

## Voltammetry in a sulfur and iron-containing soda–lime–silica glass melt

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With the aid of square-wave voltammetry soda–lime–silica melts with sulfate fining were investigated in order to enable a quantitative in-situ determination of sulfur and iron. In this study, glass melts with low iron and high sulfate contents, typical for technical white glasses, were examined. The current-potential curves are predominantly influenced by sulfur and not solely controlled by diffusion. This behavior is supposedly caused by deposition of a sulfur layer on the surface of the working electrode. However, a simultaneous quantitative in-situ determination of iron and sulfur in melts of white glasses is possible.

### Voltammetrie in einer schwefel- und eisenhaltigen Kalk-Natronsilicatglasschmelze

Mit Hilfe der Square-Wave-Voltammetrie wurden sulfatgeläuterte Kalk-Natronsilicatglasschmelzen untersucht, um eine quantitative In-situ-Bestimmung von Schwefel und Eisen zu ermöglichen. Für diese Veröffentlichung wurden Glasschmelzen mit niedrigen Eisen- und hohen Sulfatgehalten, wie sie für technische Weißgläser typisch sind, untersucht. Die Strom-Spannungskurven werden von Schwefel dominiert und sind nicht ausschließlich diffusionskontrolliert. Dieses Verhalten wird vermutlich durch eine Belegung der Oberfläche der Arbeitselektrode mit einer Schicht von Schwefel verursacht. Dennoch ist eine quantitative In-situ-Bestimmung von Eisen und Schwefel in Weißglasschmelzen möglich.

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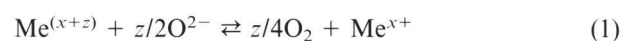
### 1. Introduction

Various voltammetric methods such as cyclic voltammetry [1 to 3], alternating current voltammetry [1], differential pulse voltammetry [1, 3 and 4] and square-wave voltammetry (SWV) [1 and 5 to 14] were applied in the past few years to examine glass melts at high temperatures. On the one hand, the determination of thermodynamic properties and diffusion coefficients of polyvalent elements in glass melts were important purposes [5 to 10]. On the other hand, square-wave voltammetry was used for the quantitative determination of the total concentration of polyvalent ions in the glass melts [10 to 14]. This was firstly demonstrated in laboratory experiments [10] using soda–lime–silica glass melts and comparably high iron concentrations. Later, this method was applied to industrially melted green and amber glass melts [11], also in industrial glass tanks [12 and 13]. It proved to enable the quantitative in-situ determination of iron also under industrial conditions. By improvement of the measuring and analyzing procedures, in the meantime, the determination of fairly low iron concentrations (0.004 mol% Fe<sub>2</sub>O<sub>3</sub>) is possible [14]. Up to now, all studies on the determination of the exact iron content were carried out in glass melts which contained iron as the only polyvalent element or in a fair excess by comparison to other polyvalent elements, such as sulfate. Since voltammetry also can be used in industrial glass tanks, an in-situ determination of both iron and sulfur in the

glass tank should be an important tool to control the melting conditions and to enable batch corrections in an early stage. In this paper, glass melts were applied which, by comparison to the sulfur content, contained iron in much lower concentrations, to show that a simultaneous quantitative in-situ determination of iron and sulfur in melts of technical white glasses is possible.

### 2. Theory

In glass melts polyvalent ions are in equilibrium with physically dissolved oxygen at high temperatures.



with  $z$  = number of electrons transferred,  $\text{O}_2$  = physically dissolved oxygen in the molten glass.

The equilibrium constants could be measured by equilibrating the glass melt with a gas atmosphere of a well-defined oxygen partial pressure, quenching the sample and analyzing the solid glass physically or chemically [15 to 17]. Another possibility is to calculate the equilibrium constants from voltammetrically determined standard potentials,  $E_0$ :

$$zFE_0 = RT \ln K(T) \quad (2)$$

with  $F$  = Faraday constant,  $K(T)$  = equilibrium constant, the other symbols have their usual meaning.

