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The Kinetics of Cathodic Processes at the Platinum-Borosilicate Melt Boundary

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Abstract

Stationary voltammetry is used to investigate the cathodic 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 cathodic processes was specified, taking into account the slowness of adsorbed oxygen ions' diffusion.

Keywords: liquid borosilicate, platinum electrode, polarization, diffusion

Cathodic polarization of platinum is accompanied by discharge of hydroxyl ions of oxide melt and molecular hydrogen emphasizing. These processes may lead to hydrogen embrittlement of glassmaking crucibles and reducing their performance properties. The galvanostatic method with compensation of the resistive voltage drop in the electrolyte was used to analyze the cathodic polarization of platinum in the melts $Na_2O \cdot B_2O_3 \cdot SiO_2$ (I), $Na_2O \cdot B_2O_3 \cdot 2SiO_2$ (II) и $Na_2O \cdot B_2O_3 \cdot 3SiO_2$ (III). Measurements were performed in air in the temperature range 1173—1273 К. 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 cathodic volt—ampere dependences are the presence of a rather extended linear region in the range of overvoltages $\eta = 0 \div 600$ mV.

The results were explained using the two-stage scheme, assuming the existence of a balance between oxygen and hydroxyl ions at the interface:

$$\left(O^-_{\mathrm{ads}}\right)_{\omega} + e = O^{2-} , \tag{1}$$

$$OH^- = \left(O^-_{\mathrm{ads}}\right)_0 + \tfrac{1}{2}H_2 . \tag{2}$$

As in the case of anodic polarization [1], stage (1) probably occurs in the surface regions of the electrode in equilibrium with the melt. Equilibrium (2) is observed on other surface regions where hydrogen bubbles can form and their escape into the gas phase is thus facilitated (near the micropores, cracks, and surface defects). The occurrence of stage (1) in the cathodic direction decreases the degree of surface coverage by the adsorbed oxygen particles O^-_{ads} due to which equilibrium (2) shifts toward the side of hydrogen evolution. It rapidly reacts with the atmospheric oxygen so that $P_{H_2} = \mathrm{const}$, which corresponds to the equation

$$H_2 + \tfrac{1}{2}O_2 = H_2O \quad , \tag{3}$$

$$p_{H_2} = p^{at}_{H_2O} \Big/ \left(k^{(3)}_{eq} \sqrt{p^{at}_{O_2}} \right) = p^{eq}_{H_2} . \tag{4}$$

Apparently, the rate of reaction (3) in the reverse direction is fairly small so that hydrogen does not get oxidized at the anode except for a small amount of H_2 accumulated in the near-surface layers of the metal during cathodic polarization. The linear volt—ampere characteristic of the cathodic process leads us to assume that the retarding stage of hydrogen evolution by reactions (1) and (2) is the surface diffusion of the adsorbed oxygen from the regions of equilibrium with the gas phase (2) to the regions of equilibrium with the melt (1). In other words, the volt—ampere characteristic of the cathodic process is described by equation:

$$i = K_D \eta \tag{5}$$

Thus, according to the model offered here, the volt — ampere characteristics must be linear, i.e., for the platinum — molten-oxide interface, Ohm's law must be satisfied. The constant of proportionality K_D is determined not only by the diffusional mobility of the O^-_{ads} particles but also by the equilibrium degree of coverage of the surface and, hence, by the concentration of the hydroxyl ions in the melt, and the partial pressures of O_2 and H_2O in the atmosphere.

The values of conductivity found by the nonlinear-regression technique [2] for the conductivity of the interface K_D are presented in Table. As can be seen, with temperature increasing, the diffusion rate constant increases for all the systems studied.

Thus, the investigations performed here confirmed the possibility of cathodic evolution of hydrogen from the oxide melt at platinum electrodes. A refined mechanism is offered for the discharging mechanism, which takes into account the sluggishness of the surface diffusion of the adsorbed O^-_{ads} particles.

Table. **Dependence K_D on temperature for melts of different composition**

T, K	$K_D \cdot 10^3$, $\Omega^{-1} \cdot cm^{-2}$		
	I	II	III
1173	1.1	0.50	0.24
1223	2.6	0.78	0.37
1273	2.9	1.20	0.55

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