ANODIC DISSOLUTION OF PASSIVE ZINC IN ZINCATE SOLUTIONS OF ALKALI

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The kinetics of dissolution of passive zinc and zinc oxide were studied by various methods in a wide range of potentials and concentrations of alkali and zincate. In supersaturated solutions of zincate, in which the oxide film cannot dissolve, complete retardation of the anodic dissolution of zinc does not take place but the growth of the film is limited by breaking up and by mechanical peeling. Parallel with the growth of the film, there occurs direct electrochemical dissolution of atomic zinc. Because of the overpotential, direct electrochemical dissolution of passive zinc cannot occur even in supersaturated zincate solutions. The passive film contains excess oxygen over the stoichiometric ratio in zinc oxide. It is shown that its mean concentration, beginning at a potential of 0.4 V, increases with increase in potential of passivation of the zinc electrode. With intermittent changes of potential by 0.1 V, a small temporary increase in current is obtained, which is explained by an acceleration of the direct electrochemical dissolution of zinc and, in the region of potentials where electrochemical dissolution does not depend on the potential, by an acceleration of the electrochemical stage in the formation of the film. In unsaturated solutions of zincate, the greater the relative concentration of zincate, the less is the percentage of the total rate of anodic dissolution of zinc occupied by chemical dissolution of oxides. The relation between the rate of anodic dissolution of passive zinc and composition of solution in dilute zincates is explained by the existence of chemical dissolution of the oxide film.

In connection with the use of zinc anodes in power sources, many investigators have studied the anodic dissolution and passivation of zinc in alkaline solutions. According to [1], for passivation of zinc in strong solutions of alkali, a large quantity of electricity is required, which corresponds to the formation of phase layers on the surface of the zinc. But in these experiments, no demarcation was made between the quantity of electricity consumed in the change of solution near the electrode (connected with anodic dissolution of zinc) and the formation of the passivating layer. After carrying out such a demarcation, it appeared that, in the original passivation of zinc in solutions of alkali, a quantity of electricity is required which is equivalent approximately to a monolayer of oxide [2], and with further passivation the thickness of this oxide increases and may dissolve from the surface of the layer. In [3], it was shown that the rate of dissolution of samples of roasted zinc oxide, with a rate of stirring of strong alkaline solutions of greater than 1000 rev/min, was determined by heterogenous chemical reaction. In [4], it was shown that the roasted zinc oxide was not the same as the surface oxide on passive zinc: its solubility and kinetics of dissolution were much less. All the same, the rate of dissolution of the oxide formed on the surface of the zinc is always less than the rate of anodic dissolutions of zinc and occupies a smaller percentage of the latter, the greater the concentration of zincate. The difference of these rates is the rate of direct electrochemical dissolution of zinc, independent of the composition of the solution [4]. We proposed that the slow stage of direct anodic dissolution of zinc (at least during passivation which was not very deep) is electrochemical formation of the Zn^{2+} and the slow stage of the process taking place at the same time is the chemical dissolution of zinc oxide. The aim of the present investigation was to make more precise and to confirm this idea in a wider material and also using results obtained by other methods [5-7]. In [5], it was shown that the rate of electrochemical dissolution of passive zinc has a diffusion limitation in the solid phase and in [6, 7] that the current, with a sharp increase in anodic polarization, goes either into an increase in the oxide film [6], or in dissolution of the zinc [7], depending on conditions.

The general aim of the present work was to explain the mechanism of anodic dissolution of passive and deeply passive zinc. A study was partially carried out in supersaturated solutions of zincate in which the passivating film

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did not chemically dissolve, and in these conditions the mechanism of dissolution of the passive metal could not occur according to Bonhoeffer[8]. According to this mechanism, the rate of dissolution of passive metal is limited by chemical dissolution of the surface oxide film forming on it; this normally explains why the rate does not depend on the electrode potential. But such an independence of the rate of dissolution of passive zinc on potential could be observed even in supersaturated solutions in which the film did not chemically dissolve [4, 5].

