Electrochemical Study of the behavior of molybdenum in glass melts

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In this project the electrochemical behavior of MoO_3 doped glass melts is investigated. Different types of electrochemical experiments were carried out: potential measurements as a function of time, cyclic voltammetry, square wave voltammetry. The data for the different techniques were compared in detail and analysed as a function of temperature and other variable parameters.

Introduction

All-electric melting of glass has taken an important place in glass and enamel production, because of various technical, economical and ecological advantages: a high degree of thermal efficiency, easy control, homogeneous melt and low exhaust of hazardous compounds such as NO_X, SO_2, fluorine, lead oxide etc. In all-electric melting heat is brought into the glass melt by means of the Joule effect applying an AC current through electrodes. During this process the corrosion of the electrodes may be a disturbing factor. Currently metallic molybdenum is predominantly used as electrode material in the glass and enamel industry. The decisive factor in the corrosion of molybdenum electrodes is the chemical composition of the melt. Since molybdenum is one of the less noble metals, it will be oxidised in the presence of nearly all other polyvalent ions in the melts. The temperature of the melt, density and frequency of the heating current and viscosity of the melt are other factors that can have an influence on the corrosion. The aim of this study is to understand the corrosion of molybdenum in glass melts. On the one hand the corrosion of molybdenum (99.5% purity) in molten glass is investigated with the aid of electrochemical techniques, on the other hand the electrochemical behavior of MoO_3 doped melts is studied. Only the second part will be discussed in this paper.

Experimental Set-Up

All experiments were carried out in a glass whose basic composition is given in table 1.

Table 1: (Basic) Composition of the glass melt

Oxide	Content in wt%
SiO_2	64
Na_2O	18
CaO	8
B_2O_3	5
MgO	3
Al_2O_3	1
K_2O	1
MoO_3	*1 - 2.5*

The pre-melted enamel was placed in an alumina crucible, located in an alumina tube inside a resistance-heated vertical tube furnace (T= 1150°C). A three-electrode set-up was used. The working electrode was a platinum rod (length 30 mm, diameter 5 or 3mm) embedded in an alumina tube with ceramic mortar. In this way only the cross section of the rod was used as electrode surface. Before the start of each experiment the surface was treated in the following way. Polishing with emery paper type 1200 grit results in a fresh but relatively rough surface that is further smoothed by polishing with Al_2O_3 powder of particle size 1.0 µm for 5 min. The counter electrode was a platinum plate with an area of approximately 3 cm^2; the reference electrode was a zirconia/air probe. All potentials given in this study refer to this zirconia/air electrode. A schematic drawing of the experimental set-up is shown in figure 1.

