POTENTIOSTATIC PASSIVATION AND GALVANOSTATIC ACTIVATION OF ZINC IN SUPERSATURATED ZINCATE SOLUTIONS OF KOH

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The passivation of zinc occurs as a result of the formation of an adsorption layer of the oxide ZnO_{1+m} (where $m < 1$), containing excess oxygen (over the stoichiometric amount in ZnO [1]). Only after this can the formation of a phase passivating layer begin, when the rate of dissolution of zinc has already been reduced by approximately two orders of magnitude. The anodic oxidation of zinc, coated with a phase oxide layer, occurs when there is an increase in the potential essential for ensuring migration of ions in the oxide layer, which, in turn, is necessary for increasing the thickness of the solid oxide layer. At potentials above 0.5 V, on account of the discharging of hydroxyl ions, the content of excess oxygen in the film is increased, whereas its thickness remains practically constant [2].

We were interested in determining the influence of the composition of the solution on the mechanism and kinetics of the passivation process and on the content of excess oxygen in the oxide film formed in the anodic polarization of a zinc electrode in alkaline solutions saturated with zincate, in which the oxide film is not chemically soluble.

For the investigation we used a potentiostatic method of recording the anodic polarization curves on a rotating disc electrode. The anodic curves were taken in the region of potentials corresponding to the dissolution of active zinc and in the region of transition from the semipassive state to the passive state. Close to the potential of the transition, a 2-5 mV potential change occurred. High reproducibility of the experimental data was observed.

The cathodic activation curves were taken at a constant current density of 5 mA/cm² on a zinc electrode preliminarily passivated at various constant values of the potential in the region from −1.0 to 1.8 V (normal hydrogen electrode). A potentiostat of the Central Laboratory of Automation was used as the polarization source; the current passing through the cell was recorded by a rapid-action potentiometer. The electrode of zinc wire with ϕ 0.5 mm, containing 99.999% Zn, had an area of the working surface of 0.002 cm². All the experiments were conducted in a thermostatically controlled glass cell at a temperature of 25 ± 0.1°C in a medium saturated with purified argon. The grades of the reagents used as methods of their supplementary purification were described earlier [2].

An analysis of the potentiostatic curves of φ versus log i obtained (Fig. 1) shows that for alkaline solutions supersaturated with zincate, in the investigated concentration region, there is a linear dependence of the electrode potential φ_p, corresponding to transition from the semipassive state to the passive state, upon the logarithm of the activity of free alkali in solution (Fig. 2). This dependence can be expressed by an empirical function, analogous to that obtained for iron [3] and for nickel [4], but with a different coefficient:

$$\varphi_p = -0.95 - 0.03 \lg a_{OH^-}, \tag{1}$$

Consequently, the electrode process resulting in passivation of the electrode, occurs at a potential approximately 0.3 V more positive than the potential corresponding to the formation of the oxide ZnO. OH^- ions participated in it. Under these conditions the electrode process in which an oxide with an excess oxygen content over the stoichiometric ratio, ZnO_{1+m}, is formed,

$$Zn(OH)_4^{2-} + 2/m ZnO + 2OH^- = 2/m ZnO_{1+m} + 3H_2O + ZnO + 4e \tag{2}$$

is most probable, which confirms the earlier hypothesis of [1]. The formation of this oxide is responsible for the passivation of zinc.

