Determination of iron, nickel and cobalt in glass melts : a comparison of non steady state and steady-state techniques.

J. De Strycker[a,b], P. Westbroek[a], E. Temmerman[a]
[a]*Ghent University, Department of Analytical Chemistry, Krijgslaan 281 S12, B-9000 Gent Belgium*
[b]*Research assistant of the Fund for Scientific Research-Flanders (Belgium, FWO),*

The determination of polyvalent elements in glass melts has been the subject of many different studies during the last decades. Electrochemical techniques proved to be very efficient for this purpose. However, most of these methods were transient techniques resulting into time dependent electrode signals. Recently, a rotating disc configuration for molten glass environment was developed [1]. This configuration gives rise to time independent electrode signals, which can be used for continuous concentration determination. In this work the determination of the concentration of the polyvalent elements iron, nickel and cobalt in glass melts was performed at a rotating platinum disc electrode in combination with chronoamperometry in a wide concentration and temperature range. Alternatively, square wave voltammetry at a static platinum disc electrode was used. The current signals for both techniques were analysed as a function of the concentration. For the three species a linear relationship was obtained. The sensitivities and detection limits were compared at different temperatures.

Introduction

During the past decades much research work has been executed on the study of polyvalent elements in glass. Often these studies had to do with the oxidation-reduction equilibria of these polyvalent elements for very different glass compositions. Electrochemical techniques such as linear sweep voltammetry, cyclic voltammetry, pulse voltammetry, chronopotentiometry, impedance spectroscopy and square wave voltammetry have proven to be very useful for measurements in molten glass environments. However, most of these methods are transient techniques resulting into time dependent electrode signals.

In aqueous solutions, time independent electrode signals showed many advantages in the study of the oxidation-reduction behaviour and the properties of polyvalent elements. An expected advantage of time independent electrode signals in glass melts is also the continuous and on-line determination of the concentration of metal ions. This opens new perspectives concerning the on-line monitoring and automatic control of glass production processes.

In this work an electrode configuration, which gives rise to time independent electrode signals in glass melt environments was tested. The results were compared with data obtained from square wave voltammetric experiments.

Experimental

In figure 1 a schematic drawing of the experimental set-up is shown. The furnace was home modified with a DC power supply to avoid distortion of the original AC power supply on the electrochemical experiments. A high-torque variable speed motor was used on top to obtain and control a wanted rotation rate. The working disc electrode consists of a platinum rod fixed in an alumina tube with a ceramic binder in such a way that only the cross section of the rod is exposed to the glass melt. Before each experimental series a pre-

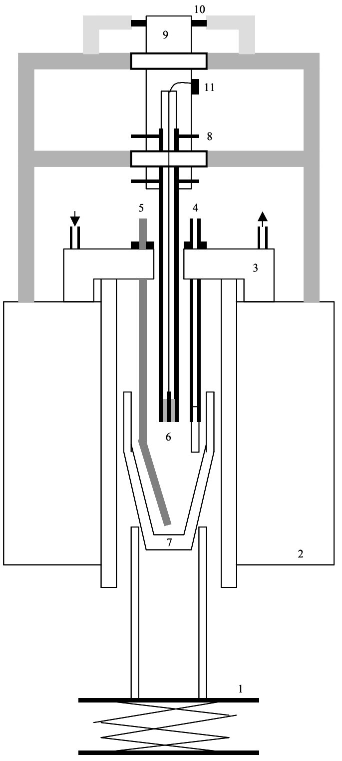

Figure 1. Schematic drawing of the rotating disc configuration. 1: lift, 2: furnace, 3: cooling flange, 4: reference electrode, 5: counter electrode, 6: working electrode, 7: crucible, 8: press screws, 9: copper holder, 10: contact brushes, 11: contact screw.

treatment of three polishing steps and an ultrasonic cleaning step was introduced to obtain a fresh surface. The counter electrode is a long small platinum foil, which is stuck to the wall of the electrochemical cell. The reference electrode is a zirconia probe flushed with air. All potentials mentioned refer to this reference.

The basic chemical composition (mass %) of the glass used is: 64 % SiO_2, 18 % Na_2O, 8 % CaO, 5 % B_2O_3, 3 % MgO, 1 % K_2O and 1 % Al_2O_3. After preparing this glass from analytical grade reagents, it was crushed and a certain amount of a polyvalent element added and melted in the electrochemical cell. The cell consisted of a 99.7 % pure aluminium oxide crucible.