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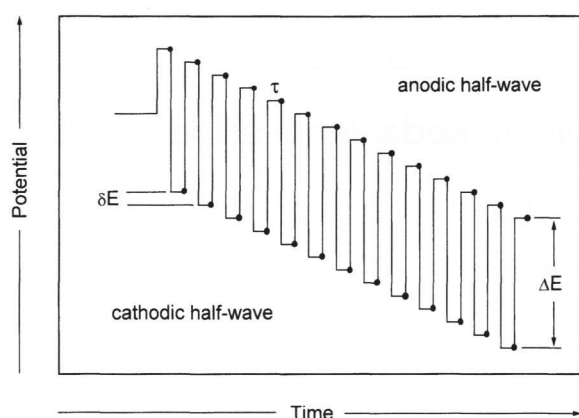


Figure 1. Schematic potential-time dependence for the square-wave voltammetry.

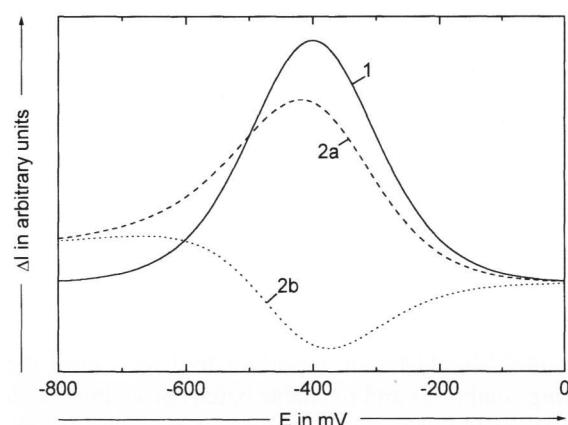


Figure 2. Theoretically calculated square-wave voltammogram for a two-electron step (curve 1) and the corresponding cathodic (curve 2a) and anodic (curve 2b) half-waves at 1200 °C.

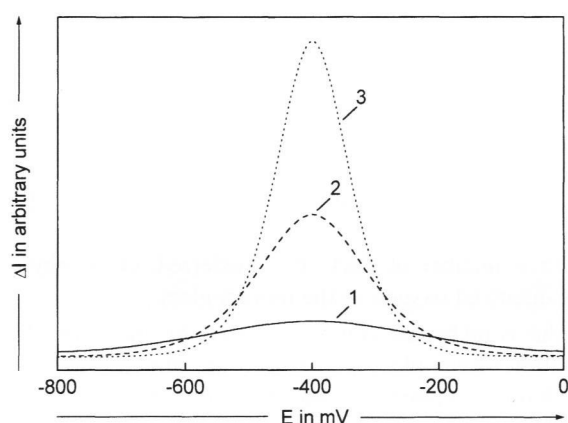


Figure 3. Theoretically calculated square-wave voltammogram for a one (curve 1), a two (curve 2) and a three (curve 3) electron step at 1200 °C.

In the course of voltammetric measurements, current-potential curves are recorded. Dependent on the method used, i.e. the potential-time dependence applied,

the curves exhibit distinct maxima and/or minima, from which the standard potential can be calculated.

In the case of SWV, the applied potential is a staircase ramp, superimposed by a rectangular wave of comparably short pulse time ( $\tau = 1$  to 500 ms) and amplitude ( $\Delta E = 50$  to 250 mV). The current is measured at the end of every half-wave (anodic and cathodic half-waves; figure 1) and then differentiated [18 and 19].

Currents due to the reactions of polyvalent elements during voltammetric measurements can theoretically be calculated using equations quoted in the literature [18 and 19]. Here, it is assumed that the transport of the electroactive species to and from the electrode is the rate-determining step and hence the currents are solely controlled by diffusion.

$$I_j = \frac{z F A D^{1/2} c_0}{\pi^{1/2} \tau^{1/2}} \sum_{m=1}^j \frac{Q_{m-1} - Q_m}{(j - m + 1)^{1/2}} \quad (3)$$

with

$$Q_m = \frac{\exp[z F (E_m - E_0) / (R T)]}{1 + \exp[z F (E_m - E_0) / (R T)]} \quad (4)$$

with  $I_j$  = current at the end of every half-wave,  $z$  = number of electrons 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.

