Original Paper

Voltammetric studies in a soda–lime–silica glass melt containing two different polyvalent ions[1])

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By the aid of electrochemical methods, a quantitative determination of polyvalent ions in glass melts is possible. This paper investigates the square-wave voltammetry in soda–lime–silica glass melts doped with iron and additionally with arsenic or antimony. In principle, a simultaneous, quantitative determination of these elements is possible, but the experimental parameters should be chosen with care and the recorded current-potential curves should be carefully analyzed.

Voltammetrische Untersuchungen an einer zwei verschiedene polyvalente Ionen enthaltenden Kalk–Natronsilicatglasschmelze

Mit Hilfe elektrochemischer Methoden können polyvalente Elemente in Glasschmelzen quantitativ bestimmt werden. Die vorliegende Arbeit beschäftigt sich mit der Square-Wave-Voltammetrie von Kalk–Natronsilicatglasschmelzen, die neben Eisen zusätzlich noch Arsen oder Antimon enthalten. Die quantitative Simultanbestimmung dieser Elemente bei Glasschmelztemperaturen ist zwar prinzipiell möglich, doch erfordert die Auswahl der experimentellen Parameter einige Sorgfalt ebenso wie die Auswertung der Meßkurven.

1. Introduction

The oxidation state of a glass melt influences many physical properties of the final glass product. This oxidation state is determined by the type and amount of the polyvalent ions and the oxygen activity of the glass melt. For many years, it has been possible to measure the oxygen activity by sensors, based on oxygen ion-conducting solid electrolytes (mainly CaO- or Y_2O_3-stabilized zirconia) [1 and 2]. These sensors can also be used to continuously determine the oxygen activity during technical melting of glass.

For a complete description and control of the oxidation state, it is necessary to know the concentration of the polyvalent ions. It is already possible to determine a multivalent ion quantitatively by voltammetric methods [3]. But up to now, all voltammetric investigations were carried out in glass melts containing only one type of polyvalent element [3 to 7]. In technical glass melting, however, more than one type of multivalent elements is often present. Besides iron oxide, present in the most technical glass melts, refining agents like arsenic oxide or antimony oxide are widely used. This paper provides a study of glasses, doped with iron oxide and additionally with arsenic oxide or antimony oxide.

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2. Theory

The redox behavior is usually described by the equilibrium constant of the redox reaction, according to equation (1):

$$Me^{(x+n)+} + n/2\,O^{2-} \rightleftharpoons n/4\,O_2 + Me^{x+} \qquad (1)$$

where n is the number of electrons transferred, and O_2 is the physically dissolved oxygen.

The equilibrium constant $K(T)$ can be measured by equilibrating the glass melt with an atmosphere of well-defined oxygen partial pressure, quenching the sample and analyzing the cooled glass physically or chemically. But the equilibrium constants can also be calculated by the help of equation (2) from the normal potentials E_0 of the redox pairs which can be measured by electrochemical methods.

$$\Delta G^0(T) = -\,n\,F\,E_0(T) = -\,R\,T \ln K(T) \qquad (2)$$

with $\Delta G^0(T)$ = standard free enthalpy; the other symbols have the usual meaning.

One of these methods for determining the normal potentials of a redox pair is the Square-Wave Voltammetry (SWV). This method has already been applied to glass melts [3, 8 and 9] and has been proven to have higher sensitivity and resolution than the most commonly used Cyclic Voltammetry (CV) [8 and 9]. SWV is a potentiodynamic method, which has already been described in detail elsewhere [4, 5, 8 and 9]. The applied potential is a staircase ramp, superimposed by a rectangular wave of comparably high frequency ($f = 5$ to $500\ s^{-1}$) and amplitude (at

