

VOLTAMMETRIC MEASUREMENT OF THE Pt ELECTRODE CAPACITY AND THE DETERMINATION OF THE POLYVALENT IONS DIFFUSION COEFFICIENTS IN THE GLASS MELT

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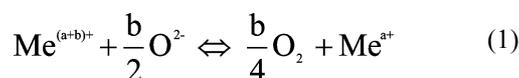
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The cyclic voltammetry has been used to investigate the kinetic behaviour of polyvalent ions in a silicate glass melt within a temperature range from 900 to 1300°C. Standard potentials of oxidation-reduction reactions of the polyvalent elements present in glass melt as refining or colouring agents (Fe and Cr) were measured. Diffusion coefficients of Fe³⁺ and Cr³⁺ ions in the melt were calculated from the shape of cyclic voltammograms. Their values were found from 10⁹ to 10⁷ cm²s⁻¹ respectively. Double layer capacity (480 μF/cm²) measured in the basic glass without of polyvalent elements corresponds to the high concentration of ions in the melt.

INTRODUCTION

Polyvalent elements, which are present in glass as refining or colouring agents, are tightly bonded with redox state of glass (partial pressure of physically dissolved oxygen) and subsequently with many important properties of glass, e.g., refining behaviour, solubility of gasses as well as the mechanical properties of glass melt. The oxidation-reduction reactions of polyvalent elements can be described by the reaction:



where Me means a polyvalent element, O²⁻ means chemically bonded oxygen and O₂ means physically dissolved oxygen. The partial pressure of physically dissolved oxygen is measurable thermodynamic quantity by the electrochemical potentiostatic method.

The various electrochemical techniques, especially cyclic or square wave voltammetry were used to investigate the behaviour of polyvalent ions in a glass melt [1-8], in some cases in high temperature range - up to 1500°C [9]. These electrochemical methods are suitable for determining the standard potential (E°) of a redox pair. The standard potential is related to equilibrium constant (K) of the redox reactions.

Kinetic behaviour and the structure characterisation of polyvalent elements present in the glass can be expressed through the diffusion coefficients and oxidation-reduction characteristics. At high temperatures the redox ratio of polyvalent element can be controlled by diffusion.

In series of papers, Claussen, Gerlach, Rüssel and co-workers [3,4,8-12], measured diffusion coefficients of polyvalent elements as a function of temperature in silicate melts using square-wave voltammetry. A linear correlation between $\log D$ and $1/T$ for all polyvalent elements and glass melt compositions was found in the temperature range of 700 to 1500°C. In further works the thermodynamics of polyvalent ions were studied and linear dependence of standard potential on temperature was found in the temperature range from 1000 to 1600°C [13,14].

In this work the cyclic voltammetry wiring applying triangular wave of potential between the working and reference electrodes and the application of three-electrode cell (the Pt working, reference as well as auxiliary electrodes) has been used. The diffusion coefficients and standard electric potential E° of polyvalent elements have been measured. Because of using the three electrode system, where the reference electrode is in the form of Pt wire, the routine determination of Pt electrode double layer capacity has been provided in the three component SiO₂-Na₂O-CaO glass.

The temperature dependence of diffusion coefficients of the polyvalent ions (iron and chromium) is one of characteristic structure parameters in given glass melt. The diffusion coefficients of Fe³⁺ and Cr³⁺ ions have been calculated by using the voltammetry measurements in a modified soda-lime-silica glass melt. Modified glasses were doped by two additions of the polyvalent oxides (Fe₂O₃, Cr₂O₃). The cyclic voltammetry allowed a rough estimation of the Pt electrode double layer capacity as well. All electrochemical measurements have been provided at high temperatures (900 - 1300°C).

THEORETICAL PART

Behaviour of an inert electrode

Let us consider an electrode in an electrolyte. No electrochemical reaction of electrode material with an electrolyte is expected in this case. A noble metal electrode and an electrolyte not containing reactive species is an example of a such system. The only reactions possible are the decomposition of the electrolyte itself either cathodically or anodically. In the case of glass electrolytes, evolution of gaseous oxygen and reduction of silicon or alkali metals should be expected as the possible reactions.

