Original Paper

Square-wave voltammetry as a method for the quantitative in-situ determination of polyvalent elements in molten glass

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Many properties of glasses, especially the color are strongly influenced by the concentration of multivalent elements. Up to now the concentration of multivalent elements can only be determined from the solid glass by chemical or physical methods. This paper introduces a method which makes possible to determine the total concentration of the multivalent ion in-situ in the glass melt by an electrochemical method. In this paper the square-wave voltammetry is used for the quantitative determination of iron in a soda–lime–silica glass melt. The area of the test electrode can be adjusted by conductivity measurements. The Fe_2O_3 concentration can be detected down to a lower limit of 0.015 mol%.

Anwendung der Square-Wave-Voltammetrie zur quantitativen In-situ-Bestimmung polyvalenter Elemente in der Glasschmelze

Viele Glaseigenschaften, insbesondere die Farbe, werden stark von der Konzentration polyvalenter Elemente beeinflußt. Bis jetzt kann diese Konzentration nur mit physikalischen und chemischen Methoden am abgekühlten Glas ermittelt werden. Die vorliegende Arbeit stellt ein elektrochemisches Verfahren vor, das es ermöglicht, die Gesamtkonzentration eines polyvalenten Ions direkt in der Glasschmelze zu bestimmen. Hierzu werden quantitative Eisenbestimmungen in einer Kalk-Natronglasschmelze mit Hilfe der Square-Wave-Voltammetrie durchgeführt. Die Oberfläche der Arbeitselektrode wird dabei durch Leitfähigkeitsmessungen eingestellt. Die untere Erfassungsgrenze liegt derzeit bei einem Stoffmengengehalt von 0,015 % Fe_2O_3.

1. Introduction

The oxidation state of a glass melt is important for many properties of the molten glass and the final glass product. Not only the color, but also many other properties like mechanical strength, crystallization, volatilization and solubility of gases are influenced by the oxidation state. In technical systems desired oxidation states are obtained by adjusting the batch composition. The oxidation state is determined by the kind and amount of multivalent ions and the oxygen activity. For many years it is possible to measure the oxygen activity of a glass melt [1 to 5] by oxygen sensors which are based on oxygen ion-conducting solid electrolytes (CaO- or Y_2O_3-stabilized zirconia) [3 to 5]. In order to describe the oxidation state completely, it is necessary to know the kind and amount of multivalent ions in the glass melt. Till now, a check was only possible by quenching the glass melt and analyzing the solid glass physically or chemically.

Melts of oxide glasses are good ionic conductors. Therefore, electrochemical techniques developed for aqueous solutions can also be used for investigations in glass melts. Recently some methods like Cyclic Voltammetry (CV) [6 to 10], chronoamperometry [11] and Square-Wave Voltammetry (SWV) [12] were successfully applied to glass melts. By means of voltammetric methods current–potential curves are obtained, which show characteristic peaks for the most multivalent ions. From the peak currents the concentrations of the multivalent ions could be calculated, if the area of the working electrode is known. If the working electrode consists of a platinum wire, inserted in the glass melt, the electrode area is unknown. Since the level of the molten glass changes, in technical glass melts the electrode cannot be adjusted properly enough. It is the aim of this work to further develop the SWV in order to determine multivalent ions in the molten glass quantitatively.

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2. Theory

Voltammetry means, that current–potential curves are recorded under potential control, a time-dependent potential is applied to the working electrode of an electrochemical cell. With this technique, the following reaction can be observed:

$$Me^{x+} + n\,e^- \rightleftharpoons Me^{(x-n)+}. \quad (1)$$

In relevant literature [12 to 15], SWV is described as a technique which has a much higher sensitivity and resolution than CV, which was used for the most voltammetric investigations in molten glass. SWV was already successfully applied to glass melts and an experimental comparison with CV also proved the better sensitivity and higher resolution of SWV in molten glass [12]. The applied potential is a staircase

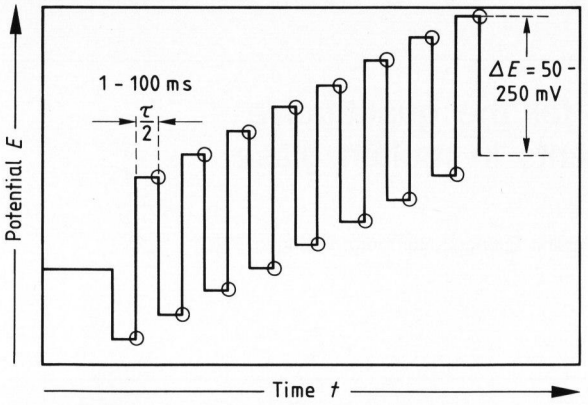


Figure 1. Potential–time dependence for Square-Wave Voltammetry (SWV).