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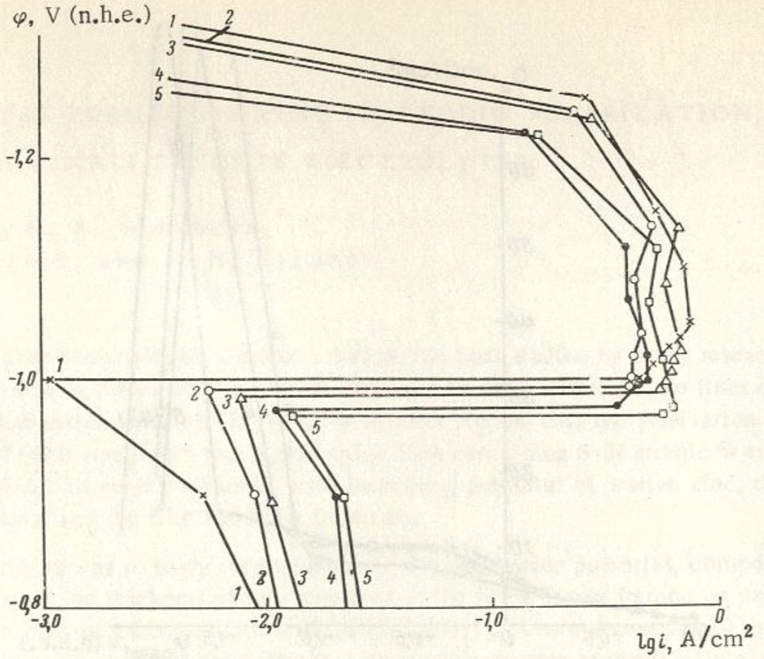

Fig. 1. Potentiostatic anodic curves taken on a Zn electrode in solutions supersaturated with zincate, with a concentration of free alkali, mole/kg: 1) 4.89; 2) 3.9; 3) 3.51; 4) 2.14; 5) 1.84.

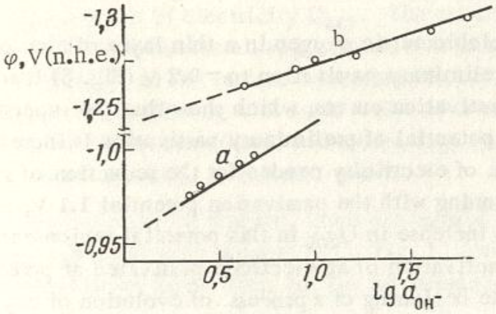

Fig. 2

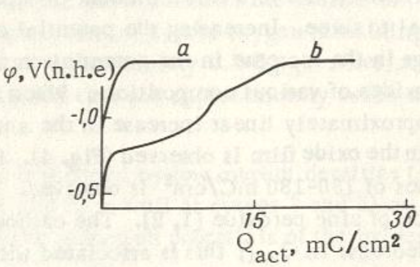

Fig. 3

Fig. 2. a) Theoretically calculated dependence of the potential of the reaction: $Zn + 2OH^- = Zn(OH)_2 + 2e$ on the logarithm of the hydroxyl ion activity (corrected for the influence of dissolved zincate); b) dependence of φ_p – the potential of transition of zinc from the semipassive state to the passive state – on the logarithm of the activity of free alkali in solution.

Fig. 3. Curves of cathodic activation, taken in a solution supersaturated with zincate with 4.89 mole/kg of free alkali on a Zn electrode preliminarily passivated for 5 min: 1) 0.5 V; 2) 0.2 V.

If we assume that the content of excess oxygen is 5-10% [5], then a calculation based on Eqs. (1), (2) gives a value of the standard free energy ΔF^0 of the oxide ZnO_{1+m}, formed as a result of process (2), equal to 80-82 kcal, substantially higher than for the oxide ZnO (76 kcal). These data are evidence that the passivation of zinc in supersaturated solutions of KOH occurs not as a result of formation of a phase layer of zinc oxide (ZnO), but due to a process of absorption of superstoichiometric oxygen in the surface oxide ZnO; the oxide ZnO_{1+m} of the peroxide type, responsible for passivation, is formed not by precipitation from a supersaturated solution, but as a result of the electrode process of discharging of OH^- ions [2].