Measurement of the Pt electrode capacity

If the electrode potential increases linearly in time with the scan rate ν (V/s), then the electrode capacity C requires a charging current I_c and if it is measured, then permits the estimation of the capacity itself in this manner

$$I_c = C \cdot dE/dt = C \cdot \nu \quad (2)$$

Measurement of the Fe and Cr diffusion coefficients

The polyvalent ions can be present in two or more forms, which differ in their valency state. At voltammetric condition, when a potential increases linearly, the current begins to flow if the potential moves further from the reversible potential. The current - potential profile exhibits a peak of characteristic shape. Randles - Ševčík - Matsuda equation can be used for evaluation of the diffusion coefficient D :

$$I_p = 0.4463 n F A C_o (n F/R T)^{1/2} \nu^{1/2} D^{1/2} \quad (3)$$

from the current of the peak I_p , the electrode surface area A , ion concentration C_o , scan rate ν and general constant F , R and temperature T . The parameter n is the number of electrons involved in the reaction (denoted as the quantity b in the equation (1)).

EXPERIMENTAL PART

Glass preparation

The measurement of the Pt electrode capacity has been done using three-component glass (SiO₂ - Na₂O - CaO) without electrochemically reactive ions. The composition of this glass was: 74 mol% SiO₂, 16 mol% Na₂O, 10 mol% CaO. The batch has been prepared from the pure chemicals and melted in Pt/Rh crucible for 6 hours at 1350°C. Prepared glass has been crushed to small pieces and melted again for 4 hours.

The glasses containing polyvalent ions were prepared from the pure chemicals by melting at 1450°C for 2.5 hours in laboratory conditions and by additions of Fe or Cr species. The basic composition of batch is presented in table 1. The concentration of Fe₂O₃ was 1 and 2 wt.% of glass and Cr₂O₃ to the concentration 0.5 and 1 wt.% of glass, respectively. The additions of polyvalent species are presented in tables 2 and 3.

Table 1. The composition of modified glass in weight (X_w) and molar (X_m) %.

Oxide	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	K ₂ O
X_w (wt.%)	72.54	14.16	8.70	3.85	0.56	0.15
X_m (mol%)	71.30	13.47	9.26	5.64	0.32	0.094

Table 2. The addition of Fe species in modified glass.

Glass	Fe ₂ O ₃ (wt.%)	Total conc. of Fe species (wt.%)	(mol%)	C_{Fe} (mol/m ³)
Fe - 1.0	1	0.70	0.73	286.5
Fe - 2.0	2	1.40	1.46	573

Table 3. The addition of Cr species in modified glass.

Glass	Cr ₂ O ₃ (wt.%)	Total conc. of Cr species (wt.%)	(mol%)	C_{Cr} (mol/m ³)
Cr - 0.5	0.5	0.34	0.37	150.6
Cr - 1.0	1.0	0.68	0.76	301.2

All together, the six kinds of glass have been prepared. The basic glass, without tested polyvalent elements, has been used as blank sample and its data were subtracted from the measured lines of glasses containing polyvalent ions in the case of diffusion.

Cyclic voltammetry setting

The measuring equipment includes the melting furnace (up to 1500°C) where a Pt/Rh crucible is placed, a potentiostat, a PC control unite (see scheme at figure 1) and a glass level signal box.

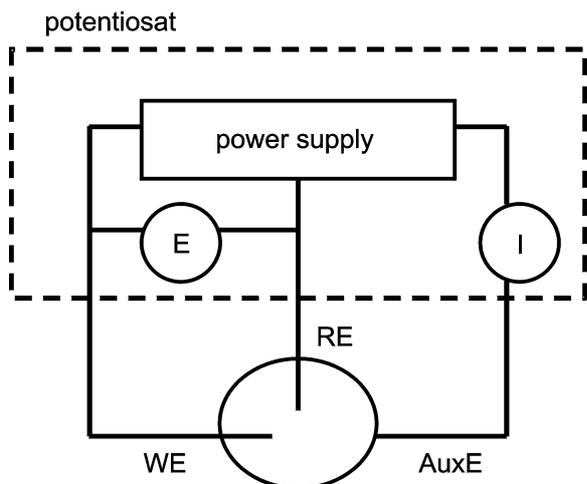


Figure 1. Wiring scheme for cyclic voltammetry measurements in glass melt.

