Quantitative in-situ determination of iron in a soda–lime–silica glass melt with the aid of square-wave voltammetry

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Square-wave voltammetric measurements are fairly convenient to determine thermodynamic data and diffusion coefficients of polyvalent elements in glass melts. In principle, these methods also allow the quantitative in-situ determination of the total concentrations of polyvalent ions. For the in-situ determination of small quantities, however, improvements of the measuring and analyzing procedures were necessary. This was achieved by approximating background currents using polynomials and describing Faradaic currents using theoretically derived equations. Simulations using least square approximations then allow a much more detailed analysis of the current potential curve. Further improvements were possible by pre-electrolyzing the melt at negative potentials and then shifting the potential to zero while recording the square-wave voltammogram. Using both procedures, a quantitative determination of iron concentrations as low as 0.004 mol% Fe₂O₃ is possible.

1. Introduction

In the past few years, voltammetric methods proved to enable the determination of thermodynamic properties and diffusion coefficients of polyvalent elements in glass melts at high temperature [1 to 14]. The voltammetric method firstly applied to investigate glass melts was the cyclic voltammetry [1 and 2]. In the meantime, other voltammetric methods, such as alternating current voltammetry [14], differential pulse voltammetry [14] and square-wave voltammetry [2 to 14] also have been applied to glass melts. Here, the square-wave voltammetry proved to be the method, possessing the highest sensitivity and resolution of all methods applied up to now to glass melts. For the determination of diffusion coefficients, the total concentration of the multivalent elements must be known [9]. By analogy, the quantitative in-situ determination of the total concentration of polyvalent ions is possible, if the diffusion coefficients are known [8, 11 and 12]. This was firstly demonstrated with the aid of laboratory experiments [8] using soda–lime–silica glass melts and comparably high iron concentrations. Later this method was applied to industrially melted green and amber brown glasses also using laboratory equipment [6]. In the meantime, voltammetry has also been carried out in industrial glass tanks [11 and 12] and proved to enable the quantitative in-situ determination of iron also under industrial conditions. Up to now, however, the method was restricted to comparably high iron concentrations. By comparison to voltammograms recorded in aqueous solutions at room temperature, current potential curves recorded in glass melts at high temperatures exhibit fairly broadened peaks. This is in accordance with the theory which predicts an increase of the half-width proportional to the absolute temperature. Additionally, matrix effects are much higher if the voltammograms have been recorded in glass melts. This is mainly caused by the fact that also the basic glass melt (without polyvalent elements) is decomposed if cathodic potentials < −800 mV are applied. In the anodic direction, the accessible potentials are limited by the formation of oxygen bubbles. Thus, only a fairly small “potential window” can be used to investigate polyvalent ions in molten glass. In this paper, improvements of the square-wave voltammetry are described.
The applied potential of the square-wave voltammetry is a staircase ramp, superimposed by a rectangular wave (Figure 1) of high frequency (5 to 500 Hz) and comparably high amplitude (50 to 200 mV). The current is measured at the end of every half wave and then differentiated [18 and 19].

Voltammetrically recorded current potential curves can be treated as a superimposition of currents due to matrix decomposition, currents due to the occurrence of polyvalent elements, and currents due to charge and discharge of the electrochemical double layer.

\[ I(E) = I_M(E) + I_{PE}(E) + I_{DL} \]  

with \( I(E) \) = total current, \( I_M(E) \) = currents due to matrix decomposition, \( I_{PE}(E) \) = currents due to the occurrence of polyvalent elements, \( I_{DL} \) = currents due to charge and discharge of the electrochemical double layer.