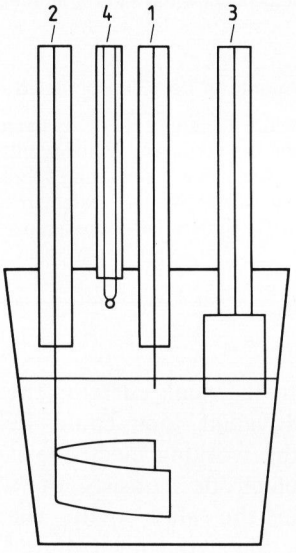


Figure 2. Schematic presentation of the electrochemical cell.
1: working electrode,
2: counter electrode,
3: reference electrode (ZrO_2 probe),
4: Pt/PtRh thermocouple.

ramp, superimposed by a rectangular wave (see figure 1) of high frequency (5 to 500 Hz) and comparably high amplitude (50 to 250 mV). The current is measured at the end of every half wave (see circles in figure 1) and then differentiated [13 to 15]. The recorded current–potential curve of a melt containing one multivalent cation like Fe^{3+}, which can be reduced in a one-electron step, will exhibit a current maximum. The peak potential equals the normal potential of the redox reaction (see equation (1)). The peak current is proportional to the total concentration of the multivalent ion and the area of the working electrode:

$$I_p = K \cdot c_0 \cdot A \,, \tag{2}$$

I_p: peak current; c_0: total concentration of the multivalent ion; A: area of the working electrode; K: constant.

When the scan rate is low and ΔE (see figure 1) is smaller than $\frac{R\,T}{n\,F}$ the constant K in equation (2) can be calculated by equation (3):

$$K = \frac{n^2 \cdot F^2 \cdot D^{1/2} \cdot \Delta E \cdot a}{R \cdot T \cdot \tau^{1/2}} \tag{3}$$

with D = diffusion coefficient; a = 0.31; n = number of the electrons transferred, T = temperature, R = gas constant, ΔE = differential potential, F = Faraday constant, τ = pulse time.

3. Experimental

Figure 2 shows the electrochemical cell. Three electrodes are inserted into the glass melt. The working electrode is a platinum wire (diameter: 1 mm), the counter electrode is a platinum plate with a size of about 2 cm^2. The third electrode is the reference electrode, it is a rod of yttria-stabilized zirconia, which is stuck to an alumina tube with a ceramic binder. Inside there is a platinum wire as electrode and air as reference gas [16]. All mentioned potentials in this paper refer to this reference. The platinum crucible with the glass melt is inside a resistance-heated furnace (SiC) with a vertical alumina tube. A water-cooled flange at the top carries the electrodes. The platinum crucible is placed on another, smaller alumina tube, which can be adjusted from the bottom flange in that way, that the level of the molten glass can be varied exactly.

Electronics for voltammetry are self-constructed. The electrodes are connected with the potentiostat, which is in principle an operational amplifier and adjusts the potential between working and counter electrode in such a manner that the potential between working and reference electrode has the required value. A microcomputer is connected with a potentiostat via an analog/digital and a digital/analog converter and with a printer, plotter and floppy disc. This computer gives the potential–time dependence (see figure 1) to the potentiostat and records the current–potential curves. Conductivity measurements were made with an impedance analyzer (HP 4192) between working and counter electrode.

The experiments were carried out in the following manner: The electrodes were placed in the furnace at a position, in which the working electrode does not dip in the glass melt and therefore, the impedance analyzer indicates a conductivity of zero. The crucible is slowly lifted up, till the working electrode dips in the molten glass and the impedance analyzer indicates a certain conductivity. This position of the crucible was defined as zero-immersion depth. Then the melting pot could continuously be lifted with a screw till the electrodes immersed 10 mm deep. In that way peak currents from voltammetric measurements and the measured conductivity between working and counter electrode can be correlated with each other and the immersion depth. In the most voltammetric experiments ΔE (see figure 1) of the