The measuring cell has been constructed as the three-electrode system. The working and reference electrodes have the form of Pt wires with diameter of 1 mm and the counter electrode is directly the Pt/Rh crucible contacted by Pt wire under their bottom. (See detail in figure 2). The electrodes have been dipped approximately 2 cm into a glass melt. The area of the working electrode (A) has been calculated from the dip-in length, which has been adjusted using the glass level signal box.

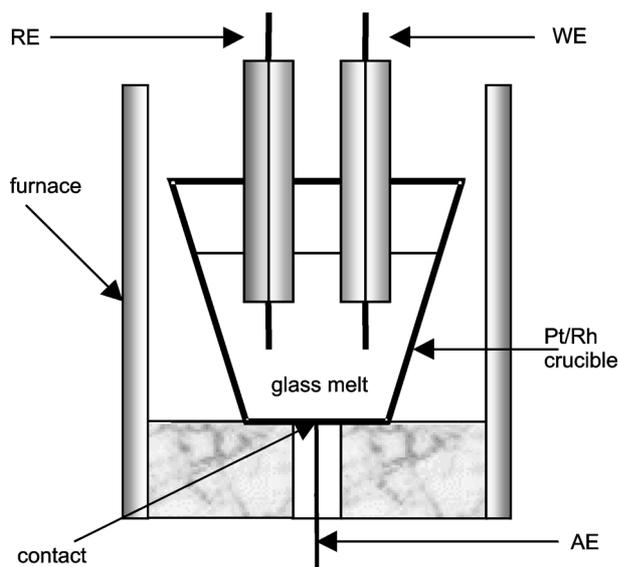


Figure 2. Detailed arrangement inside the furnace. RE - reference electrode (Pt wire, 1 mm in diam.), WE - working electrode (Pt wire, 1 mm in diam.), AE - auxiliary electrode (Pt wire, 0.5 mm in diameter which is in contact with Pt/Rh crucible).

Diffusion coefficients

The measurements of diffusion coefficients have been done using modified glass with addition of Fe or Cr species according tables 2 and 3. The batches have been prepared from the pure chemicals and melted in Pt/Rh crucible for 6 hours at 1350°C. Prepared glasses have been broken down to small pieces and melted again for 4 hours. The glasses were then used for diffusion coefficients determination for both cations by cyclic voltammetry. Anodic and cathodic parts of cyclic voltammograms were used for the calculation of anodic (D_a) and cathodic diffusion (D_c) coefficients.

Double layer capacity of Pt electrode

The measurement of the Pt electrode capacity has been done using three-component basic glass (SiO_2 - Na_2O - CaO) without electrochemically reactive ions. The batch has been prepared from the pure chemicals and melted in Pt/Rh crucible for 6 hours at 1350°C. Prepared glass has been broken down to small pieces and melted again for 4 hours.

Because of using the three electrode system, where the reference electrode is in the form of Pt wire, the routine determination of Pt electrode electric capacity has been provided.

RESULTS AND DISCUSSION

Iron containing glass

In figure 3, the voltammetric curves of the glass containing 2 wt.% of Fe_2O_3 at various scan rates are plotted. As the diffusion controlled process was expected, the coordinates in units EF/RT and $I\nu^{-1/2}$ were used. The redox wave is well developed there and its height and position is rather independent on the scan rate. The control by diffusion is confirmed in this way.

Chromium containing glass

On contrary to figure 3, the behaviour of chromium containing glass (see figure 4) is not so easy to understand. The voltammetric wave is more complex and the cathodic reduction branch is better developed and more constant. Most likely it is due to the fact that there is less Cr^{4+} ions at temperatures over 1000°C, and only these generated by previous anodic oxidation participate in the process of subsequent reduction.