Whereas the charge currents, in a first approximation, are independent of the potential (the double layer capacitance is constant), currents due to matrix decomposition and those due to polyvalent elements strongly depend on potential. \( I_{PE}(E) \) can theoretically be calculated using equations quoted in the literature [18 and 19].

\[ I_{PE}(E) = \frac{zFAD^{1/2}C_0}{\pi^{1/2} \tau^{1/2}} \sum_{m=1}^{\infty} \left( \frac{(-1)^m Q_{m-2} Q_{m-1} + Q_{m-2}}{(1 + m)^{1/2}} \right) \]  

with \( Q_m = \frac{\exp[zF(E_m - E_0)/(RT)]}{1 + \exp[zF(E_m - E_0)/(RT)]} \)  

with \( z \) = numbers of electron transferred, \( F \) = Faraday constant, \( D \) = diffusion coefficient, \( C_0 \) = total concentration of the polyvalent element, \( \tau \) = pulse time, \( A \) = area of the working electrode, \( E_m \) = potential applied, \( E_0 \) = standard potential of the polyvalent element.

In figure 2, theoretically calculated current potential curves are shown for a one, a two and a three electron transfer reaction. The peak width, \( E_{PW} \), decreases if more than one electron is transferred.

\[ E_{PW} = T \cdot b/z \]  

with \( b = 0.30 \) mV/K.

The peak current, \( I_p \), depends on the surface area of the electrode, the total concentration of the polyvalent element, and the number of the electrons transferred; it is proportional to \( z^2 \) and can be calculated from:

\[ I_p = A \cdot C_0 \cdot D^{1/2} \cdot z^2 \cdot \text{const} \]  

for small \( \Delta E \): const = 0.31 \( F^2 \Delta E / (\pi^{1/2} \tau^{1/2} R T) \).

3. Experimental

The experiments were carried out in a resistance-heated furnace with a vertical alumina tube with water-cooled flanges at the top and at the bottom. A platinum...
crucible which contains the glass melt and which can be adjusted from the bottom flange is located in the centre of the tube. The electrodes are inserted into the furnace from the top flange and dipped into the glass melt. The working electrode consists of a platinum wire, the counter electrode is a platinum plate and the reference electrode is a zirconia probe. All mentioned potentials in this paper are with reference to the zirconia/air electrodes. The details of the experimental equipment has already been described in [4 and 14].

The electronics were self-constructed, the main part being a potentiostat. It is connected to a microcomputer via a digital/analogue and analogue/digital converter so that any potential time dependence can be supplied. The potential time dependence of the conventional square-wave voltammetry is shown in figure 1. Figure 3 shows another potential time dependence supplied in another series of experiments. Here, the potential was first shifted to a negative potential (e. g. of -900 mV), hold for e. g. 2 s, then the measurement was carried out while shifting the mean potential to 0 or -100 mV.

All experiments were carried out in a glass melt with the basic composition (in mol%) of 74 SiO₂, 16 Na₂O, 10 CaO, which was modified by adding Fe₂O₃.

The dip-in length of the working electrode into the glass melt was adjusted while measuring the electric (alternating current) conductivity between working and counter electrode using the procedure in detail described in [8].

4. Results and discussion
4.1 Numerical simulation of the current potential curves
Figure 4a shows a square-wave voltammogram recorded in a soda–lime–silica glass melt without any addition of polyvalent elements. At potentials above 0 V, the current increases due to the oxidation of the silicate network and hence to the formation of O₂. At potentials more negative than -500 mV, a steady increase of the current can be registered. This current is due to the cathodic decomposition, i.e. the reduction of the silicate network and the formation of elementary silicon or platinum silicide on the surface of the electrode. The shape of the current potential curve changes slightly, but systematically with temperature. The shape, however, does not change significantly, if experimental parameters, such as step time and step potentials are altered. The current, however, increases with increasing step potential and decreasing step time (see also equation (7)). Furthermore, also the current offset is mainly determined by those experimental parameters. According to theory, the current offset should mainly be caused by charge and discharge of the electrochemical double layer. The current potential curve shown in figure 4b was approximated by a polynom as described by equation (8) using least square fits.

\[ I_{sl}(E) = \sum_{n=1}^{10} A_n \cdot E^n + B. \]  

The coefficients \( A_n \) have to be optimized for any temperature, the coefficient \( B \) is mainly a function of the
Figure 5. Square-wave voltammogram recorded in a soda-lime-silica glass melt doped with 0.25 mol% Fe₂O₃ at 1300 °C (τ = 10 ms, ΔE = 100 mV).

