quad (5)$$

where E = measured emf, E_{Th} = thermoelectric voltage of the zirconia ceramic. The standard Seebeck coefficient, $dE_{\text{Th}}/d(\Delta T)$, of yttria-doped zirconia measured in separate experiments was found to be independent of temperature and temperature gradient but dependent on the yttria content of the ceramic. Consequently,

$$\int_{T_r}^{T_m} (dE_{\text{Th}} / d(\Delta T)) = (dE_{\text{Th}} / d(\Delta T)) (T_m - T_r), \quad (6)$$

where, e.g. for $(\text{ZrO}_2)_{0.954} \cdot (\text{Y}_2\text{O}_3)_{0.046}$ usually applied,

$$(dE_{\text{Th}} / d(\Delta T)) = (-0.4739 \pm 0.0015) \text{ mV K}^{-1} [1].$$

Under identical conditions, dissolving zirconia electrodes can reach life-times 50 to 100 times as long as those of zirconia tube electrodes. Besides, arrange-

3. Modes of electrode construction

3.1. ZrO_2 reference electrodes

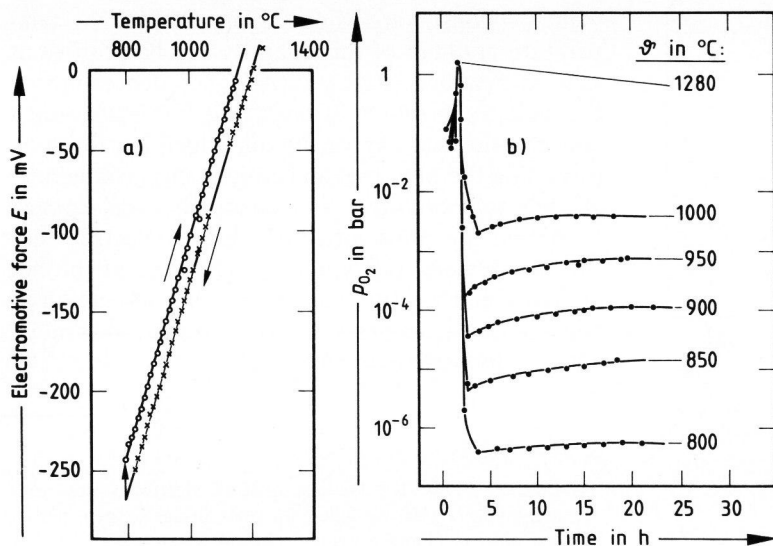
Different kinds of zirconia reference electrodes have been constructed [1 to 3], see also [4]. Figure 1a shows a zirconia tube electrode originally proposed by Plumat [5] and Besson [6]. An yttria-doped zirconia tube immersed in the melt contains the Pt, O_2 electrode and a thermocouple insulated by a four bore-alumina tube, through which also the reference gas is introduced. This construction is most accurate because of the truly isothermal arrangement of the vital electrode parts. It is, however, sensitive to thermal shock and has a limited life-time due to corrosion of the thin zirconia wall. The zirconia tube electrode is thus ideally suited for research and development and is applied for laboratory measurements.

Figure 1b presents a "dissolving zirconia electrode", which was developed for technical melters [1, 7 and 8]. A zirconia bridge connects the Pt, O_2 electrode and the melt. The arrangement is continuously lowered as the bridge is slowly dissolved away by the melt. It is particularly suited for application in streaming melts since dissolved zirconia is continuously removed thus eliminating errors caused by changes of melt composition and by diffusion potentials. Since, however, the temperatures of Pt, O_2 electrode and melt differ usually, cells employing these electrodes are nonisothermal cells whose emf must be corrected for the thermoelectric voltage of the zirconia bridge. Correspondingly, the oxygen fugacity of the melt is obtained from [1]

ments with an alumina electrode shaft as in figure 1b eliminate the costly zirconia tube [8]. Dissolving zirconia electrodes are thus both economical and ideally suited for technical service.

3.2. Platinum measuring electrodes

Although the construction of the Pt measuring electrodes does not present any basic problems, it must be considered that it is contacted by parts of the melt with different oxygen fugacities. Since an insulation of the metal is impossible because of the lack of inert materials, the platinum electrode in itself forms a short-circuited gas concentration cell whose mixed potential is measured. This deficiency can be overcome by electrode kinetics [1] in that a large surface area of the platinum is employed at the depth of interest and a small surface area in other parts, e.g. the surface ranges of the melt. The small current densities through the large electrode areas of interest



Figures 2a and b. Temperature-dependent redox equilibria in oxidic glass-forming melts, a) dynamic measurement of $E(T)$ of cell I (Pt, O_2 reference electrode ($p_{O_2} = 1$ bar) | ZrO_2 | melt | Pt; melt = sodium borate; fining agent: Sb_2O_3 ; $dT/dt = 450$ K h^{-1} ; $dE/dT = 0.63$ mV K^{-1}); b) oxygen partial pressure of a melt as a function of time and temperature during melting. Fining agent: 0.3 wt% As_2O_3 ; fining conditions: 1280 °C, 30 min.

and the large current densities through the small deteriorating surface areas of the electrode, which are thus created, result in a small polarization of the potential of interest. The mixed potential of the electrode can thus be made almost equal to the equilibrium potential to be measured if a ratio of the different surface areas of 20 to 60 is chosen.

4. Application

4.1. Temperature dependence of oxygen fugacity; redox fining

An important redox equilibrium is the combination of the intrinsic redox system (equation (1)) and the redox system of a polyvalent ion, e.g.