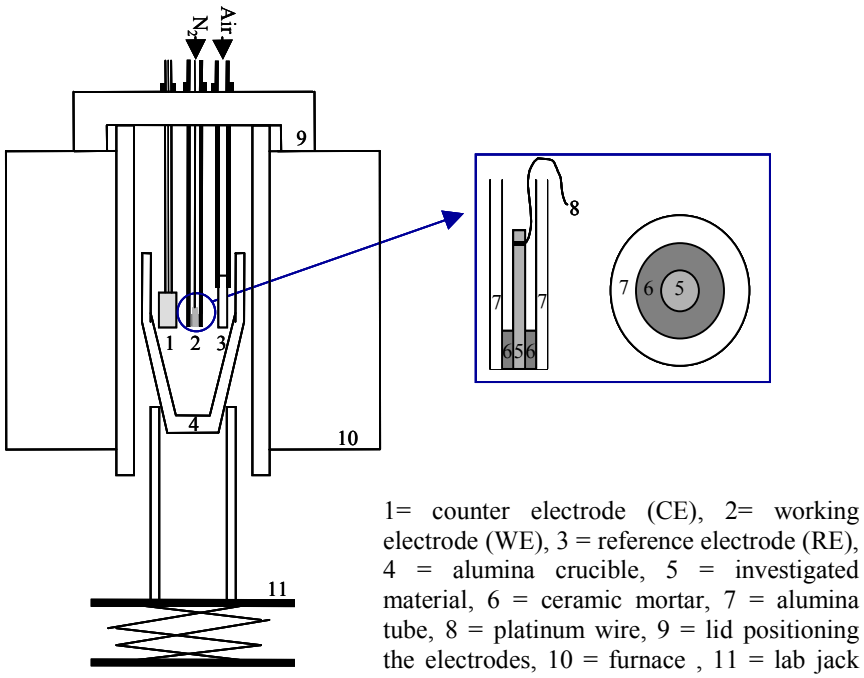

Figure 1: Schematic drawing of the experimental set-up

Results and discussion

Square wave voltammetric curves were recorded at different frequencies, as shown in fig. 2 for a glass melt containing 1.71 mass% MoO_3. The curves were recorded from 0.1 to –1.2 V vs. yttria stabilised ZrO_2/air. Three reduction waves can be observed (fig. 2). The reduction peaks with E_p = ca. -760 mV vs. yttria stabilised ZrO_2/air and E_p = ca. -930 mV vs. yttria stabilised ZrO_2/air are due to reduction reactions of the added MoO_3. Evidence for this assumption was found by changing the mass concentration of MoO_3 in the glass melt. Similar peaks were obtained for the other investigated MoO_3 concentrations and the excepted linear relationship between I_{peak} and MoO_3 concentration was found (fig. 3). For the

reduction wave observed at ca. 400 mV, this evidence could not be found. At the moment there is no explanation for this wave.

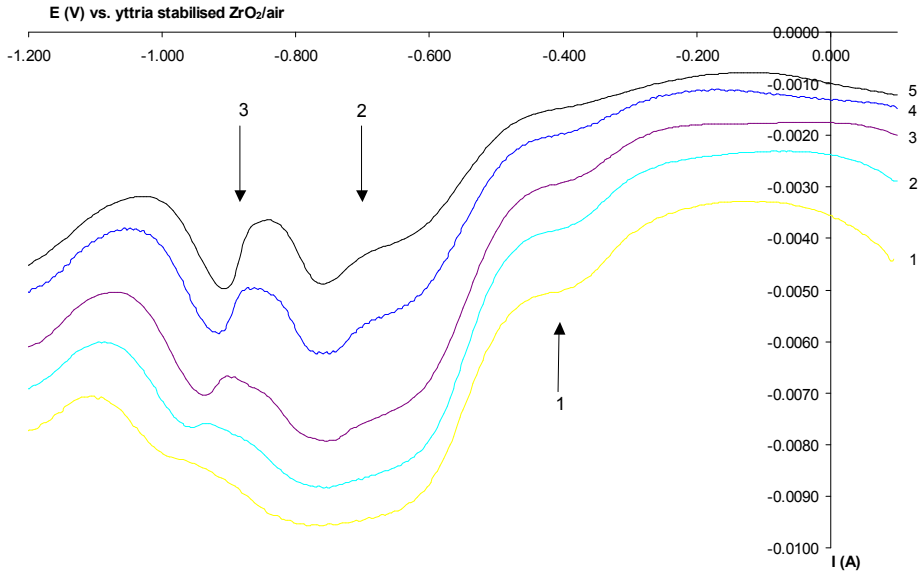

Figure 2 : Square wave voltammetric curves recorded at a platinum electrode at 1150°C for different frequencies in a glass melt containing 1.71 mass % MoO_3. Square Wave Amplitude = 50mV. Frequencies are (1) 200, (2) 100, (3) 50, (4) 20 and (5) 10 Hz.