Figure 6. Square-wave voltammogram (curve 1) recorded in a soda-lime-silica glass melt doped with 0.035 mol% Fe₂O₃ at 1200 °C (τ = 2 ms, ΔE = 100 mV) and background current (curve 2) optimized using equation (9) and the procedure described in the text.

Figure 7. Square-wave voltammogram of figure 6 (background current subtracted, curve 1) in comparison to simulated Faraday current (curve 2).

Figure 8. Square-wave voltammogram recorded in a glass melt containing 0.035 mol% Fe₂O₃ and using two different potential time dependences. Figure 8 (curve 1) shows a square-wave voltammogram recorded in a conventional manner according to the potential time dependence shown in figure 1, applying a pulse time of 10 ms. The mean potential was shifted from +100 to −900 mV. Figure 8 (curve 2) shows a square-wave voltammogram recorded in the same glass melt, the potential, however, was first shifted to −900 mV and held for 2 s, then the mean

experimental parameters used. The curves calculated are in good agreement with the experimental ones, as it can be seen by comparison of figures 4a and b.

Figure 5 shows a square-wave voltammogram recorded in a soda-lime-silica glass melt doped with 0.25 mol% Fe₂O₃. A well-pronounced peak due to the reduction of Fe³⁺ to Fe²⁺ can be observed. In the potential region shown in this figure, the shape of the current potential curve is predominantly due to the occurrence of iron but the asymmetric shape of the peak is evidence that the curve is also influenced by background currents, which increase with decreasing potential. Figure 6 (curve 1) shows a square-wave voltammogram recorded in a melt doped by 0.035 mol% Fe₂O₃. The shape of the curve is predominantly due to the background current, only a small shoulder indicates the occurrence of iron. A quantitative determination of the iron content is possible without subtraction of the background current. The curve was therefore analyzed using equation (9):

\[ I(E) = X_1 \cdot I_M(E) + X_2 \cdot I_{PE}(E + X_3) + X_4 \]  

(9)

With respect to matrix decomposition, the empirical function \( I_M(E) \) according to equation (8) was used. The Faraday currents, \( I_{PE} \), were calculated using equations (4 and 5). The coefficient \( B \) in equation (8) is represented by the parameter \( X_4 \).

The simulated curve \( I(E) \) was adjusted to the experimental curve by varying the parameters \( X_1 \) to \( X_4 \) using least square approximation. The variation of parameter \( X_3 \) also includes an optimization of the peak potential and hence the standard potential of the redox pair. The resulting background current is also shown in figure 6 (curve 2). Figure 7 (curve 1) shows the experimental current potential curve from which the background current was subtracted and the optimized theoretically calculated term \( X_2 \cdot I_{PE}(E + X_3) \). Within the potential region of 0 to −750 mV, the curves are in good agreement, while at lower potentials slight deviations can be observed. These slight deviations may be due to a second reduction step, the reduction of Fe²⁺ to metallic iron at potentials more negative than −750 mV.

