PASSIVATING LAYERS FORMED ON ZINC IN ANODIC POLARIZATION IN CONCENTRATED ALKALI ZINCATE ELECTROLYTES

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The passivation of zinc electrodes in alkaline solutions has been studied by many researchers. It has been shown in [1-3] that there is less zinc in the passivating oxide film than in ZnO. However, no lines of zinc peroxide have been detected on x-ray diffraction patterns. In [4-6] the authors propose that the passivation of zinc is caused by films of zinc oxide. In [7-9] it was shown that a thin oxide film containing 5-20 atomic % excess oxygen is sufficient for the passivation of zinc in oxide solutions. With increasing potential of passive zinc, the amount of excess oxygen in the film increases, and the film thickness increases.

The purpose of this work was to study the influence of the passivation potential, composition of the electrolyte, and conditions of diffusion on the thickness and composition of the oxide layers formed on passive zinc. The conditions of the measurements and the electrodes were the same as in [7]. The composition of the oxides on passive zinc was determined according to the shape of the cathodic curves taken on zinc preliminarily passivated at various potentials in alkaline solutions containing zincate.

Figure 1 presents the cathodic activation curves, taken on a zinc electrode after exposure at 0.0, 0.6, and 1.0 V (normal hydrogen electrode). After passivation at 0.0 V, judging by the cathodic activation curves taken at low current densities (for example, Fig. 1, curve 1), reduction begins at a potential of −0.3 V and ends at −1.3 V* after the passage of a certain amount of electricity Q_{act}. The presence of a region of the most sloping portion of the cathodic curves at −0.8 to −1.0 V indicates an approximately semilogarithmic dependence of the reduction potential φ or the electrochemical potential on the surface concentration or on the amount of excess oxygen remaining in the film, equivalent to $(Q_{act}-Q)$, beginning with some value of Q equal to approximately 0.3 Q_{act}. After profound passivation (at 1.0 V) on the curves of cathodic reduction, lags are obtained that are approximately twice as prolonged and at more positive potentials (Fig. 1, curves 1 and 3).

In unsaturated solutions of zincate, when the passive zinc is reduced by low current densities (0.23 mA/cm²), an increase in the rate of mixing reduces Q_{act} (Fig. 1, curves 1 and 2, as well as curves 3 and 5) on account of chemical dissolution of the oxide film, but has no influence on the reduction potentials of the oxides.

Increasing the cathodic current density leads to a shift of the reduction potentials of the excess oxygen in the negative direction. This is especially distinctly observed in alkaline solutions supersaturated with zincate, in which there is no distortion of the curve of activation on account of chemical dissolution. An 11-fold increase in the density of the reduction current gives a displacement of the potentials of the lag on passive zinc of approximately 0.18 V (Fig. 1, curves 9 and 11).

*A sharp rise in the potential from −1.1 or −1.2 to −1.3 V is observed especially distinctly on the curves of spontaneous activation, taken without current, and is almost absent on the curves obtained at high current densities, for example, at 100 mA/cm². This rise is apparently associated with self-activation of the electrode according to the reaction:

$$ZnO_{1+m} + m\,Zn = (1+m)ZnO.$$

Therefore the upper portions of the curves are extrapolated in the case of low current densities (dotted line).