The differential current is obtained by subtracting the currents flowing during the anodic and cathodic half-waves.

$$\Delta I = I_j - I_{j-1} \text{ for } j = 1, 3, 5, 7 \dots \quad (5)$$

Figure 2 shows the theoretical cathodic (curve 2a) and anodic (curve 2b) half-waves and the subtracted current-potential curve (curve 1) for a two-electron step. While the peak potential of curve 1 is equal to the standard potential, the maximum in curve 2a and the minimum in curve 2b are shifted in cathodic and anodic direction, respectively.

Figure 3 shows a theoretical current-potential curve for a one, a two and a three-electron step. The half-width of the peak decreases with an increasing number of electrons transferred

$$E_{p/2} = T b / z \quad (6)$$

with  $b = 0.30 \text{ mV/K}$ .

If the reactions of polyvalent elements during voltammetric measurements are controlled by diffusion, the peak current ( $\Delta I_p$ ) is proportional to the surface of the electrode, the total concentration of the polyvalent element and the number of the electrons transferred.

$$\Delta I_p = A c_0 D^{1/2} z^2 \text{const} / \tau^{1/2} \quad (7)$$

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

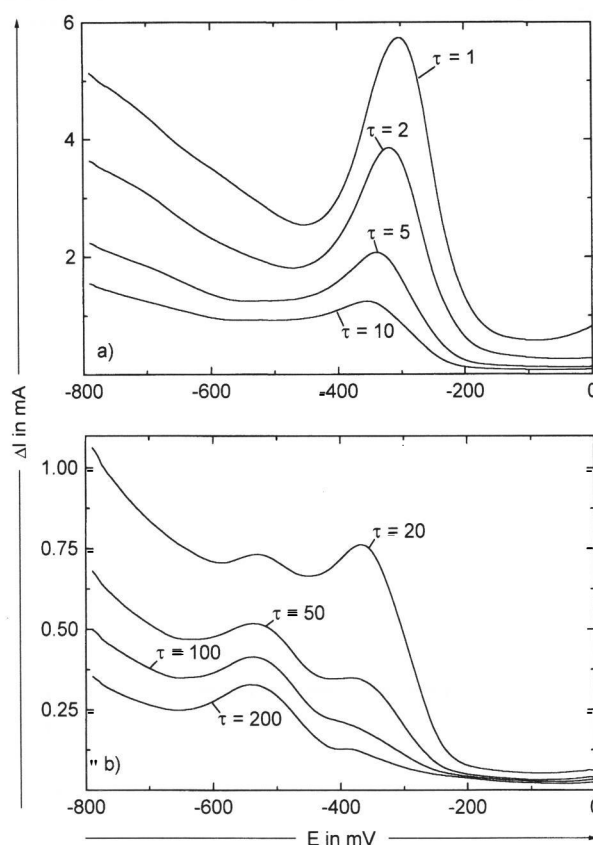
### 3. Experimental

The experiments were carried out in an electrically heated furnace, using a vertical alumina tube with water-cooled flanges at the top and the bottom. Approximately in the middle of this tube a platinum crucible with the molten glass was located. Three electrodes were inserted from the top flange and dipped into the glass melt. The working electrode is a platinum wire (diameter 1.0 mm), the counter electrode is a platinum plate (size: about 2 cm<sup>2</sup>) and the reference electrode is a zirconia probe flushed with air. All mentioned potentials in this paper are with reference to the zirconia/air electrode. The experimental equipment has been described in detail in [10].

The electronics were self-constructed, the main part being a potentiostat. It is connected to a microcomputer via digital/analogue and analogue/digital converter, so that any potential-time dependence could be supplied. The microcomputer also recorded the measured current. All experiments were carried out in a glass melt with the basic composition (in mol%): 74 SiO<sub>2</sub>, 16 Na<sub>2</sub>O and 10 CaO, which was modified by adding Fe<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>. 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 a procedure described in detail in [10]. The voltammograms are illustrated by a drawing of the differentiated current against the mean potential supplied. With the exception of figure 6, they are not corrected with respect to the background.