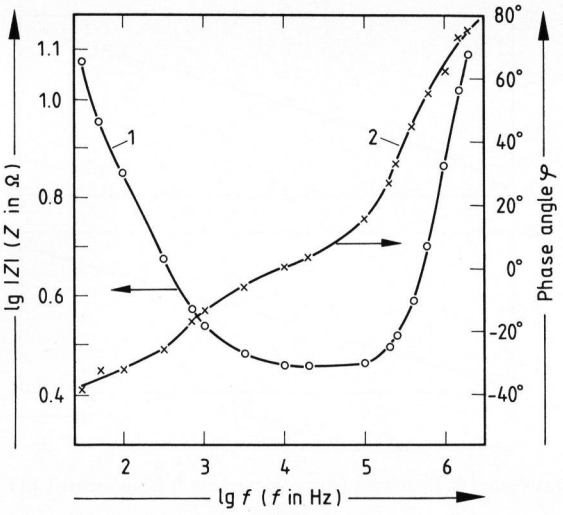


Figure 3. Impedance Z and phase angle φ as a function of frequency f. Curve 1: impedance, curve 2: phase angle.

square-wave was 100 mV, the frequency was 25 Hz und the scan rate 125 mV/s.

All experiments were carried out with glasses of the basic composition (in mol%) 74 SiO_2, 16 Na_2O, 10 CaO, which were modified by adding up to 2 Fe_2O_3.

4. Results and discussion

For conductivity measurements an optimized frequency must be found to eliminate capacitive and inductive effects. For this purpose, the measuring frequency of the impedance analyzer was varied in a wide range from 30 Hz to 1.8 MHz, the total impedance Z and the phase angle φ were registered (see figure 3). The total impedance exhibits a broad minimum from 3 to 100 kHz, in which the value is almost constant. At decreasing frequency $f < 3$ kHz, the impedance is influenced more and more by capacitive effects, the phase angle in this region is negative. At high frequency $f > 100$ kHz, the impedance increases again, it is influenced by inductive effects; the phase angle is positive. As in the frequency region from 3 to 100 kHz nearly no influence of inductive and capacitive effects can be observed and the impedance is nearly constant, all frequencies in this range can be used. In this work a frequency of 10 kHz was used generally for all the following experiments.

Figure 4 shows a typical SWV curve ($\Delta E = 100$ mV, $f = 25$ Hz, scan rate = 0.125 V/s) at 1300 °C and a Fe_2O_3 concentration of 0.38 mol%. The record exhibits a definite current maximum at −480 mV. The further increase of the current at potentials more negative than −780 mV belongs to the background of the matrix and may be due to the reduction of the silicate glass to elementary silicon or platinum silicid.

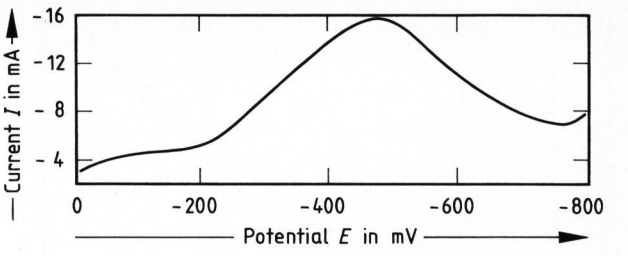
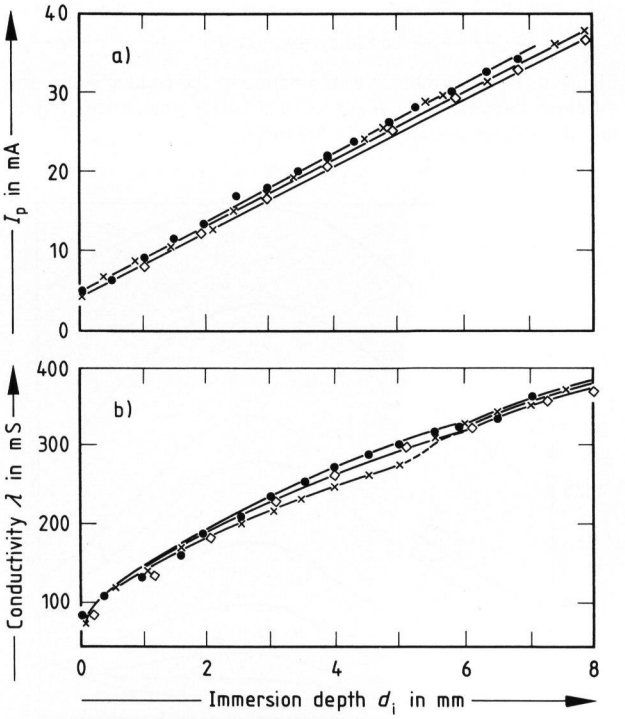


Figure 4. SWV curve of a soda–lime–silica glass melt, containing 0.38 mol% Fe_2O_3; $\vartheta = 1300$ °C ($\Delta E = 100$ mV, $f = 25$ Hz, scan rate = 0.125 V/s).