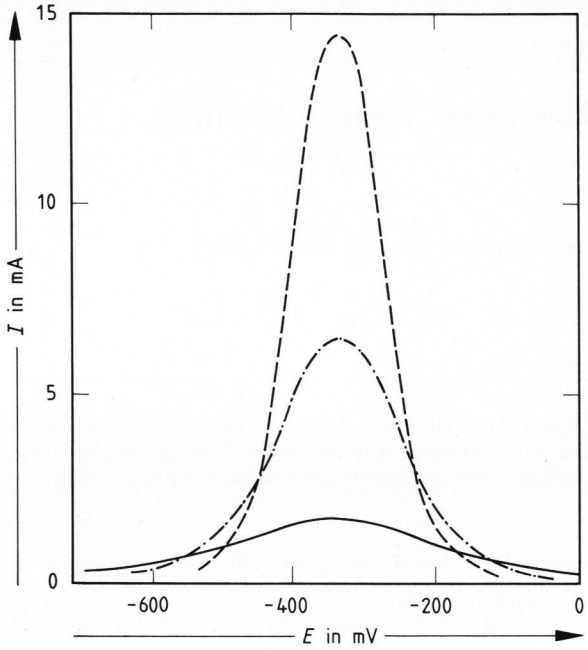


Figure 1. Theoretical Square-Wave Voltammograms (SWV) for a one- (———), a two- (– · – · –) and a three- (– – –) electron step at 1100 °C. $D = 10^{-7}$ cm²/s, $\Delta E = 100$ mV, $\tau = 10$ ms, $C_0 = 1$ mol%, $A = 10$ mm².

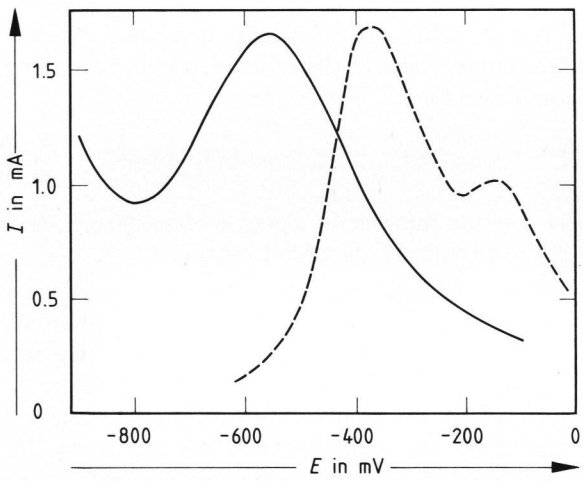


Figure 2. SWV of a soda-lime-silica glass melt, measured at 1150 °C and doped with 1 mol% Fe_2O_3 (———) and 1 mol% As_2O_5 (– – –). $\tau = 2$ ms, $\Delta E = 50$ mV.

1000 °C: $\Delta E = 50$ to 250 mV). The current is measured at the end of every half-wave and then differentiated [4 and 5]. In the presence of polyvalent ions characteristic peaks are visible in the SWV.

A theoretical current-potential curve for a one-, a two- and a three-electron step is shown in figure 1. It is actually only valid if educt and product are dissolved. The half-width of the peak ($E_{p/2}$) is given in equation (3); it decreases if more than one polyvalent ion is transferred:

$$E_{p/2} = T \cdot b / n \tag{3}$$

where $b = 0.30$ mV/K. The peak current I_p is proportional to the bulk concentration C_0 and depends on the diffusion coefficient D of the polyvalent ion and the number of electrons transferred:

$$I_p = C_0 D^{1/2} n^2 \tau^{-1/2} \cdot \text{const} \tag{4}$$

with τ = pulse time; for a small pulse amplitude ΔE: const $= 0.17\, A\, F^2\, \Delta E / R\, T$ (A = surface area of the electrode). The peak potential equals the thermodynamic normal potential E_0.

If more than one multivalent element is present, the current-potential curve can be described by the superposition of two or more current-potential curves. It should be remarked that this is only valid when the concentrations of the polyvalent ions are not too high and there are no complexes, like M–O–M′ (M, M′: polyvalent ions), which greatly influence the thermodynamics.

3. Experimental

The experiments were carried out in a resistance-heated furnace with a vertical alumina muffle tube. A platinum crucible with the glass melt was located in the middle of the tube. The electrodes were inserted from the top and dipped into the glass melt. The working electrode consists of a platinum wire. The counter electrode is a platinum plate with a size of around 2 cm², and the reference electrode is a zirconia probe [1 and 2]. All mentioned potentials in this paper are referenced to the zirconia/air electrode.