### 4. Results and discussion

Figures 4a and b show square-wave voltammograms recorded at 1200°C in a glass melt doped with 0.163 mol% Na<sub>2</sub>SO<sub>4</sub>, using different pulse times  $\tau$  in the range of 1 to 200 ms. Two peaks could be observed: one peak is in the range of -300 to -375 mV (first peak) and another one at about -540 mV (second peak). The intensities of these peaks strongly depend on the pulse time: in principle, the currents decrease with increasing pulse times. The shape of the curves, however, also changes. For short pulse times ( $\leq 10$  ms), the first peak is well-pronounced, while the second one can only be observed as a shoulder-shaped curve. For long pulse times ( $\geq 20$  ms), the first peak decreases strongly whereas the second peak becomes even more well-pronounced and more intensive than the first peak. In figure 5, square-wave voltammograms of glass melts doped with 0.070 (curve 3), 0.163 (curve 2) and 0.240 (curve 1) mol% Na<sub>2</sub>SO<sub>4</sub> are shown, recorded with a pulse time of 10 ms. In curve 3, solely the first peak can be seen. At curve 2, the first peak is well-pronounced and the second one could be observed as shoulder, while curve 3 shows two relatively well-separated peaks. Thus, the shape of the voltammograms recorded in glass melts doped with sulfate strongly depends on both the pulse time and the sulfur content. Figure 6 (curve 1) shows a voltam-



Figures 4a and b. Square-wave voltammograms recorded in a soda–lime–silica glass melt doped with 0.163 mol% Na<sub>2</sub>SO<sub>4</sub> for different pulse times at 1200°C, a)  $\tau = 1, 2, 5, 10$  ms,  $\Delta E = 100$  mV; b)  $\tau = 20, 50, 100, 200$  ms,  $\Delta E = 100$  mV.

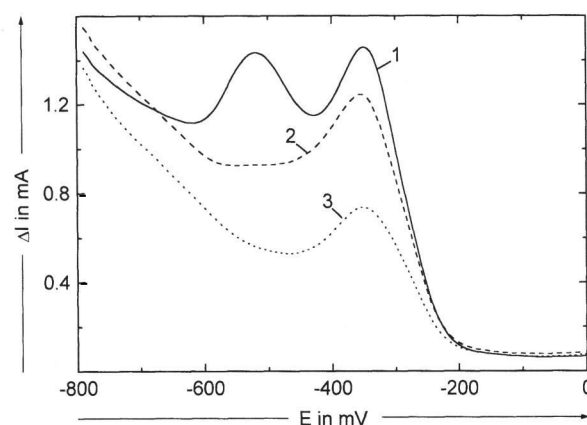


Figure 5. Square-wave voltammograms recorded in soda–lime–silica glass melts doped with different contents of Na<sub>2</sub>SO<sub>4</sub>: 0.070 mol% (curve 3), 0.163 mol% (curve 2), 0.240 mol% (curve 1).  $\vartheta = 1200^\circ\text{C}$ ,  $\tau = 10$  ms,  $\Delta E = 100$  mV.

mogram of a glass melt doped with 0.240 mol% Na<sub>2</sub>SO<sub>4</sub>. Curve 3 was obtained by subtracting the matrix current (curve 2) recorded in a melt without polyvalent elements from curve 1. Curve 4 shows a superimposition of the theoretically calculated curves 4a and 4b. Curves 4a and

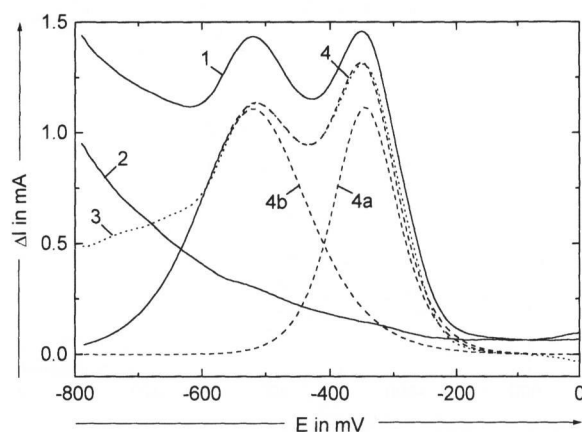


Figure 6. Square-wave voltammograms recorded in a soda–lime–silica glass melt doped with 0.240 mol%  $\text{Na}_2\text{SO}_4$  (curve 1); curve 2: matrix current; curve 3: curve 1 – curve 2; curves 4a and b: theoretical voltammograms, curve 4: curve 4a + curve 4b.  $\vartheta = 1200^\circ\text{C}$ ,  $\tau = 10$  ms,  $\Delta E = 100$  mV.

