Voltammetric methods for determining polyvalent ions in glass melts

Eberhard Freude
Hahn-Meitner-Institut Berlin GmbH, Berlin (FRG)

Christian Rüssel
Institut für Werkstoffwissenschaften, Lehrstuhl III: Glas und Keramik, Universität Erlangen-Nürnberg, Erlangen (FRG)

Voltammetry is an in situ technique to investigate redox equilibria in glass melts. Its sensitivity and resolution have been improved by introducing the square-wave voltammetry. The results reported in this paper clearly demonstrate the superiority of this method over the cyclic voltammetry, which had been used so far in glass melts.

1. Introduction

A variety of properties of a glass or a glass melt are influenced by the oxidation state, especially the color. Normally a desired oxidation state is achieved by adjusting the batch composition [1]. This requires an exact analysis of all raw materials including impurities and their oxidation states. A further difficulty is given by the interaction of the melt with the atmosphere and the bubbling gases. In the past, a check was only possible by analyzing the solid glass chemically or physically. Since a few years ago it has become possible to measure the oxygen activity in the melt [2], but it is necessary to know more about the redox equilibria of polyvalent ions at melt conditions to completely describe the oxidation state.

Glass melts are electrolytes. Therefore, electrochemical techniques, developed for aqueous solutions, can be used for investigations of redox equilibria in glass melts, too. Some of these techniques, especially cyclic voltammetry, have recently been applied to glass melts [3 and 4]. It is the aim of this work to further develop voltammetry to improve sensitivity and resolution.

2. Theory

Voltammetry is the general name for measurements of current-potential curves under potential control, i.e., a definite potential varied with time is applied to the working electrode of an electrochemical cell and the resulting current is registered. The following reaction occurs at the working electrode:

\[ \text{Me}^{+\, z^+} + z^+ e^- = \text{Me}^{(z-2)+} \]

In this paper two techniques will be considered, i.e., cyclic voltammetry (CV) and square-wave voltammetry (SWV).

In CV the applied potential shows a triangular wave form. The recorded curve exhibits a cathodic and an anodic current peak (see figure 1a). The normal potential \( E_n \) can be calculated from the peak potential \( E_p \) according to equation (1) — all symbols with the usual meaning:

\[ E_p = E_n \pm 1.1 \left( \frac{R T}{z F} \right) \]

It is seen from equation (1) that with increasing temperature the peak separation between cathodic and anodic peak also increases. This is accompanied by a broadening of the peaks, thus reducing sensitivity and resolution.

SWV, though basically developed in the late 50s [5], is a relative new technique in application, for it capitalizes on the evolution in electronics. The applied potential is a staircase ramp superimposed by a fast rectangular wave, thus needing quick data handling. The current is measured at the end of every half wave and differentiated. The advantage of this measuring method is a much higher sensitivity and resolution of the peaks. The peak potential equals the normal potential. A short description of both methods [6] provides further information.

Voltammetric measurements not only provide information about normal potential but are also

Received 14 October 1986.

\(^1\) Presented in German by E. Freude on May 28 1986 at the 60th Annual Meeting of the German Society of Glass Technology (DGG) in Bremen.
Voltammetric methods for determining polyvalent ions in glass melts

suitable for determining total concentration or diffusion coefficients of polyvalent ions by means of equations for calculating theoretical current-potential curves [5 and 7].

Measurement of the actual potential \( (E) \) of the glass melt can be done with a \( \text{ZrO}_2 \) sensor [2]. Thus, all information is provided to calculate the redox equilibria according to Nernstian equation (2):

\[
E = E_0 + \frac{RT}{zF} \ln \left( \frac{C_{\text{red}}}{C_{\text{ox}}} \right).
\]

3. Experimental

All experiments were carried out in a resistance heated oven with a vertical alumina tube. A flange at the top carries the electrodes in small alumina tubes and an alumina or platinum crucible can properly be adjusted from the bottom. The working electrode consists of a platinum wire; a platinum plate acts as counter electrode, which is also used to measure the actual potential of the melt. The reference electrode is, in principle, described in [2]. It is modified in such a way that an yttria stabilized zirconia rod is stuck to an alumina tube with a ceramic binder instead of the more complicated platinum-assisted heat bonding. Air is used as reference gas and all quoted potentials refer to this reference.

Electronics are selfconstructed and consist mainly of the potentiostat, which adjusts the voltage between working and counter electrode in such a manner that the potential working/reference electrode is equal to any required value. The potentiostat is connected to a microcomputer via an analog/digital and a digital/analog converter. By that way the microcomputer can apply any potential-time function to the electrochemical cell and records the current.

All experiments were carried out with glasses having a basic composition of (mol%) 74 \( \text{SiO}_2 \), 16 \( \text{Na}_2\text{O} \), 10 \( \text{CaO} \), which were modified by adding oxides of polyvalent elements.

4. Results and discussion

Figures 1a and b show theoretical current-potential curves for cyclic voltammetry (figure 1a) and for square-wave voltammetry (figure 1b) for an ideal reversible single-electron reaction. The curves are calculated according to equations given in the literature [5 and 7]. (The parameters used were: \( \vartheta = 1100 \text{ °C} \), surface area of working electrode \( A = 0.025 \text{ cm}^2 \), diffusion coefficient \( D = 4 \cdot 10^{-8} (\approx 4 \cdot 10^{-8}) \text{ cm}^2/\text{s} \), \( E_0 = -560 \text{ mV} \), scan rate is 1 V/s, amplitude of the square wave is 100 mV and half-wave duration is 5 ms.) It is obvious that, contrary to SWV, in the case of CV the peak is very broad and flat due to the high temperature. An assignment of any peak potential is difficult even in this ideal case. Therefore, this technique does not show great promise.

Figures 2a and b show experimental results of measurements at 1100 °C in a glass doped with 1 mol% iron calculated as \( \text{Fe}_2\text{O}_3 \). Parameters for the measurements were the same as above. Figure 2a is the record of a CV; in the cathodic scan the peak is reduced to a shoulder, the related reaction is the reduction of Fe III to Fe II. The further increase in the current belongs to the background of the matrix and may be due to the reduction of the silicate glass. Figure 2b is the record of a SWV. The peak is pronounced well even though the background has a noticeable influence clearly seen by comparing the curve with the theoretical one. Even though not shown here, it was possible with this method to get a well-shaped peak in a glass with 0.1 mol% iron.

The record of a SWV experiment in a glass with 1 mol% \( \text{As}_2\text{O}_3 \) is shown in figure 3b. The tempera-
ture was 1100 °C, the amplitude 50 mV and the half-wave duration 10 ms. The first peak is assigned to the As V/As III equilibrium, the second one to As III/As VI. It was not possible to get the As V/As III peak in CV, as seen in figure 3a. Obviously the lack of this peak easily leads to misinterpretations.

5. Conclusions
Voltammetry has been developed to a useful instrument to investigate redox equilibria in glass melts by introducing the square-wave voltammetry. The results reported in this paper clearly demonstrate the superiority of this method over the cyclic voltammetry, which had been used so far in glass melts. Consequently further laboratory measurements will serve as a basis for thermodynamic interpretations. This technique could also be applied to industrial glass melts.

The authors want to thank Mr. Friese, Mr. Matinske and Mr. Rabe from the Hahn-Meitner-Institut, Berlin, for construction of the electronic equipment and for help with the computer software.

Parts of these investigations were conducted with the kind support of the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF), Köln, by agency of the Hüttentechnische Vereinigung der Deutschen Glasindustrie, Frankfurt am Main, through the resources of the Bundesministerium für Wirtschaft.

6. References