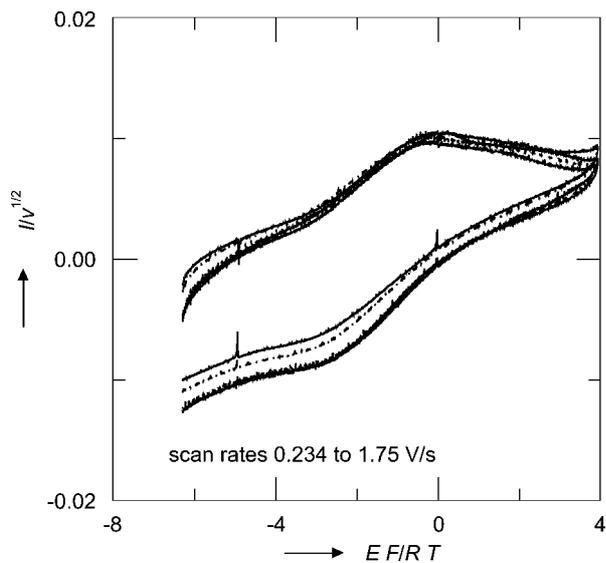


Figure 3. Cyclic voltammograms of 2 wt.% Fe_2O_3 in modified glass melt at 1200°C and different scan rates from 0.234 to 1.75 V/s.

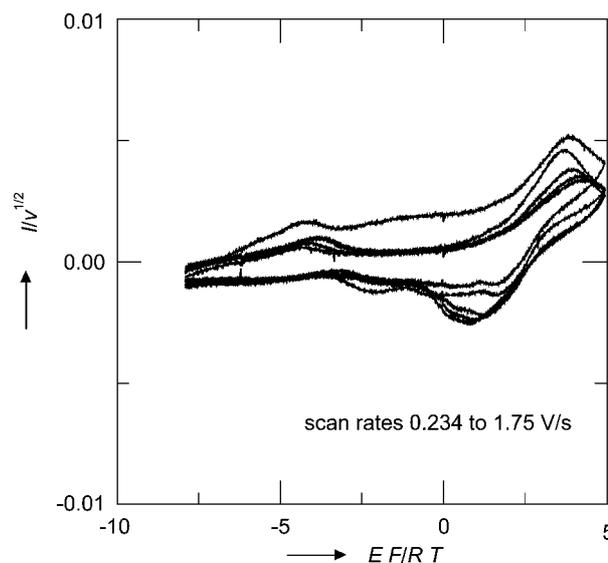


Figure 5. Cyclic voltammograms of basic unmodified glass melt at 900°C and different scan rates from 0.234 to 1.75 V/s.

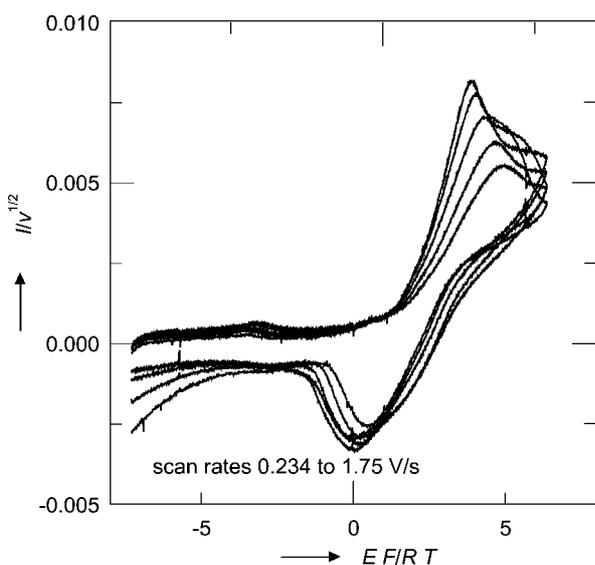


Figure 4. Cyclic voltammograms of 1 wt.% Cr_2O_3 in modified glass melt at 900°C and different scan rates from 0.234 to 1.75 V/s.