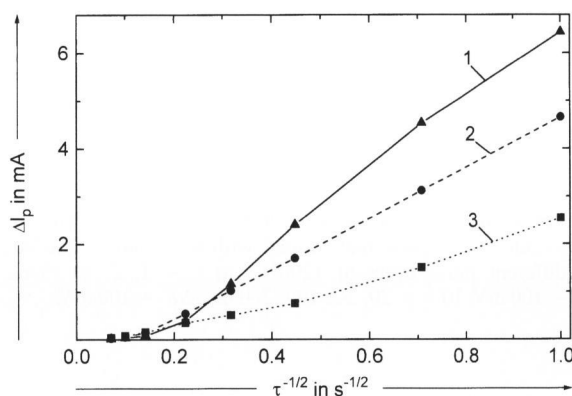


Figure 7. Peak currents of the first peak as a function of the pulse time for different contents of  $\text{Na}_2\text{SO}_4$ : 0.070 mol% (curve 3), 0.163 mol% (curve 2), 0.240 mol% (curve 1).  $\vartheta = 1200^\circ\text{C}$ ,  $\Delta E = 100$  mV.

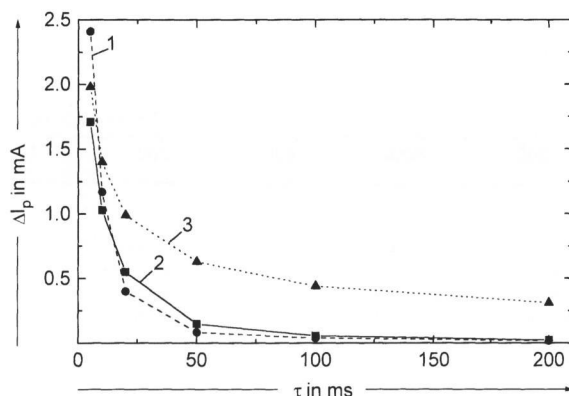


Figure 8. Peak currents of the first peak as a function of the pulse time for different contents of  $\text{Na}_2\text{SO}_4$ : 0.163 mol%, extrapolated from step times 1 and 2 ms (curve 3); 0.163 mol%, recorded (curve 2); 0.240 mol%, recorded (curve 1).  $\vartheta = 1200^\circ\text{C}$ ,  $\Delta E = 100$  mV.

4b were optimized in such a manner that curves 3 and 4 are in maximum agreement using least square approximation. The half-width of curve 4a corresponds to a four-electron step, while that of curve 4b is attributed to a two-electron step. At potentials higher than  $-600$  mV, excellent agreement between curves 3 and 4 is observed. Therefore, the first peak is related to equation (8) and the second one to equation (9). The attribution of these two peaks has previously been reported in [11]. The increase of the current of curves 1 and 2 at potentials lower than  $-600$  mV is due to the decomposition of the glass melt, forming elemental silicon or platinum silicide at the surface of the electrode. The additional presence of sulfide (curve 1) possibly promotes the forming of silicon or silicide. Therefore, at potentials lower than  $-600$  mV the theoretical curve 4 and the measured curve 3 show a discrepancy.