Figures 5a and b. Increase of a) peak currents I_p, b) conductivity λ between working electrode and counter electrode for different immersion depths d_i of the working electrode of a glass melt containing 0.88 mol% Fe_2O_3, $\vartheta = 1250$ °C. × = first increase of immersion depths; ● = the immersion depth is decreased; □ = the immersion depth is increased again.

Figure 5a shows the dependence of the peak current upon the immersion depth at an iron concentration of 0.88 mol% and a temperature of 1250 °C. When the immersion depth is increased, the area of the platinum electrode, in contact with molten glass, is enlarged. Then, according to equation (2) the peak current increases, too. The experiments shown in figure 5a, were made in the following manner: Starting from the immersion depth "zero", the crucible was lifted up to 8 mm and then screwed down again to "zero" and lifted up again. All these motions were made step by step. Figure 5a shows, that the dependence predicted by equation (2) can be observed, but the exact value of the peak current slightly depends on the direction of the movement.

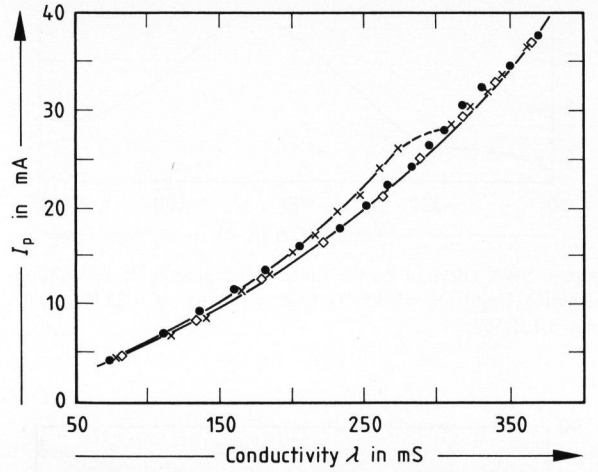


Figure 6. Peak currents I_p as a function of the conductivity λ for different immersion depths d_i of the working electrode. Explanation of symbols see figures 5a and b.

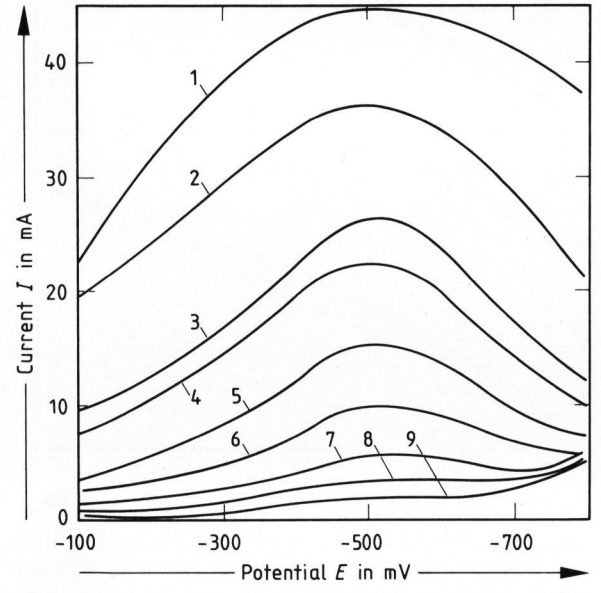
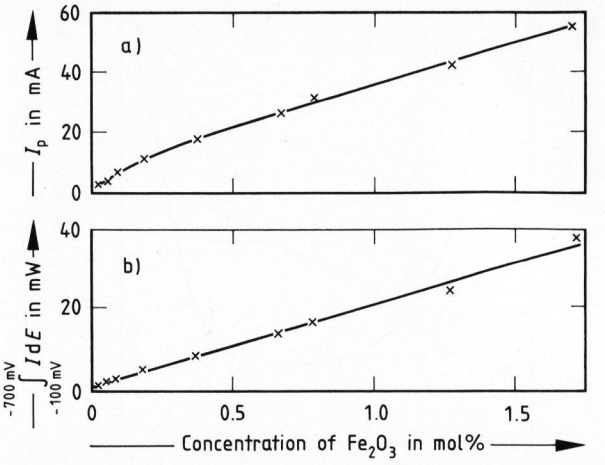


Figure 7. SWV curves of glass melts with different Fe_2O_3 concentrations. 1 = 1.72, 2 = 1.28, 3 = 0.78, 4 = 0.67, 5 = 0.37, 6 = 0.19, 7 = 0.086, 8 = 0.049, 9 = 0.015 mol% Fe_2O_3.