The electronics were self-constructed. The main part is a potentiostat, connected to a microcomputer via a digital/analog and an analog/digital converter. The experimental equipment has already been described in detail [3 and 8]. Starting from a potential of 0 V, the applied potential was shifted cathodically at all voltammetric measurements.

All experiments were carried out in a model glass melt with the basic composition (in mol%) of 74 SiO_2, 16 Na_2O and 10 CaO, which was modified by adding oxides of iron, arsenic and antimony.

4. Results and discussion

Figure 2 shows square-wave voltammograms ($\tau = 2$ ms; $\Delta E = 50$ mV), measured at 1150 °C in a glass melt, doped with 1 mol% Fe_2O_3, and in a glass melt, doped with 1 mol% As_2O_5. The Fe^{3+} ion is reduced in a one-electron step to the Fe^{2+} ion.

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} . \tag{5}$$

The potential of the Fe^{2+}/Fe^{3+} peak equals to −550 mV. The iron peak is quite broad, as expected for a one-electron step (compare figure 1).

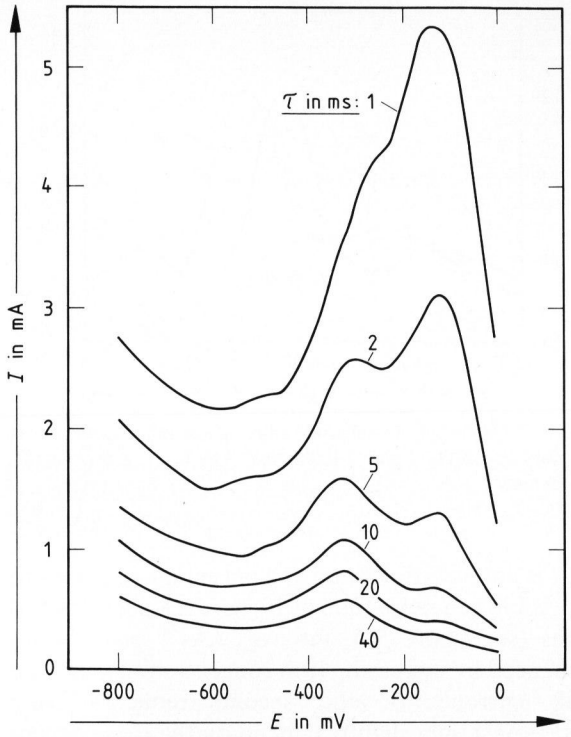


Figure 3. SWV of a soda–lime–silica glass melt, doped with 0.2 mol% As_2O_5 and 0.05 mol% Fe_2O_3 at 1200 °C. $\Delta E = 75$ mV, $A \approx 10\ mm^2$, $\tau = 1, 2, 5, 10, 20, 40$ ms.

The As^{5+} ion is reduced in a two-electron step to the As^{3+} ion and at further negative potentials in a three-electron step to metallic arsenic (As^0).

$$As^{5+} \xrightleftharpoons{2\,e^-} As^{3+} \xrightleftharpoons{3\,e^-} As^0 . \qquad (6)$$

The peak potential of the As^{5+}/As^{3+} step at 1150 °C is equal to −130 mV and that of the As^{3+}/As^0 step to −370 mV. The peaks are not so broad as the peak for the Fe^{3+}/Fe^{2+} reduction step. The shape of the SWV in the case of glass melts doped with iron is nearly independent of the experimental conditions (τ, ΔE).

For glass melts doped with As_2O_5, however, the shape is strongly influenced by the pulse time τ. Figure 3 illustrates this behavior for a glass, doped with 0.2 mol% As_2O_5 and 0.05 mol% Fe_2O_3. The small amount of iron has only little influence on the shape of the curves; only a small increase of the current can be observed in the potential region at about −500 to −550 mV. At relatively high pulse times in the range of 10 to 20 ms, the shapes of the curves are nearly the same and the ratio of the peak currents of the As^{5+}/As^{3+} and the As^{3+}/As^0 step are about 4:9 as predicted by theory (see equation (4)). At shorter pulse times, the shape of the SWVs changes. The peak current of the As^{5+}/As^{3+} step increases relatively to the peak currents of the As^{3+}/As^0 step with decreasing pulse time. At a pulse time of 2 ms, the As^{5+}/As^{3+} peak is already higher than the As^{3+}/As^0 peak. At a pulse time of 1 ms, the