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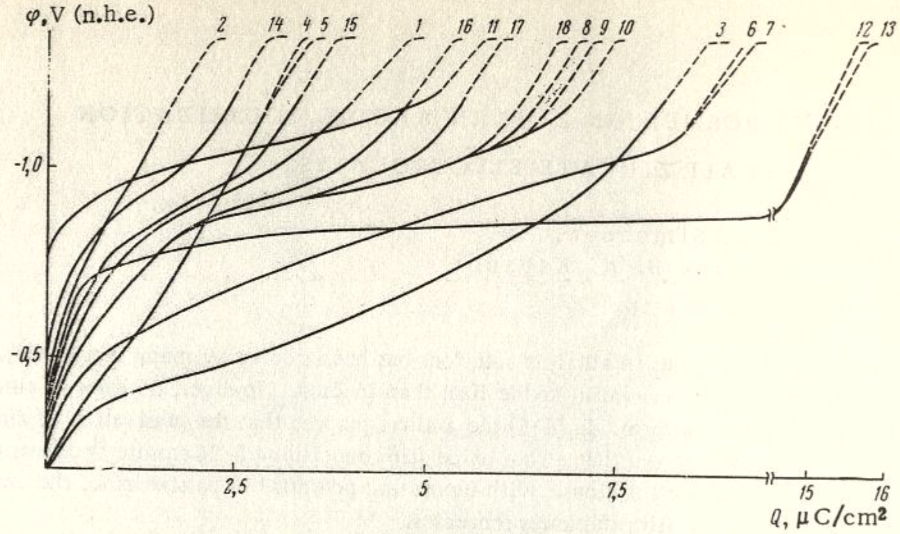

Fig. 1. Curves of cathodic activation (7.9 moles of free alkali/kg in solution). Mixing: 1, 3, 6, 10, 13, 18) 60 rpm; 4, 17) 300 rpm; 2, 7, 9, 11, 16) 1000 rpm; 5, 8, 12, 15) 3000 rpm. The solution contains 2.5 mole/kg of ZnO, duration of preliminary passivation 10 min: 1-5) $i_c = 0.23$ mA/cm^2; 6, 7) $i = 4.3$ mA/cm^2. Passivation potential: 1, 2) 0.0 V; 3-7) 1.0 V. Duration of passivation 5 min: 8-10, 12-18) i_c=3.3 mA/cm^2; 11) i_c = 37 mA/cm^2. The solutions contain: 8-11) 4.5 mole/kg ZnO; 12, 13) the same, with 0.25% H_2O_2; 14-18) 1.9 mole/kg ZnO. Passivation potential: 8-13) 1.0 V; 14-18) 0.6 V.

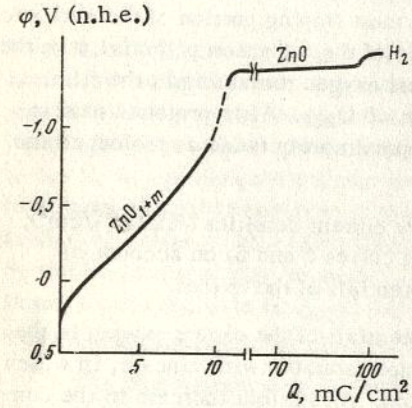

Fig. 2. Curve of activation taken at 4 mA/cm^2 in 10 N KOH on a zinc electrode, passivated for 30 min at 1.0 V, mixing 60 rpm.

Q_{act} is practically unchanged in this case. It may be assumed that up to a potential of −1.3 V, all the superstoichiometric oxygen contained in the passivating film is reduced according to the reaction:

$$1/m \cdot ZnO_{1+m} + H_2O + 2e^- \rightarrow 1/m \cdot ZnO + 2OH^-, \quad (1)$$

where 1 > m > 0. An oxide film consisting of zinc oxide remains on the electrode. In a 10 N solution of KOH containing no zincate, it was determined according to the amounts of electricity consumed for the reduction of superstoichiometric oxygen to −1.3 V and zinc oxide at −1.37 V that the oxide film contains up to 5-7 atomic % superstoichiometric oxygen after shallow passivation and about 10% after profound passivation (for example, Fig. 2).*