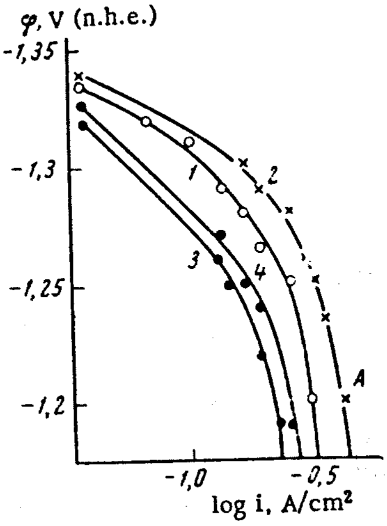

Fig. 1. Galvanostatic anodic curves recorded on a Zn electrode in solutions with concentrations of free alkali 7.9 mole/kg and the content of ZnO of 1.9 (1 and 2) and 3.8 mole/kg (3 and 4); with stirring rates of: 1) 60, 3) 300, and 2, 4) 2500 rev/min.

EXPERIMENTAL PROCEDURE

In the investigation, we used galvanostatic and potentiostatic methods for recording polarization curves on disc electrodes (diameter 0.5 to 2 mm) rotating with a speed of from 60 to 5000 rev/min. The use of the rotating disc electrode was necessary to create a similar concentration on the whole surface of the electrode in conditions of concentration polarization. All the experiments, in which the rate of stirring was not particularly studied, were carried out with a rate of rotation of the electrode of 1000 rev/min.

Cathodic curves for activation (charge curves) were also recorded on the passive zinc. In order to do this, the zinc electrode was potentiostatically passivated at a chosen constant potential for a definite time (5-30 min) and afterwards, with the help of a special relay, the zinc electrode was switched onto a galvanostatic schedule and was polarized at a constant cathodic current density. The change in potential during activation was recorded with a ENO-1 oscillograph.

Prolonged passivation was also carried out on zinc electrodes at potentials from −0.9 to 1.0 V with an analysis of the zincate solution before and after passivation and also with a determination of the weight loss of the zinc electrodes after cathodic activation and after removing the oxide film remaining on the surface. On the basis of these data, a balance was established for the consumption of electricity in anodic formation of the film and in anodic dissolution of the metallic zinc.

For the experiments, electrodes were used from zinc of purity 99.996%, with the surface cleaned with moist glass powder. All the experiments were carried out in a closed glass electrolytic cell at a temperature of 28 ± 0.1°C with a platinum auxiliary electrode separated from the main solution by a glass filter. The potential of the zinc electrode was measured against a mercuric oxide electrode in the same solution and was converted for the normal hydrogen electrode. The experiments were carried out in an atmosphere of purified nitrogen or argon. Before the experiment, the KOH solutions were purified by prolonged polarization with a zinc cathode and platinum anode separated from the main solution by a glass filter. In order to prepare the zincate solution, zinc oxide and KOH of chemical purity were used.

In the solutions of zincate, the content of zinc ions was determined polarographically after dilution of the solution to 1 N KOH. The total and free alkali in the zincate solutions was determined by titration with phenolphthalein and methyl orange.

EXPERIMENTAL RESULTS AND DISCUSSION

The stationary critical current densities at which the active zinc electrode is strongly passivated were determined by galvanostatic and potentiostatic methods, i.e., when the gradient of the polarization curve becomes extremely large (greater than 0.5 V). Figure 1 gives typical anodic polarization curves recorded galvanostatically on a disc electrode at various rates of rotation for two concentrations of zincate (curves 3 and 4 for solutions close to saturated). The rate of recording of the curves was about 2.5 min per curve.

Figure 2 gives the potentiostatic anodic curves recorded on a disc electrode in solutions with a concentration of free alkali from 2.0 to 10 mole/kg, holding at each potential for 2-3 min. The relative calculated concentrations of zincate at the surface of the electrode, c^*_{ZnO}, are indicated underneath Fig. 2.