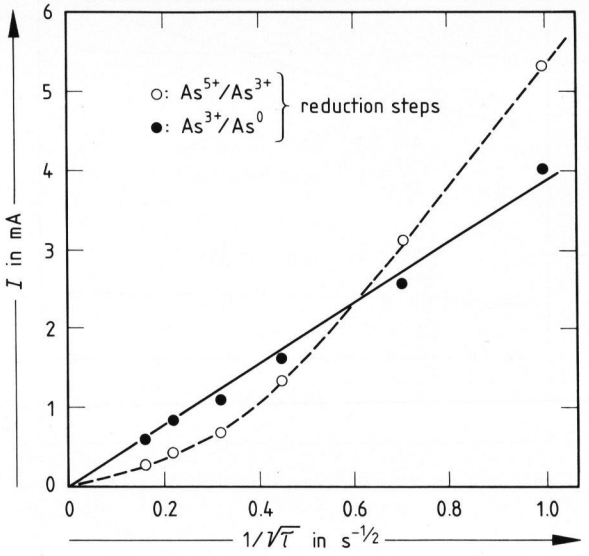
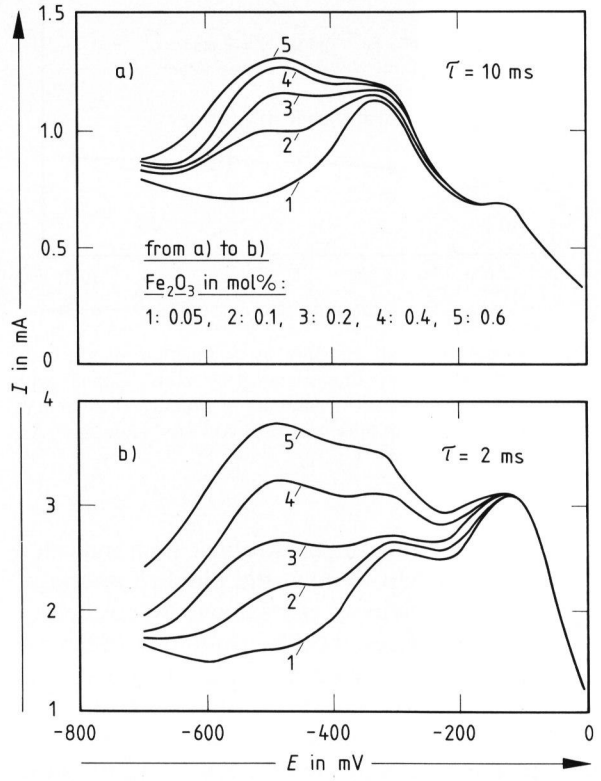
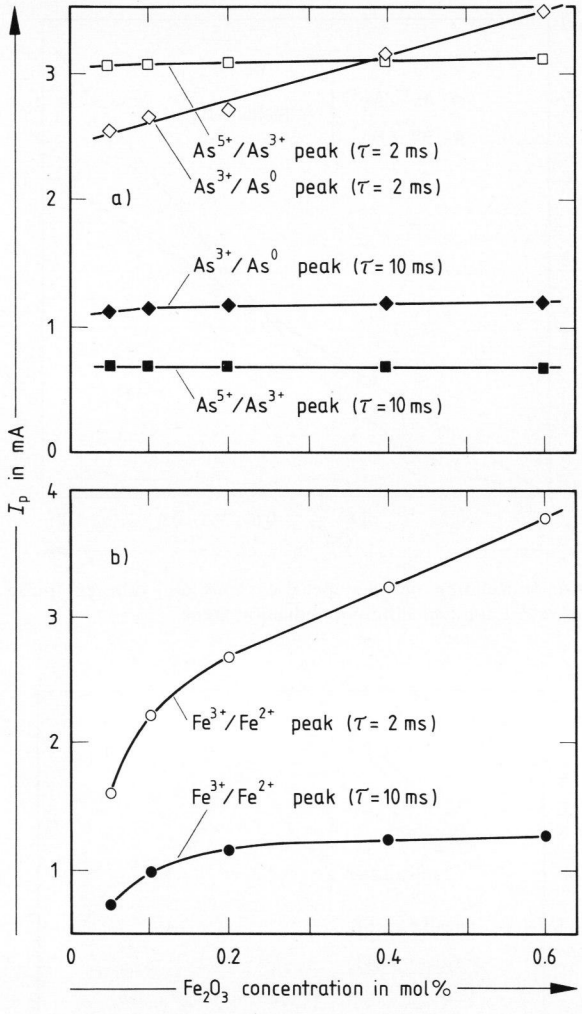