Results and discussion

The first polyvalent element studied with the rotating disc electrode was iron. Therefore melts containing 2.5 up to 10 mass% Fe_2O_3 were prepared. In a normal linear sweep voltammogram at a static disc electrode two reduction waves can be observed, one assumed to correspond with the Fe(III) to Fe(II) reduction and the other one with the reduction of Fe(II) to metallic iron.

For testing the rotating disc electrode configuration a chronoamperometric measurement at a potential (-0.9 V vs. zirconia probe) slightly more negative than the peak potential of the Fe(III) to Fe(II) linear sweep reduction wave was performed. During rotation a time-independent steady state current is obtained after 150 s. Results of these experiments were shown in figure 2 for four different rotation rates. The highest rotation rate gives rise to the highest limiting current as predicted by the Levich-equation[2]. When these limiting currents were drawn versus the concentration of the iron in the melt, a linear relationship is obtained over the whole investigated concentration range (2.5 up to 10 mass% Fe_2O_3). This relationship is shown in figure 3. At a rotation rate of 1000 rpm and 1473 K a detection limit of 0.16 ± 0.01 mass% and a sensitivity of 0.63 ± 0.01 mA massa%$^{-1}$ is obtained with the rotating disc electrode for the determination of Fe(III) in the melt. At other rotation rates the detection limit is always higher and the sensitivity lower. The rotation rate of 1000 rpm is also the optimal value for calibration curves at lower temperatures.

In a second series of experiments, cyclic and square wave voltammetric curves were recorded in melts containing the same amounts of iron as for the experiments with the rotating disc electrode. A plot of the obtained peak current versus the iron concentration is given in figure 4. It can be seen that again a linear relationship is obtained over the entire investigated concentration range for the optimal frequency and scan rate of 20 Hz and 200 mV s^{-1} respectively. For square wave voltammetry a detection limit of 0.11 ± 0.01 mass% is

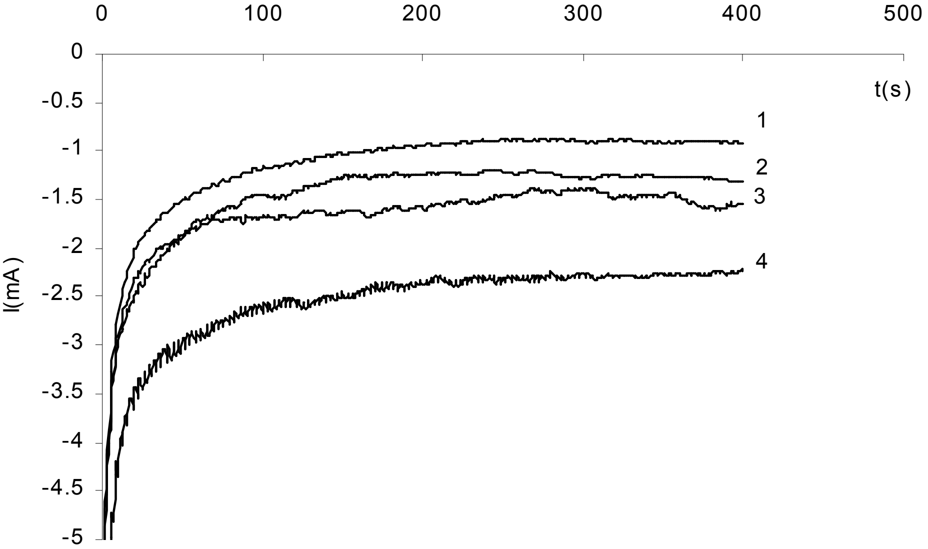

Figure 2 Chronoamperometric experiments at a platinum rotating disc electrode at –0.9 V and 1200 °C with electrode rotation rates of (1)250, (2)440, (3)750 and (4)1000 rpm.