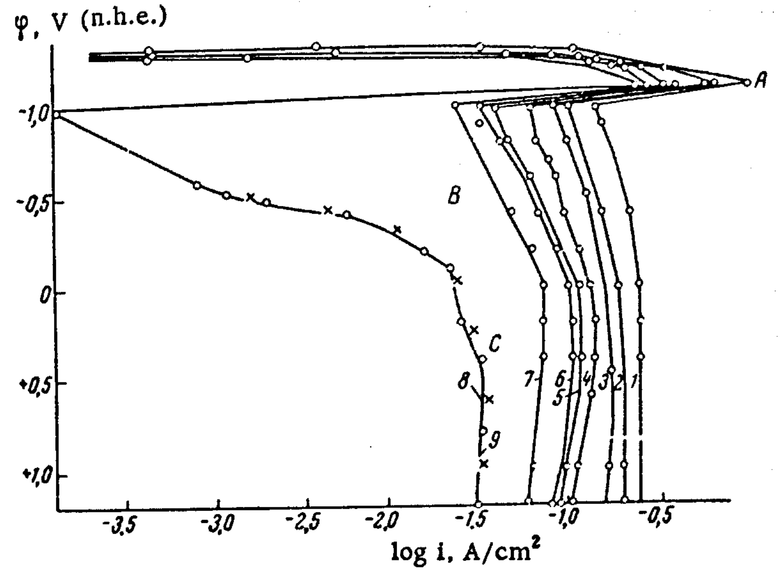

Fig. 2. Potentiostatic anodic curves recorded with stirring rate of 1000 rev/min in alkaline solutions containing ZnO 8-9% of saturation point, with a concentration of free alkali of: 1) 7.5, 2) 5.0, 3) 3.0 mole/kg: 37-40% from saturation of ZnO with concentration of free alkali of: 4) 10.0, 5) 6.3, 6) 4.4, 7) 2.5 mole/kg; supersaturated relative to ZnO: 8) 0.65 mole/kg ZnO with concentrations of free alkali of 2.05 mole/kg; 9) 6.2 mole/kg ZnO with concentration of free alkali 9.2 mole/kg.

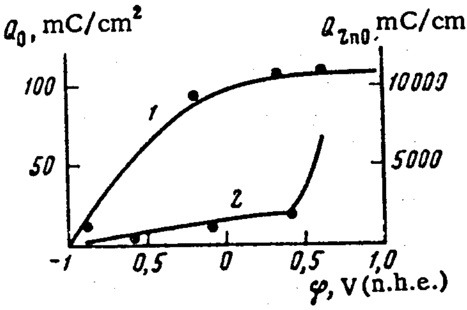

Fig. 3. 1) Dependence of thickness of oxide film Q_{ZnO}; 2) dependence of quantity of excess oxygen in the oxide film Q_0, on the potential for passivation of the zinc electrode φ (passivation time 1 h).

In the region of potentials B (from −1.0 to −0.2 V, Fig. 2) in which passivation was not deep, the stationary rate of dissolution of passive zinc depends on potential. On curves 8 and 9 (Fig. 2), obtained in supersaturated solutions of zincate, in the limits from −1.0 to −0.3 V there is an approximate linear relationship between φ and log i with a gradient of about 0.35 V. This agrees with the hypothesis about the limitation of the rate of dissolution by the electrochemical stage [4, 7]. The direct electrochemical dissolution of metal may occur even in solutions supersaturated with zincate on account of the high overpotential. The relation between log i and φ, existing at low concentrations of zinc (Fig. 2), shows that the rate of anodic dissolution in these conditions is partially determined by the electrochemical stage. This dependence is less, the lower the relative concentration of zincate. This is explained by the fact that with decrease in concentration of zincate in the solution the constituent of the total rate of dissolution of passive zinc, which does not depend on potential, increases. In these conditions it is determined by the rate of chemical dissolution of the basic film [4]. However, with a sharp (intermittent) small increase in potential and in solutions unsaturated with zincate, a temporary increase in current is obtained, which obviously cannot be explained by an increase in the rate of dissolution of zinc oxide because the rate of the chemical reaction does not depend on the electrode potential. The increase in current in this case consists of only 5-10% in relation to the whole anodic current. It was shown that practically the whole of this excess current, which for several tenths of a second flows after increasing the potential, is consumed in the region of potentials B in the dissolution of zinc, and not in a thickening of the oxide film [7], i.e., the increase in potential in this case causes mainly not a thickening of the film, as follows from the theory [8], but a temporary acceleration of the direct electrochemical dissolution of the metal, which consists here of 10-15% of the total current passing through the electrode. (The thickening of the film does not exceed 0.1%.)