Figure 7 shows the pulse time dependence of the peak current of the first peak after correction for the matrix curve for different quantities of  $\text{Na}_2\text{SO}_4$ . According to equation (7), the peak current should linearly depend on  $\tau^{-1/2}$ . As this obviously is not the case, another, non-diffusional effect must take part in the electrode reaction. To elucidate this effect, figure 8 shows the peak currents of the first peak as a function of the pulse time. For pulse times higher 10 ms, the peak currents of the glass melt containing 0.240 mol%  $\text{Na}_2\text{SO}_4$  are lower than those for a concentration of 0.163 mol%  $\text{Na}_2\text{SO}_4$ . From the peak currents at pulse times of 1 and 2 ms, peak currents for higher pulse times were calculated assuming a decrease according to  $\tau^{-1/2}$  (see equation (7)). In figure 8, it can be observed that the peak currents measured in glass melts containing 0.163 and 0.240 mol%  $\text{Na}_2\text{SO}_4$  are distinctly lower than the theoretical peak currents of a glass melt doped with 0.163 mol%  $\text{Na}_2\text{SO}_4$ . On summarizing, it can be stated that longer pulse times and higher quantities of sulfate are leading to an overproportional decrease of the attributed peak currents. Higher concentrations of  $\text{Na}_2\text{SO}_4$  and longer pulse times lead to an increasing formation of elemental sulfur on the surface of the working electrode, which results in a, at least partial desactivation of the working electrode, supposedly caused by a sulfur layer deposited on the surface.

Figure 9 (curve 1) shows a voltammogram recorded in a glass melt doped with 0.163 mol%  $\text{Na}_2\text{SO}_4$ . Curves 2a and b represent the cathodic and the anodic half-waves, respectively. Curve 2 is the sum of curves 2a and 2b. In the range between  $-200$  and  $-350$  mV, curve 2 shows a well-pronounced peak. This means that during the cathodic half-wave, more  $\text{SO}_2$  is reduced to  $\text{S}^0$  than during the anodic half-wave  $\text{S}^0$  is oxidized back to  $\text{SO}_2$ . The surface of the working electrode dipped into the

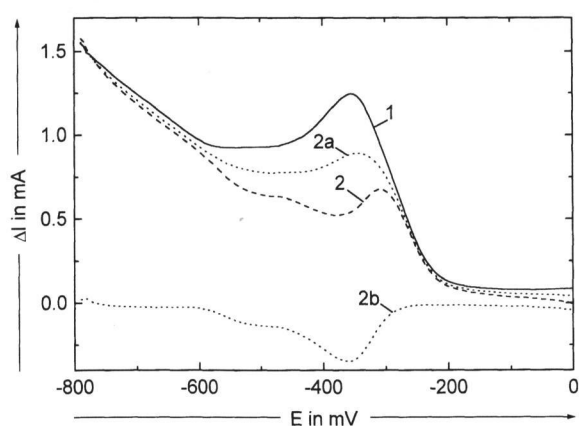


Figure 9. Square-wave voltammogram recorded in a soda-lime-silica glass melt doped with 0.163 mol%  $\text{Na}_2\text{SO}_4$  (curve 1); curve 2a: cathodic half-wave, curve 2b: anodic half-wave, curve 2: curve 2a + curve 2b.  $\vartheta = 1200^\circ\text{C}$ ,  $\tau = 10$  ms,  $\Delta E = 100$  mV.

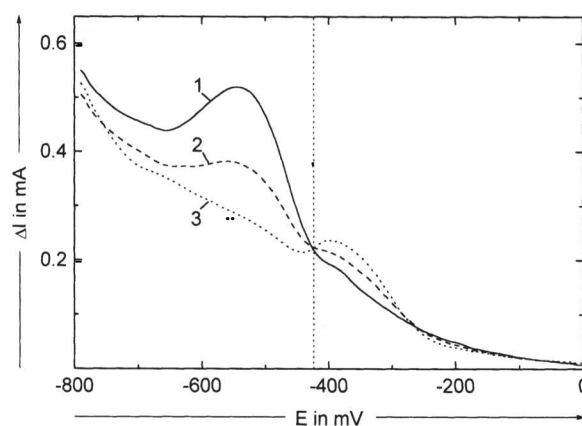


Figure 11. Cathodic half-waves recorded in soda-lime-silica glass melts doped with different contents of  $\text{Na}_2\text{SO}_4$ : 0.070 mol% (curve 3), 0.163 mol% (curve 2), 0.240 mol% (curve 1).  $\vartheta = 1200^\circ\text{C}$ ,  $\tau = 100$  ms,  $\Delta E = 100$  mV.