Basic glass

For comparison, the voltammetry in the basic glass (without polyvalent ions) was measured (see figure 5, in the same scales). We can see that the main redox wave observed there is much weaker and shifted to the zero potential of O_2 electrode.

Double layer capacity

The double layer capacity was estimated from the width of the voltammograms in pure glass with negligible amount of dopants. The value of potential -0.2 V (against O_2 reference electrode) was chosen. Capacity $C = 480 \mu\text{F}/\text{cm}^2$ at 900°C was found in this way.

Diffusion coefficients

Comparison of data measured with those from literature is shown in table 4. Researchers who measured the diffusion coefficient of polyvalent elements in glass melt used the square wave voltammetry [1-4] or cyclic voltammetry with triangular shape of potential [5].

Table 4. The diffusion coefficients of Fe^{3+} and Cr^{3+} ions in the studied glasses.

Dopant (wt.%)	T ($^\circ\text{C}$)	D_a ($10^{-7} \text{ cm}^2/\text{s}$)	D_c ($10^{-7} \text{ cm}^2/\text{s}$)	D [lit.] ($10^{-7} \text{ cm}^2/\text{s}$)
Fe_2O_3 (1)	1200	1.32	1.1	4.7
Fe_2O_3 (1)	1300	2.02	1.44	10
Fe_2O_3 (2)	900	0.073	0.0183	0.02
Fe_2O_3 (2)	1100	1.072	0.711	1.47
Cr_2O_3 (0.5)	1150	0.437	-	1.38
Cr_2O_3 (0.5)	1300	3.114	1.90	2.19
Cr_2O_3 (1)	1000	0.071	0.067	0.0927
Cr_2O_3 (1)	1150	0.194	0.14	0.162
Cr_2O_3 (1)	1300	1.13	0.62	2.19

Experiments have been provided in soda-lime-silica glass samples in the temperature range from 700 to 1300°C. The three electrodes settings have been used, where the working electrode has most often the shape of Pt wire with diameter from 0.6 to 1 mm. Counter electrodes were in the shape of the Pt plate and reference electrodes were used in the form Pt wire [5] or ZrO₂ air flushed sensor [6]. Anodic D_a and cathodic diffusion coefficients D_c are differentiated in this paper.

CONCLUSIONS

The possibility to investigate glass melts by electrochemical instrumentation was verified with success. The behaviour of Fe containing melt corresponds to a redox system in which an one-electron reaction occurs. More complex is the behaviour of the chromium glass melt as an evidence of at least two successive steps appeared. The values of diffusion coefficients were found in reasonable limits of 10^{-9} to 10^{-7} cm²/s, the higher values being found in the case of Fe ions. This is clearly understandable from the fact that chromium can enter the basic glass structure in the form of heteropolyanions the mobility of which can be lower. The method is worth of further investigations. The cell will be improved using ZrO₂ air flushed sensor [9] as reference electrode.

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VOLTAMETRICKÉ MĚŘENÍ KAPACITY ELEKTRICKÉ DVOJVRSTVY PLATINOVÉ ELEKTRODY A STANOVENÍ DIFUZNÍCH KOEFICIENTŮ POLYVALENTNÍCH IONTŮ VE SKELNÉ TAVENINĚ

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Kinetické chování polyvalentních iontů ve sklovině bylo studováno za pomoci cyklické voltametrie v rozmezí teplot 900-1300°C. Byly měřeny standardní potenciály oxidačně-redukčních reakcí polyvalentních prvků, které ve sklovině plní úlohu čeriv nebo barvicích látek. Z tvaru cyklických voltogramů byly vypočteny hodnoty difúzních koeficientů pro ionty Fe³⁺ a Cr³⁺ v řádu 10^{-9} - 10^{-7} cm²/s. Zjištěná kapacita elektrické dvojvrstvy, 480 μF/cm², odpovídá koncentraci iontů v tavenině.