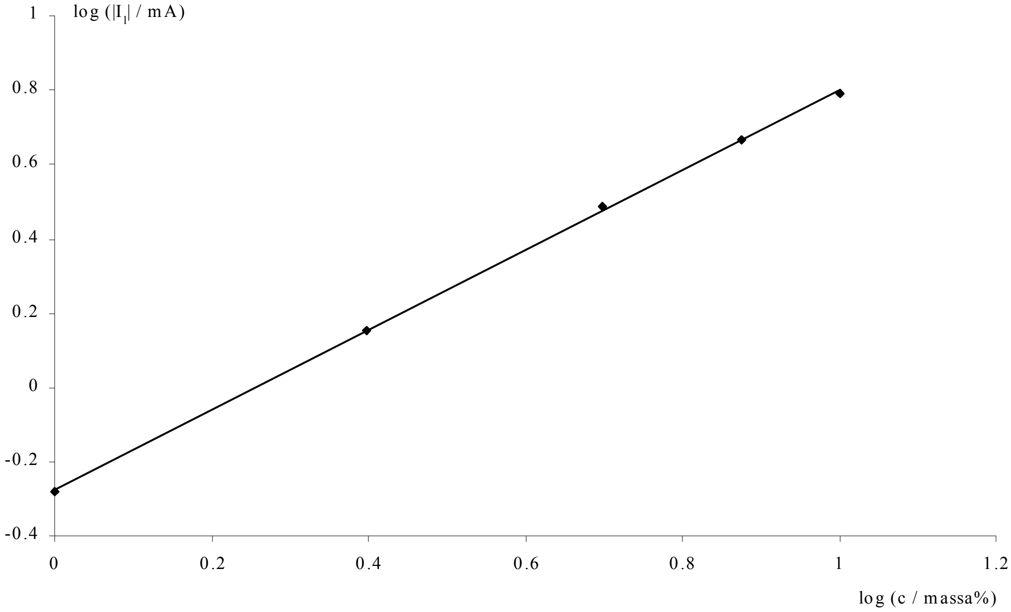

Figure 3 Calibration plot for detection of Fe(III) at a rotating disc electrode at 1473 K and 1000 rpm.

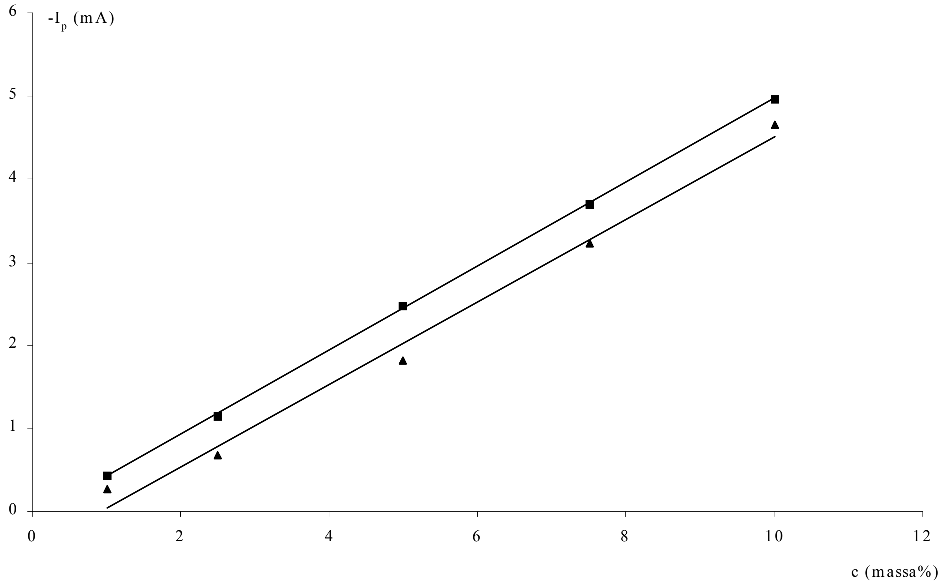

Figure 4 Plot of the peak current versus concentration of Fe_2O_3 at 1473 K obtained with (■) square wave voltammetry, f = 20 Hz en (▲) cyclic voltammetry, v = 200 mV s^{-1}.

obtained. This is five times lower than for cyclic voltammetry. The sensitivity is comparable, about 0.50 ± 0.01 mA massa%$^{-1}$.

For the polyvalent elements nickel and cobalt were the same type of experiments carried out in a concentration range of 0 up to 2.5 mass%. Also for these elements a linear calibration plot is obtained over the investigated concentration range with the rotating disc electrode as well as with square wave and cyclic voltammetry. The sensitivity and detection limits were comparable to those obtained for glass melts doped with iron.

Conclusion

In this work the results obtained at a rotating disc electrode were compared with square wave and cyclic voltammetric data. A linear calibration plot was found for iron, nickel and cobalt in the investigated concentration ranges. With the aid of the rotating disc electrode the detection limit is in the same order of magnitude as for square wave voltammetry but considerably lower than for cyclic voltammetry. The best sensitivity is obtained with the rotating disc electrode. The rotating disc electrode can be used as a detection method in the analysis of glass melts and opens new possibilities for continuous determination of metal ions under steady-state conditions.

---

[1] De Strycker, J.; Westbroek, P.; Temmerman, E. *J. Non-Cryst. Solids,* **2001***, 289,* 106-112.

[2] Bard, A., J.; Faulkner, L., R. *Electrochemical methods Fundamentals and Applications*, John Wiley & Sons, New York, 2001.