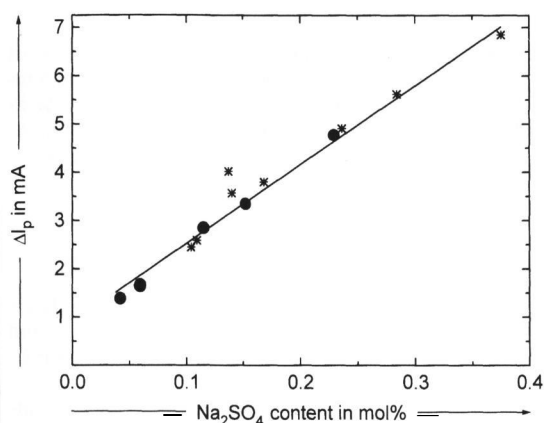


Figure 10. Peak currents of the first peak ( $\tau = 2$  ms) as a function of the  $\text{Na}_2\text{SO}_4$  content.  $\vartheta = 1200^\circ\text{C}$ ,  $\Delta E = 100$  mV. \*: glass melts doped with  $\text{Na}_2\text{SO}_4$  and  $\text{Fe}_2\text{O}_3$ , ●: glass melts doped with  $\text{Na}_2\text{SO}_4$ .

glass melt was about  $14 \cdot 10^{-6} \text{ m}^2$ . The van-der-Waals radius of a sulfur atom is  $180 \cdot 10^{-12} \text{ m}$ . To cover an area of  $14 \cdot 10^{-6} \text{ m}^2$  with a monomolecular sulfur layer  $2.3 \cdot 10^{-10}$  moles are necessary. Proceeding from the voltammograms recorded with pulse times of 1, 2, 5 and 10 ms, the amount of sulfur formed on the surface of the working electrode was evaluated to be around  $1.7 \cdot 10^{-9}$  mol for a concentration of 0.163 mol%  $\text{Na}_2\text{SO}_4$  sulfate and a pulse time of 10 ms. For longer pulse times and higher concentrations, this amount would be much higher. Hence, it could be assumed that the surface of the working electrode is covered with a film of sulfur if longer pulse times were applied. To determine the sulfur content in the glass melt, it is obviously more promising to use short pulse times. Figure 10 shows the peak currents of the first peak (after peak correction) as a function of the  $\text{Na}_2\text{SO}_4$  content (pulse time 2 ms). A good linear correlation is given. Only in

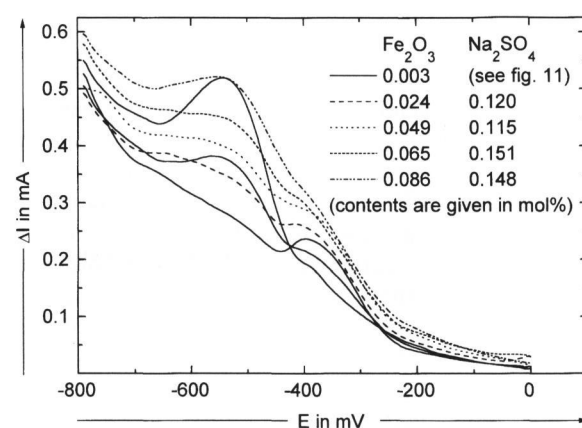


Figure 12. Cathodic half-waves recorded in soda-lime-silica glass melts doped with different contents of  $\text{Na}_2\text{SO}_4$  and  $\text{Fe}_2\text{O}_3$ .  $\vartheta = 1200^\circ\text{C}$ ,  $\tau = 100$  ms,  $\Delta E = 100$  mV.

the glass melts containing  $>0.06$  mol%  $\text{Fe}_2\text{O}_3$  deviations from the regression line could be observed. In technical white glasses the iron concentration is usually  $<0.05$  mol%  $\text{Fe}_2\text{O}_3$ . Therefore, it is possible to determine the sulfur content in white glasses using a pulse time of 2 ms with fairly good accuracy. Figure 11 shows the cathodic half-waves for different concentrations of sulfate. At a potential of  $-425$  mV, the currents measured for different concentrations are almost equal at this temperature of  $1200^\circ\text{C}$  and at  $\tau \geq 100$  ms. This behavior is supposedly caused by the desactivation of the working electrode by sulfur. In principle, the same behavior is also observed applying other temperatures or using other glass melt compositions. Figure 12 shows voltammograms for glass melts doped with different concentrations of sulfur and iron. By contrast to figure 11, the currents obtained at a potential of  $-425$  mV are notably