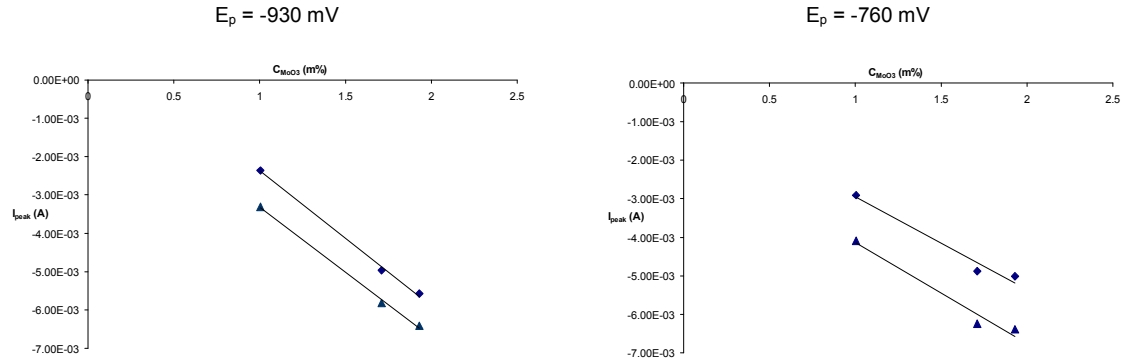

Figure 3: Relationship between MoO_3 concentration and peak current obtained with square wave voltammetry (Amplitude = 50 mV, frequencies ♦ = 10 Hz and ▲ = 20Hz)

In addition to Square wave experiments cyclic voltammetry was carried out. These current-potential curves, as a function of polarization rate, are shown in figure 4. The voltammograms were measured at a potential region between the open circuit potential (OCP) and –1150 mV vs. yttria stabilised ZrO_2/air. Two reduction waves and two cathodic peaks can be seen. The half-wave potentials of the reduction waves $E_{1/2,1}$ = -700 mV and

$E_{1/2,2}$ = - 945 mV vs. yttria stabilised ZrO_2/air are in agreement with the peak potentials of the square wave curves.

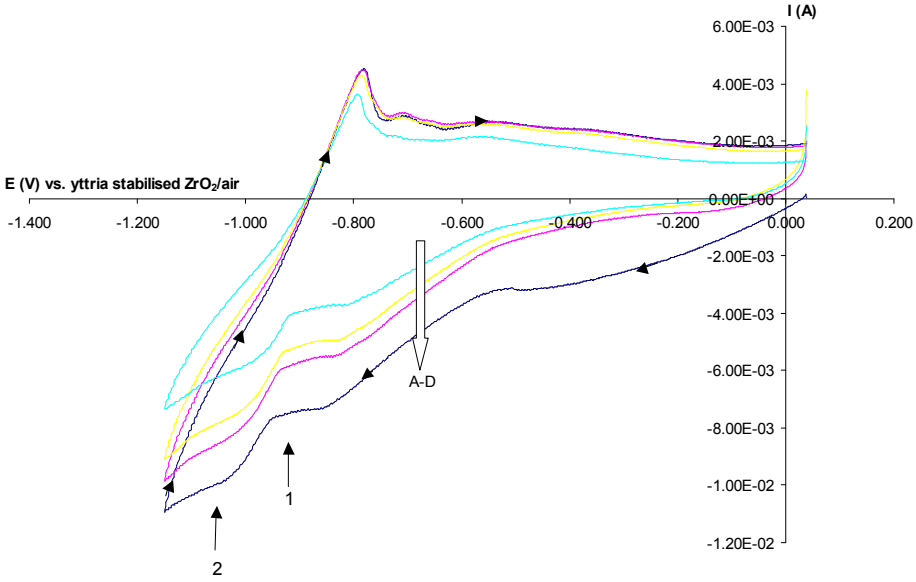

Figure 4: Cyclic voltammetric curves recorded from OCP to -1150 mV back to OCP vs. yttria stabilisised ZrO_2/air in a glass melt containing 2.0 mass% MoO_3 as a function of polarisation rate at a platinum electrode. Polarisation rates are (A) 100, (B) 200, (C)250 and (D) 300 mV s^{-1}.

In order to characterize the reduction reactions, a potential of –875 mV vs. yttria stabilised ZrO_2/air was applied for a certain interval of time (1000 s) and then the electrode was pulled out of the melt and rapidly cooled to room temperature. The same experiment was repeated for a potential of –1000 mV vs. yttria stabilised ZrO_2/air. The electrode surfaces were examined using a scanning electron microscope, for both samples a molybdenum phase was observed. To obtain more information about the composition of the phases (and thus the reduction reactions) XRD analyses has to be done.

Conclusion

The electrochemical behavior of glass melts containing MoO_3 can be characterized with the aid of square wave voltammetry as well as cyclic voltammetry. The results of both techniques are in good agreement with each other. In square wave and cyclic voltammetric curves two reduction waves, wich can be attributed to the reduction of Mo ions, are observed. SEM analyse of the electrode surface confirm this. In order to obtain more information about the reaction products XRD analyse has to be done.