In alkaline solutions saturated with zincate, in the case of shallow passivation of zinc, the oxide films contain up to 1-2% superstoichiometric oxygen, while in the case of profound passivation they contain up to 3%. The observed difference in the concentrations of superstoichiometric oxygen in the films formed at various zincate concentrations is explained by the fact that in solutions supersaturated with zincate, the total thickness of the oxide film is greater than in the case of solutions in which the film dissolves. After more profound and prolonged passivation of zinc, the reduction process already begins 1-1.5 V more positive than the equilibrium potential of the system $Zn/ZnO, OH^-$ (Figs. 1 and 2), and the content of superstoichiometric oxygen becomes higher (Fig. 3a and 3b). It might have been assumed that this is explained by the formation of zinc peroxide (ZnO_2) on the electrode surface [1-3]. To test this hypothesis, tentative thermodynamic calculations were performed in [7], using the data of [10] on the determination of the equilibrium potential of the formation of analogous peroxides of alkaline earth metals, since there are no data in the literature for ZnO_2. Such calculations give a value of the standard potential of the system $ZnO_2/ZnO, OH^-$ equal to 0.4 V (normal hydrogen electrode). The direct addition of hydrogen peroxide to an alkaline solution supersaturated with zincate during passivation of the electrode (Fig. 1, curves 12 and 13, compare with curve 10), leads

*In this case we arbitrarily assume that with weak mixing, the chemical dissolution both of ZnO and of ZnO_{1+m} proceeds at approximately the same rate.

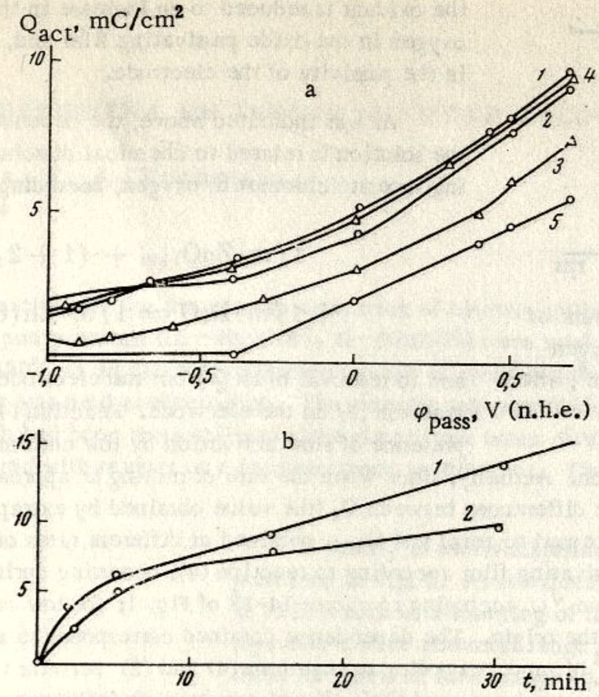

Fig. 3a. Dependence of Q_{act} on the potential of passivation of a Zn electrode with mixing 1000 rpm and time of passivation 5 min in solutions with 7.9 moles of free alkali/kg, at a cathodic current of 100 mA/cm² and ZnO content (in moles/kg): 1) 5.6; 2) 2.9; 3) 1.9; and at a cathodic current of 3.3 mA/cm²: 4) 5.6 moles/kg; 5) 1.9 moles/kg. b) Dependence of Q_{act} on the duration of preliminary passivation at a potential of 0.0 V in solutions with 7.9 moles of free alkali/kg at a ZnO content: 1) 5.6 moles/kg; 2) 2.9 moles/kg.

only to a lengthening of the lags on the activation curves and a small shift of them in the direction of positive values of the potential, i.e., in this case even the beginning of reduction occurs at potentials approximately 1 V more negative than the calculated reduction potential of ZnO_2. The large value of the slope $\partial\varphi/\partial \log i$ and the very large (of the order of 2 V) overvoltage are also characteristic of the reduction of hydrogen peroxide on mercury [11]. However, the shape of the reduction curves of the oxide film in the presence of zinc peroxide* on an oxidized zinc electrode with a semilogarithmic dependence of the potential on $Q_{act}-Q$ (Fig. 1, curves 12, 13) indicates the formation of peroxide-type compounds on the electrode of variable composition ZnO_{1+m} or a solid solution of oxygen in zinc oxide. It may be assumed that in an alkaline solution supersaturated with zincate, peroxide compounds of zinc are partially hydrolyzed, forming hydrogen peroxide. Hydrogen peroxide can enter into a reaction with the oxide film on the surface of zinc:

$$1/m\cdot ZnO + HO_2^- = 1/m\cdot ZnO_{1+m} + OH^-. \tag{3}$$

The addition of another oxidant, for example, K_2CrO_4, also leads only to an increase in the areas on the activation curves and a negligible displacement of the curve in the direction of more positive potentials. Thus, the action of

* Hydrogen peroxide reacts with zincate in solution, forming a peroxide compound of zinc, for example:

$$Zn(OH)_4^{2-} + HO_2^- = ZnO_2 + 3HO^- + H_2O. \tag{2}$$

Zinc peroxide is insoluble and is readily suspended; it does not come in contact with the electrode. In unsaturated solutions of zincate, when hydrogen peroxide is added, at first a white precipitate of ZnO_2 is formed; at the same time catalytic decomposition of the HO_2^- ion by zincate ions to complete disappearance of the ZnO_2 precipitate begins (there is practically no decomposition of hydrogen peroxide in the absence of zincate). However, no decomposition is observed in saturated solutions of zincate, since the equilibrium (2) is shifted to the right.

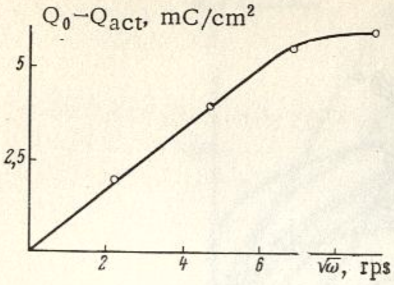

Fig. 4. Dependence of the amount of chemically dissolved excess oxygen upon $\sqrt{\omega}$ rps, at $i_c = 3.3\ \mathrm{mA/cm^2}$, after passivation at 1.0 V.

the oxidant is reduced to an increase in the content of superstoichiometric oxygen in the oxide passivating film and, correspondingly, to an increase in the passivity of the electrode.

As was indicated above, the dependence of Q_{act} on the mixing of the solution is related to chemical dissolution of the oxide film, containing superstoichiometric oxygen, according to the reaction

$$1/m\cdot ZnO_{1+m} + (1+2/m)OH^- + 1/m\cdot H_2O \rightleftarrows 1/m\cdot Zn(OH)_4^{2-} + HO_2^- \quad (4)$$

and to removal of HO_2^- from the electrode, preventing the occurrence of reaction (3) on the electrode. Reaction (4) should occur primarily in the presence of slow activation by low current densities and should depend on the rate of mixing of the solution. Actually, since when the rate of mixing ω approaches zero the rate of chemical dissolution approaches zero, the differences between Q_0 (the value obtained by extrapolating the direct dependence of Q upon $\sqrt{\omega}$ to a value of ω equal to zero) and Q_{act}, obtained at different rates of mixing, are equivalent to chemical dissolution of the passivating film according to reaction (4), occurring during activation. Figure 4 gives the dependence of Q_0-Q_{act} upon $\sqrt{\omega}$ according to curves 14-18 of Fig. 1; for low rates of mixing it is expressed by a straight line, passing through the origin. The dependence obtained corresponds to a change in the concentration in solution Δc of the order of 10^{-3} M, and according to reactions (4) and (2) pertains to the removal of HO_2^-, since the zincate and alkali concentrations are large and their change can have no influence on the rate of chemical dissolution of the film.

In this work we determined the composition of passivating oxides formed on zinc and demonstrated that the observed dependence of Q_{act} on the rate of mixing of the solution is determined by the rate of removal of HO_2^- from the electrode in the chemical dissolution of ZnO_{1+m}.

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