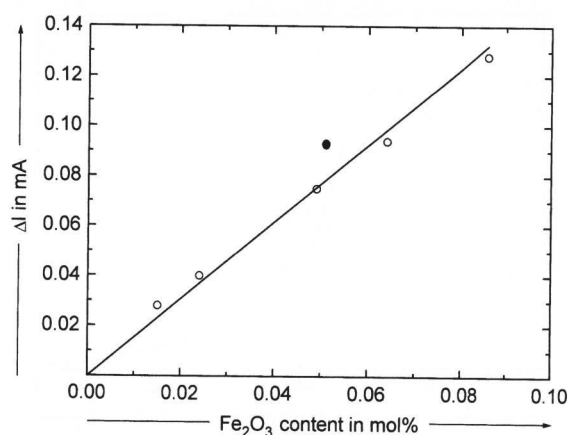


Figure 13. Current differences at  $-425$  mV of figure 12 as a function of the  $\text{Fe}_2\text{O}_3$  content.  $\vartheta = 1200^\circ\text{C}$ ,  $\tau = 100$  ms,  $\Delta E = 100$  mV. ○: glass melts doped with  $\text{Na}_2\text{SO}_4$  and  $\text{Fe}_2\text{O}_3$ , ●: glass melt doped with only  $\text{Fe}_2\text{O}_3$ .

different and depend on the iron content. Figure 13 shows the difference of the currents measured in iron-doped glass melts and those containing only trace quantities of iron ( $0.003$  mol%  $\text{Fe}_2\text{O}_3$ ) at this potential ( $-425$  mV) as a function of the  $\text{Fe}_2\text{O}_3$  content (○ in figure 13). A linear correlation is observed. In order to illustrate, whether these differences are solely caused by iron, the difference between the currents measured in a glass melt doped with  $0.05$  mol%  $\text{Fe}_2\text{O}_3$  and a glass melt without any polyvalent elements is also shown in figure 13 (●) for a potential of  $-425$  mV. The values are in the same range. Therefore, it is possible to determine in-situ the concentration of iron in melts of white glasses also if sulfur is in excess in the melts.

## 5. Conclusions

Sulfur in soda–lime–silica glasses can easily be detected by SWV. Two characteristic peaks are visible at pulse times  $>10$  ms and concentrations of  $>0.2$  mol%  $\text{Na}_2\text{SO}_4$ . The peak currents and the shape of the peaks are strongly influenced by the pulse time and the concentration of sulfate. The content of sulfur can be determined with the aid of short pulse times (e.g. 2 ms). For longer pulse times and higher concentrations, it is assumed that the surface of the working electrode is deactivated by a film of elemental sulfur. For longer pulse times the cathodic half-waves measured in sulfur-containing melts exhibit at a certain potential a constant value for the current. If these melts are additionally doped with iron, the currents at this potential are rising almost proportional to the iron concentration. This effect can be used to determine the iron content in glass melts even if sulfate is in excess.

## 6. Symbols

$A$	area in $\text{m}^2$
$b$	variable
$c_0$	concentration in $\text{mol}/\text{m}^3$
$D$	diffusion coefficient in $\text{m}^2/\text{s}$
$E_0$	standard potential in V
$E_m$	applied potential in V
$E_{p/2}$	half-width in V
$\Delta E$	amplitude in V
$\delta E$	pulse increment
$F$	Faraday constant
$I_j$	current in A
$\Delta I$	differential current in A
$\Delta I_p$	peak current in A
$j$	index number
$K(T)$	equilibrium constant
$m$	index number
$Q_m$	variable
$R$	universal gas constant
$T$	temperature in K
$z$	number of electrons
$\tau$	pulse time in s

\*

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