The curves of the cathodic activation φ versus Q_{act}, an example of which is given in Fig. 3, show that for transition to the active state of an electrode passivated close to the transition potential region (at −1.0 and −0.9 V), an amount of electricity Q_{act} = 0.7-0.9 mC/cm² is required, which is independent of the composition of the solution

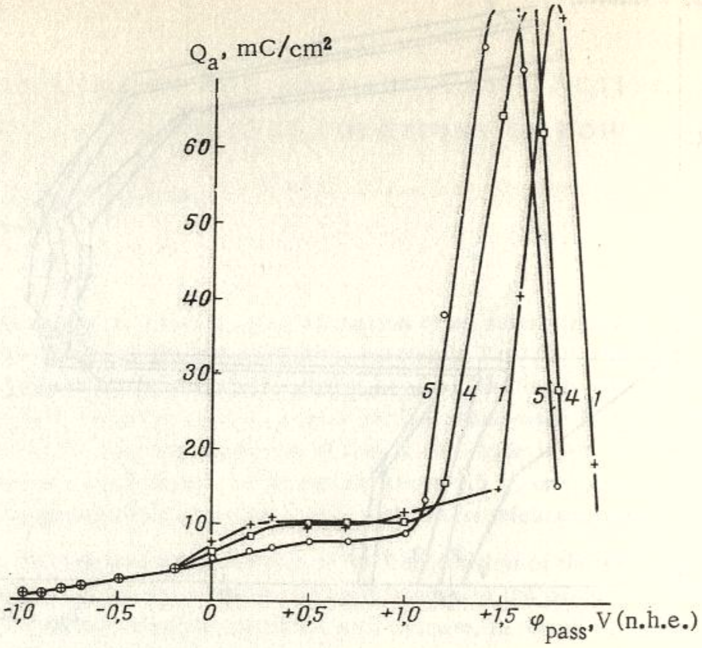

Fig. 4. Dependence of the amount of electricity needed for the activation of a zinc electrode on the potential of its passivation for solutions saturated with zincate, with various concentrations of free alkali (the notation of the curves corresponds to Fig. 1).

(Fig. 4), which corresponds to a small amount of superstoichiometric oxygen in a thin layer of zinc oxide at a roughness factor equal to three. Increasing the potential of preliminary passivation to −0.2 V (Fig. 3) leads to the appearance of two lags in the increase in the potential on the activation curves, which show that the superstoichiometric oxygen forms oxides of various compositions. When the potential of preliminary passivation is increased all the way to 1.0 V, an approximately linear increase in the amount of electricity needed for the reduction of superstoichiometric oxygen in the oxide film is observed (Fig. 4). Beginning with the passivation potential 1.1 V, a sharp increase in Q_{act} to values of 130-180 mC/cm² is observed. The increase in Q_{act} in this potential region can be explained by the formation of zinc peroxide [1, 2]. The cathodic activation of an electrode passivated at potentials from 1.4 V shows a sharp decrease in Q_{act}; this is associated with the beginning of a process of evolution of oxygen at the electrode and means a decrease in the degree of its adsorption.

The dependence of Q_{act} upon φ_{pass} obtained for various supersaturated solutions shows that a small amount of superstoichiometric oxygen is sufficient for transition from the semipassive to the passive state of a zinc electrode. In the region of potentials corresponding to the state of profound passivity, the electrode is covered with a thicker layer of the phase oxide, containing superstoichiometric oxygen. This confirms the significance of the ionic-semiconductor properties of the surface oxide layer in phenomena of passivation.

LITERATURE CITED

1. T. I. Popova, N. A. Simonova, and B. N. Kabanov, Élektrokhimiya, 2, 1476 (1966).
2. T. I. Popova, N. A. Simonova, and B. N. Kabanov, Élektrokhimiya, 3, 1419 (1967).
3. V. F. Franck, Z. Naturforsch., 4a, 378 (1949).
4. V. A. Lovachev, A. I. Oshe, and B. N. Kabanov, Élektrokhimiya, 5, 1383 (1969).
5. É. A. Ivanov, T. I. Popova, and B. N. Kabanov, Élektrokhimiya, 5, 695 (1969).