For the same experiment, the dependence of the conductivity between working and counter electrode is shown in figure 5b. When the crucible is lifted up, the area of the working electrode is enlarged and therefore, the conductivity increases. When the crucible is screwed down again, the conductivity, measured at the same immersion depth is not exactly the same. In the first lift up of the crucible (figure 5b, dots ×), there were some slight deviations from the other values (figure 5b, dots ● and □). It is assumed that the deviation of the first lift is based on the effect, that the coverage of the platinum electrode with the molten glass is not yet in equilibrium. The reason why this correlation is not linear, is that the geometry of the cell does not meet the requirements of an ideal conductivity measurement cell.



Figures 8a and b. Increase of a) peak currents I_p from figure 7 and b) the area below the peaks $\left(\int_{-100\,mV}^{-700\,mV} I \cdot \Delta E\right)$ as a function of the different Fe_2O_3 concentrations.

Figure 6 shows the peak current as a function of the conductivity for the experiments of figures 5a and b. In the first lift up there are some slight deviations, too, according to figure 5b. When the experiments were repeated all dots were placed on the same graph as the dots ● and □, the reproducibility was within 2 %.

Further experiments were made to investigate the dependence of the conductivity on the size of the counter electrode and the distance from the counter electrode to the working electrode. For this purpose, the counter electrode with a surface area of 2 cm^2 was replaced by another one with 3 cm^2, the conductivity was adjusted at 300 mS and a SWV was recorded. The peak current increased from 20.0 to 21.5 mA. Then the distance between working and counter electrode (surface area: 2 cm^2) was changed from 3 to 1 cm, the conductivity was adjusted at 300 mS and SWV was recorded again, the peak current decreased to 19.8 mA. From these two experiments one can draw the conclusion, that different geometric constellations do not have much influence on the measured conductivity. If the counter electrode is much larger than the working electrode, the conductivity depends mainly on the area of the working electrode. This is in agreement with theory, because the equipotential lines have the highest density near the working electrode. Therefore, accidential variations of the electrode constellations cannot affect seriously the conductivity between the two electrodes.

Figure 7 shows some SWV curves of molten glasses with different iron concentrations. Before recording the SWV, the level of glass melt was adjusted in such a manner, that the conductivity between working and counter electrode was 400 mS. In the concentration range from 0.1 to 0.8 mol% Fe_2O_3, the peak is pronounced very well and

the SWV curve has nearly the same shape. When the Fe_2O_3 concentration is higher, the peak is broadened significantly. At an Fe_2O_3 concentration of 0.015 mol% the peak is not pronounced well, the background effects are too high. The peak currents increase with increasing Fe_2O_3 concentrations (see figure 8a), but a linear relationship, according to equation (2) could not be observed. At Fe_2O_3 concentrations of more than 1 mol% the slope in figure 8a is significantly lower. A possible explanation for this deviation from linearity and the broadening of the peaks could be, that at higher Fe_2O_3 concentrations the iron ions are in different positions in the glass network and are energetically not equal. These positions are related to different normal potentials. The recorded current–potential curve would be a superposition of different curves of the shape from figure 4 and therefore, the peaks are virtually broadened and the peak currents from figure 8a deviate from linearity. In this case, the area below the peaks in figure 7 should be a better measure for high Fe_2O_3 concentrations than the peak currents. For this purpose, the graphs in figure 7 are integrated from −100 to −700 mV. It can be seen in figure 8b, that a good linear correlation with the iron concentration is obtained. The lower limit for the determination of the Fe_2O_3 concentration is about 0.015 mol%. But if the background current of the matrix is substracted by the microcomputer, further improvement should be possible.

5. Conclusions

Square-wave voltammetry in molten glass has been developed to a quantitative technique. For adjusting the area of the working electrode a simple conductivity measurement is necessary. This technique could be applied for industrial glass melts, too.

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