The fact that the stationary rate of dissolution of zinc in the absence of zincate depends little on potential (in the same region B) may not be explained only by the prevailing value (although in stationary conditions) of the chemical stage of dissolution. The direct electrochemical dissolution must also change little with increase in

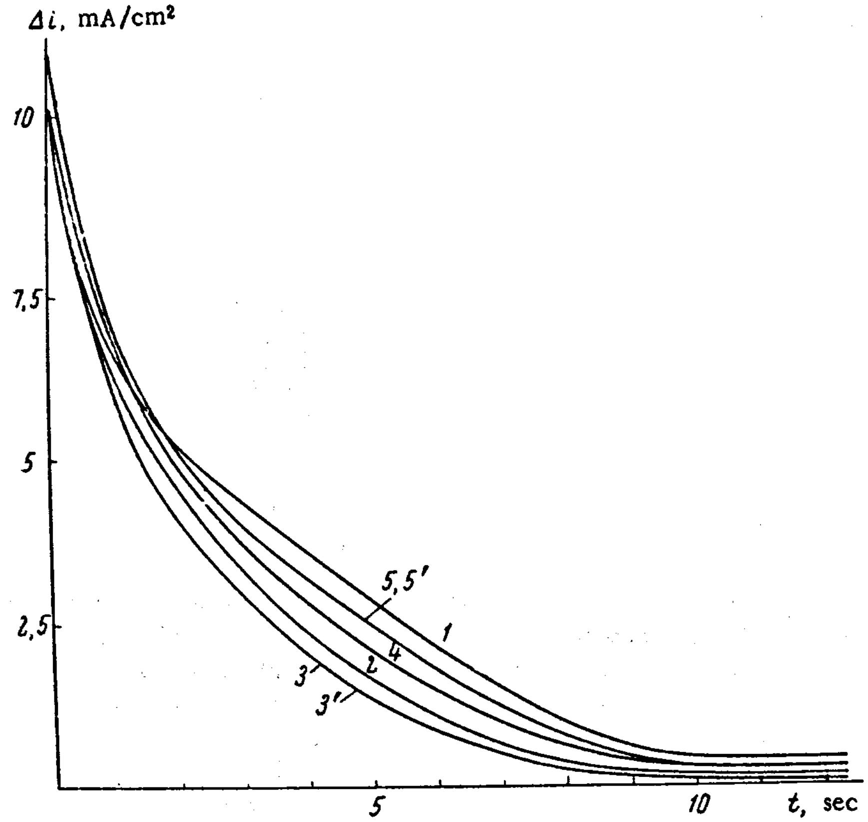

Fig. 4. Change in current for anodic oxidation of passive zinc with time after the sharp displacement of potential of the electrode by 0.1 V (after 0.05 sec) in solutions supersaturated with zincate (5.6 mole/kg ZnO and 5.6 mole/kg KOH). The time of holding the electrode at the initial value of potential was from 3 min to 1 h: 1) from 0.1 V (1 h) to 0 V; 2) from 0.1 V (1 h) to 0.2 V; 3) from 0.2 V (3 min) to 0.3 V; 3') from 0.2 V (1 h) to 0.3 V; 4) from 0.3 V (1 h) to 0.4 V; 5) from 0.6 V (3 min) to 0.7 V; 5') from 0.6 V (1 h) to 0.7 V.

potential. In fact, the strong retardation of the process of direct electrochemical dissolution of zinc in the time after increasing the potential corresponds to an increase in the quantity of excess oxygen in the oxide film with increase in potential (Fig. 3, curve 2) and possibly to an increase in the excess surface concentration of oxygen in this film. The retarding action of oxygen on the electrochemical process may be explained either by a change in the semiconducting properties of the film or by a change in the adsorption state at the boundary, responsible for the rate of the electrochemical process.