Figure 4. Relation between peak currents and different pulse times, $\tau^{-1/2}$, for two different reduction steps.



Figures 5a and b. SWV of a soda–lime–silica glass melt, doped with 0.2 mol% As_2O_5 and different amounts of Fe_2O_3 ($\Delta E = 75$ mV, $\vartheta = 1200$ °C) at a) $\tau = 10$ ms, b) $\tau = 2$ ms.

As^{3+}/As^0 peak has disappeared and only a shoulder can be observed. Figure 4 illustrates the peak currents of both reduction steps as a function of $1/\sqrt{\tau}$. For the second reduction step (As^{3+}/As^0, dots in figure 4) a nearly linear correlation, according to equation (4), can be observed. By contrast, the peak currents of the first reduction step (As^{5+}/As^{3+}, circles in figure 4) show a quite different behavior: They increase with



Figures 6a and b. Peak currents as a function of the iron concentration in a soda-lime-silica glass melt, doped with 0.2 mol% As_2O_5 and different amounts of Fe_2O_3 (ΔE = 75 mV, ϑ = 1200 °C) for different pulse times, a) As^{5+}/As^{3+} and As^{3+}/As^{0} peaks, b) Fe^{3+}/Fe^{2+} peak.

decreasing pulse time much stronger than indicated by equation (4). Up to now, the physical reason of this irregular behavior is not known. Nevertheless, for analytical purposes, if offers a method to decrease or increase the peak currents, related to a certain reduction step by the variation of the pulse time. By this method, very low concentrations of arsenic oxide could be quantitatively determined at short pulse times.

Figures 5a and b show SWVs of glasses, doped with 0.2 mol% As_2O_5 and different amounts of Fe_2O_3 (0.05; 0.1; 0.2; 0.4 and 0.6 mol%) at pulse times of 10 ms (figure 5a) and 2 ms (figure 5b). At iron concentrations $\geq$ 0.1 mol%, three potential regions can be clearly distinguished with decreasing potential: First the As^{5+} ion is reduced at around −125 mV to the As^{3+} ion, then the As^{3+} ion is reduced to the As^{0} ion at about −325 mV and finally the Fe^{3+} ion is reduced to the Fe^{2+} ion at around −500 mV. At a Fe_2O_3 concentration of 0.05 mol%, the Fe^{3+}/Fe^{2+}

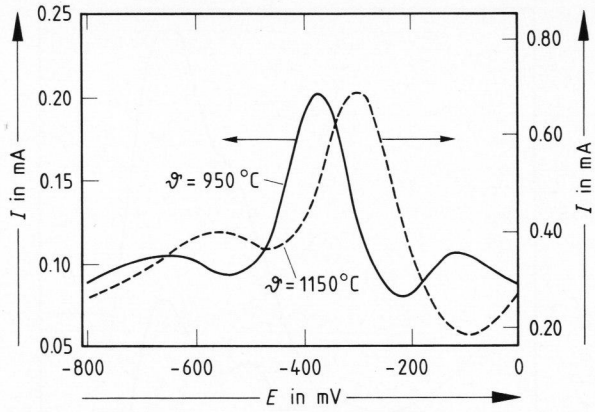


Figure 7. SWV of a soda-lime-silica glass melt, doped with 0.2 mol% Sb_2O_5 and 0.2 mol% Fe_2O_3. ΔE = 50 mV, τ = 10 ms.

peak is not well-separated at a pulse time of 2 ms and not visible at a pulse time of 10 ms. At a pulse time of 10 ms (see figure 5a), the As^{5+}/As^{3+} peak is not influenced by increasing iron concentrations, and the peak currents of the second reduction step (As^{3+}/As^{0}) only slightly depend on the iron concentration. The currents in the potential region of around −500 mV, in which the Fe^{3+} ion is reduced to the Fe^{2+} ion, increase with increasing iron concentration.

