

## The Kinetics of Anodic Processes at the Platinum-Borosilicate Melt Boundary

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### Abstract

Stationary voltammetry was used to investigate the anodic polarization of platinum in sodium borosilicate melt. The influence of the silicon oxide content is estimated for the electrode processes rate. The mechanism of the electrode processes was specified, taking into account the slowness of oxygen ions desorption.

**Keywords:** liquid borosilicate, platinum electrode, polarization, diffusion

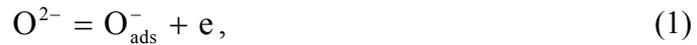
In contact with liquid oxides, platinum and the alloys based on it lose strength with time and become brittle which complicates the application of these structural materials in the production of glasses. The reaction process between platinum and oxide melts is electrochemical in nature. Meanwhile, the literature data on the mechanism and kinetics of electrode processes in such systems are limited [1—4].

The galvanostatic method with compensation of the resistive voltage drop in the electrolyte was used to analyze the stationary polarization of platinum in the melts  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$  (I),  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$  (II) и  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 3\text{SiO}_2$  (III). The electrochemical cell consisted of a platinum crucible containing the melt and the electrode under investigation in the shape of a cylinder 1 mm in diameter. Its surface area in contact with the melt was equal to  $0,32 \text{ cm}^2$ , which was substantially smaller than the value of the same for the auxiliary electrode ( $\approx 80 \text{ cm}^2$ ). Therefore, the polarization of the auxiliary electrode was omitted from consideration.

Measurements were performed in air in the temperature range 1173—1273 K. In order to decrease the concentration of the dissolved water, was degassed at the given temperature to a residual pressure of 10 Pa.

The basic characteristic feature of the anodic dependences was the presence of a rather extended linear region in the range of overvoltages  $\eta = 0 \div 240$  mV, after which the angle of slope of the curves was observed to increase.

The results were explained using the two-stage mechanism of the discharging of the oxygen ions of oxide melt on platinum's surface:



The slowest stage is the surface diffusion of the adsorbed  $\text{O}_{\text{ads}}^-$  particles from areas of their occurrence on the equilibrium (1) to the portions equilibrium with the gas phase (2) where oxygen bubbles are released.

Table. Kinetic Parameters of the Anodic Process

Melt	T, K	$K_D \cdot 10^3$ , $\Omega^{-1} \cdot \text{cm}^{-2}$	$i_0$ , mA/cm <sup>2</sup>	$\beta$
I	1173	1.2	2.6	0.4
	1223	1.8	2.9	0.5
	1273	5.5	14.0	0.3
II	1173	0.18	0.88	0.4
	1223	0.39	1.81	0.3
	1273	0.78	3.40	0.3
III	1173	0.06	0.37	0.3
	1223	0.13	0.81	0.4
	1273	0.28	1.60	0.3

It is shown that the first stage of the current-voltage characteristics is described by the equation:

$$i_1 = K_D \eta, \quad (3)$$

for the second branch of the anodic curve (after the inflection point  $\eta > \eta^*$ ), the following kinetic equation is true:

$$i_2 = K_D \eta + i_0 \left\{ \exp \left[ \frac{2\beta F (\eta - \eta^*)}{RT} \right] - \exp \left[ \frac{-2\alpha F (\eta - \eta^*)}{RT} \right] \right\}. \quad (4)$$

In this equation the symbol  $i_0$  is used for the doubled transfer current in stage (2),  $K_D$  – diffusion rate coefficient.

The diffusion rate constants of  $\text{O}_{\text{ads}}^-$  calculated by the nonlinear-regression

method, transfer current, and the transport coefficients are presented in Table. As can be seen, increasing the temperature and reducing the silica content in the melt leads to an increase of the diffusion rate constant and transfer current, which is caused by depolymerization of the oxide melt.

## References

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**Received: February 16, 2014**