The temperature-dependent equilibrium constant,

$$K(T) = a_{As_2O_3} p_{O_2(m)}^* / a_{As_2O_5} \quad (8)$$

is the basis for redox fining, i.e. the removal of gaseous impurities. Redox fining is initiated by oxygen nuclei and bubbles created by shifting the equilibrium (equation (7)) to the right at high temperatures. The undesired gases diffuse into the oxygen bubbles and increase their volume and buoyancy. After their removal, the temperature is decreased in order to redissolve remaining bubbles of

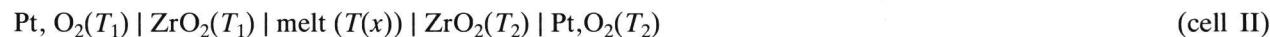
pure oxygen by shifting the equilibrium (equation (7)) to the left.

Figure 2a shows the emf of cell I in a melt containing Sb^{3+}/Sb^{5+} as a function of temperature [1]. The emf, $E = -275$ mV, reached at 800 °C after cooling the melt corresponds to an oxygen fugacity of $7 \cdot 10^{-6}$ bar, which slowly increases under constant conditions because of oxygen diffusion from the atmosphere into the melt. On raising the temperature again, the emf increases and indicates an oxygen fugacity of 1 bar at 1150 °C, above which spontaneous formation of bubbles is observed. The linear function $E(T)$ with $dE/dT \approx 0.6$ mV K^{-1} at constant total oxygen contents could be explained by thermodynamics [1].

As a typical application, figure 2b demonstrates short-time fining with As^{5+}/As^{3+} . After melting the raw materials, fining is conducted at 1280 °C for 30 min. The remaining oxygen bubbles are subsequently redissolved at five different, lower temperatures, the dissolution rates corresponding to the different diffusion coefficients of oxygen.

4.2. Measurement of standard Seebeck coefficients of glass melts

Zirconia reference electrodes are ideally suited for the measurement of thermoelectric voltages of glass-forming melts since their potential is independent of any redox systems present. The nonisothermal cell II



was applied whose thermoelectric emf,

$$E_{ZrO_2\Delta T} = (R T_2/4 F) \ln p_{O_2(r)}(T_2) - (R T_1/4 F) \ln p_{O_2(r)}(T_1) + E_{Th} \quad (9)$$

contains the term

$$E_{Th} = \varepsilon^0(T_2) - \varepsilon^0(T_1) + (R T_1/2 F) \ln a_{O_2-(m)}(T_1) - (R T_2/2 F) \ln a_{O_2-(m)}(T_2) + \Delta\varepsilon_{Pt}(T_2, T_1) + \varepsilon_m(T_1, T_2) \quad (10)$$

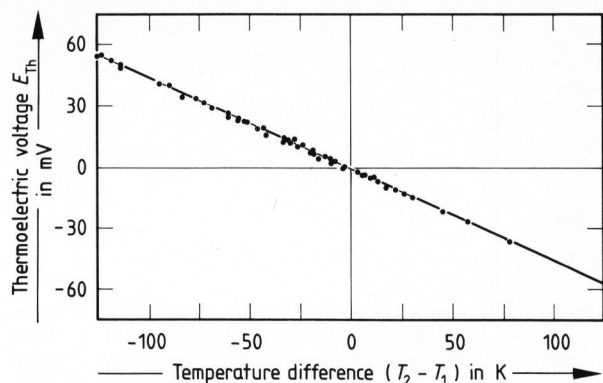


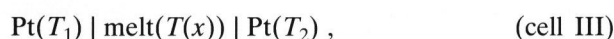
Figure 3. Standard thermoelectric emf, E_{Th} , of the nonisothermal cell II with two ZrO_2 electrodes as a function of temperature difference. Standard Seebeck coefficient: $dE_{Th}/d(\Delta T) = (-0.448 \pm 0.006) \text{ mV K}^{-1}$.

which was defined standard thermoelectric emf [9]. ($\varepsilon^0(T_1)$ and $\varepsilon^0(T_2)$ = standard potentials, $\Delta\varepsilon_{Pt}(T_2, T_1)$ = thermoelectric voltage in the Pt leads and $\varepsilon_m(T_1, T_2)$ = thermoelectric diffusion voltage of the melt, at the respective temperatures). Its derivative with respect to the temperature difference, ($dE_{Th}/d(\Delta T)$), was defined standard Seebeck coefficient [9].

Figure 3 shows an example. The standard Seebeck coefficient of this melt (composition (in mol%): 15.5 Na_2O , 10.8 CaO , 73.7 SiO_2) is

$$dE_{Th}/d(\Delta T) = (-0.448 \pm 0.006) \text{ mV K}^{-1}$$

and was found to be independent of temperature and temperature difference, at least in the temperature range 900 to 1500 °C. Its knowledge allows the determination of thermoelectric voltages also of nonisothermal cells with two Pt electrodes,



if isothermal emfs of cell I, i.e. of



with $T = \text{const.}$, are known. Surprisingly, the temperature gradient of this quantity can be positive as well as negative, $dE_{Pt, \Delta T}/d(\Delta T) \geq 0$, depending on the melt composition. It must thus be distinguished between thermal oxygen reboil, which is caused by exceeding the physical or chemical oxygen solubility at high temperatures, and electrochemical oxygen formation by short-circuiting thermoelectric cells with two Pt electrodes, which can occur at the hot or cold electrode [9]. This finding has direct consequences for the analysis of bubble formation at metal parts of industrial furnaces.

5. References

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