At a pulse time of 2 ms (see figure 5b), the As^{5+}/As^{3+} peak at around −125 mV is already slightly influenced by the iron concentration of the glass melt. The peak current, related to the second reduction step at around −325 mV, increases remarkably with increasing iron concentrations. In any case, all peak potentials are only slightly influenced by the variation of the iron concentration. The dependence of the As^{5+}/As^{3+} and the As^{3+}/As^{0} peak currents on the Fe_2O_3 concentration is summarized in figure 6a.

In figure 6b, the peak currents, related to the Fe^{3+} reduction are shown as a function of the iron concentration. The peak current at a pulse time of 10 ms increases remarkably up to a concentration of 0.2 mol% Fe_2O_3, and only a slight increase at higher Fe_2O_3 concentrations can be observed. At a pulse time of 2 ms, the peak currents increase more strongly (see the circles in figure 6b) than at a pulse time of 10 ms. At a low iron concentration, up to 0.2 mol%, the slope in figure 6b is rather high. At iron concentrations $\geq$ 0.2 mol% Fe_2O_3, the slope decreases, and a nearly linear correlation can be observed.

For the quantitative in situ determination of Fe_2O_3 and As_2O_5 in the molten glass, it is favorable to calculate the Fe_2O_3 concentration from a SWV, recorded at a short pulse time. The As_2O_5 concentration should be calculated preferably from the As^{5+}/As^{3+} peak, because the As^{3+}/As^{0} peak is

influenced by the amount of Fe_2O_3 in the glass melt, especially at short pulse times.

Figure 7 shows SWVs of a soda–lime–silica glass melt doped with 0.2 mol% Sb_2O_5 and 0.2 mol% Fe_2O_3 at a temperature of 1150 °C (dotted line) and at 950 °C (full line). At 1150 °C two peaks can be observed: The broad peak at −540 mV is related to the reduction of the Fe^{3+}ion; the peak at −300 mV coincides with the reduction of the Sb^{3+} ion to metallic antimony. In comparison to glasses, doped with As_2O_5, this peak is shifted to more positive potentials. At 1150 °C, a peak related to the reduction of the Sb^{5+} to the Sb^{3+} ion cannot be observed, but the current increases remarkably at potentials higher than −100 mV. It is assumed that the normal potential at 1150 °C has a positive value, which cannot be measured by voltammetric methods because it is outside the accessible potential range [8]. At 950 °C (figure 7, full line), three peaks can be observed. The Fe^{3+}/Fe^{2+} and the Sb^{3+}/Sb^0 peaks are shifted cathodically, as observed at every polyvalent ion in molten glass [3 and 9]. The third peak at about −120 mV is related to the reduction of the Sb^{5+} to Sb^{3+} ion, having a normal potential E_0, which is remarkably more positive than that of the As^{5+}/As^{3+} peak. This is in agreement with the observation that antimony, which delivers oxygen at lower temperatures, is a better refining agent than arsenic [10]. In SWVs, obtained from a glass melt doped with Sb_2O_5 and Fe_2O_3, the peaks are better separated than in a SWV obtained from a glass melt doped with As_2O_5 and Fe_2O_3.

5. Conclusions

In principle, in a molten glass the simultaneous in situ determination of two polyvalent cations like Fe_2O_3 and As_2O_5 or Fe_2O_3 and Sb_2O_5 is possible. But at the high temperatures, necessary to melt glass, the peaks are quite broad and not very well separated. There is always an overlap of peaks, especially, if the normal potentials are not very different or the polyvalent ions are reduced in a one-electron step. The recorded current-potential curves should be carefully analyzed to achieve reliable data.

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