4.2 Square-wave voltammetry after pre-electrolysis of the glass melt at negative potentials

Figure 8 shows two voltammograms both recorded in a glass melt containing 0.035 mol% Fe₂O₃ and using two different potential time dependences. Figure 8 (curve 1) shows a square-wave voltammogram recorded in a conventional manner according to the potential time dependence shown in figure 1, applying a pulse time of 10 ms. The mean potential was shifted from +100 to −900 mV. Figure 8 (curve 2) shows a square-wave voltammogram recorded in the same glass melt, the potential, however, was first shifted to −900 mV and held for 2 s, then the mean
potential was scanned from -900 to 100 mV while the measurement according to the potential time dependence shown in figure 3 was carried out. The applied pulse time was also 10 ms. In the latter case, the peak is more pronounced than in the square-wave voltammogram recorded in a conventional manner. This is a more advantageous prerequisite for a quantitative determination of the total iron content. The reason for a more pronounced peak should be an enrichment of iron at the electrode surface or near the electrode within the time when the potential is held at -900 mV. During the subsequent measurement, a higher quantity of iron species can be oxidized to Fe³⁺. This results in an increase of the Faraday currents.

The voltammograms recorded during shifting the potential from -900 to 0 mV were analyzed using equation (9). A series of experiments were carried out using both different step times and different total iron concentrations. All these measurements were carried out at a temperature of 1200°C. The resulting currents increase with decreasing step times. The total shape of the current potential curves, however, remains nearly constant because both, Faraday currents and background currents, increase simultaneously. The resulting peak currents after subtraction of the background current are shown in figures 9 and 10 as a function of the square root of the step times for iron concentrations of 0.023 and 0.004 mol%, respectively. The step times supplied were in the range of 1 to 50 ms. Figure 9 shows an excellent linear correlation, and hence the theoretically predicted correlation according to equation (2) is fulfilled. Fairly similar correlation was also obtained analyzing glasses with 0.016 and 0.035 mol% Fe₂O₃. The data shown in figure 10 were recorded in a glass melt possessing an iron concentration as low as 0.004 mol% Fe₂O₃. By comparison to figure 9, the resulting peak currents are notably lower. Although the correlation between the peak currents and the reciprocal value of the square root of the step time is not as good as
in figure 9, a quantitative analysis is still possible. Figure 11 shows the slopes from figures 9 and 10 and also values calculated from similar measurements using iron concentrations of 0.016 and 0.035 mol% \( \text{Fe}_2\text{O}_3 \). A strict linear correlation between the slopes and the total iron concentration is observed. From equation (7), equation (10) can easily be derived:

\[
I_p \cdot t^{1/2} = K \cdot C_0
\]

with \( K = \text{constant} = 0.31 \cdot A \cdot D^{1/2} \cdot z^2 \cdot F^2 \cdot \Delta E/(\pi^{1/2} \cdot R \cdot T) \).

Hence, the proportionality observed in figure 11 is in agreement with the theory.

Thus, using the potential time dependence shown in figure 3 while recording the current potential curve and also applying the background elimination procedure already described, drastic improvements of the sensitivity of the square-wave voltammetry are possible, allowing even a quantitative determination of iron contents as low as 0.004 mol% \( \text{Fe}_2\text{O}_3 \).

It should be noted that with the aid of square-wave voltammetry, always the total concentration of a polyvalent element, i.e. the sum of the concentrations in its oxidized and its reduced form is determined. A distinction between these two forms is only possible by carrying out additional measurements of the oxygen activity. Then from the standard potential, which is equal to the peak potential of the square-wave voltammograms, the potential measured and the total iron concentration, both the concentrations of the oxidized and the reduced form can be calculated.

5. Conclusions

Preelectrolysis of the glass melt containing small quantities of iron oxide at a potential of \(-900 \text{ mV} \) versus the zirconia/air electrode and subsequent potential shift to zero while recording the square-wave voltammogram leads to better pronounced peaks. Approximating the background currents using polynomials, empirically derived from square-wave voltammograms recorded in glass melts without polyvalent ions allows the simulation of the square-wave voltammograms recorded. Here, the Faradaic currents are calculated using the theoretically derived equations. With the aid of these two techniques, a notable improvement of the sensitivity is possible. Iron contents as low as 0.004 mol% \( \text{Fe}_2\text{O}_3 \) could be quantitatively determined.

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6. References