In the region of potentials (Fig. 2), the stationary rate of the anodic dissolution of zinc in all the solutions is practically independent of potential. In supersaturated solutions of zincate, in this region of potentials, with intermittent changes of potential of deeply passive zinc by 0.1 V, there is observed a small increase in current (approximately by 1.5 times) and afterwards a fall for several seconds to the initial value (Fig. 4). The observed jump in current in these solutions is close in absolute value to the jump observed in unsaturated solutions of zincate. As in unsaturated and in supersaturated solutions of zincate, the quantity of electricity in the jump and the value of the nonstationary current do not depend on the total thickness of the oxide film forming on zinc and this means they are not determined by the process of diffusion of the components of the reaction through the film but depend only on the values of $\Delta\varphi$, the change of potential. The total thickness of the oxide film on the zinc during the jump in current with intermittent change of potential by 0.1-0.3 V increases only by 0.2-0.5%. Such an increase in thickness of film may have no substantial influence on the rate of direct electrochemical dissolution of zinc, which in supersaturated zincate solution is 80% of the stationary current [4], and as measurements showed using alternating current [5], it is limited by diffusion in the solid phase. Therefore, it may be proposed that the nonstationary increase in current during the sharp increase in potential in the region of potentials C occurs only because of a temporary increase in the rate of thickening of the film and the increase in concentration of oxygen in it. The data of [6] agree with this hypothesis. This work shows that for solutions of alkali (0.1-0.5 N) not saturated with zincate, the nonstationary current observed during the displacement of the potential of a deeply passivated zinc electrode goes into the growth of the oxide film. In this case, the jump in current need not be related only to that part of the stationary current (the constituent in the supersaturate zincate solutions is about 20% of the total stationary current [4]), which is consumed in the growth of the film (4-5 mA/cm²). During the sharp change in potential by 0.1 V, there occurs an increase in current going into the growth of the film of three times (Fig. 4). During this, the true gradient of the curve relating log i and φ for the reaction for the formation of the film, determined from the nonstationary oscillographic measurements, is 0.2 V, which does not contradict the hypothesis of the retardation of the electrochemical stage of the formation process of the oxide film. In unsaturated solutions, the nonstationary current is only 2-5% of the whole current going through the electrode. Obviously, also in these solutions, the temporary increase in current is related to the electrochemical stage of the formation of the film. The decrease of current with time (after the sharp change of current with increase of potential), as also in the case of the less deeply passive zinc, may be connected with retardation of the electrochemical stage, in connection with the increase in the oxygen content in the corresponding part of the oxide layer.

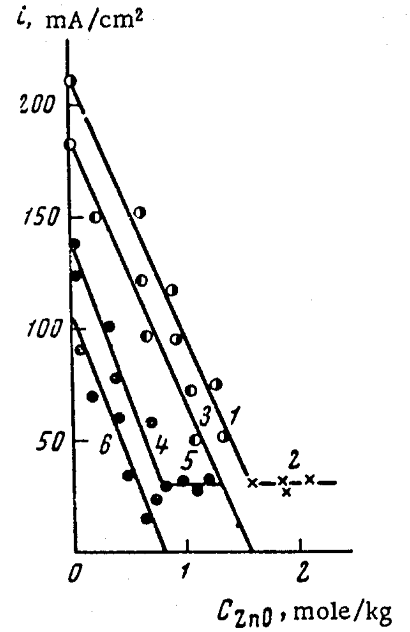

Fig. 5. Dependence of rate of anodic dissolution of passive zinc (at 0.2 V) on concentration of zincate in solutions with concentrations of free alkali of: 1 and 2) 2 mole/kg; 4 and 5) 4 mole/kg. Dependence of rate of chemical dissolution of oxide film on concentration of zincate in solutions with concentrations of free alkali of: 3) 2 mole/kg; 6) 4 mole/kg. Rate of stirring 1000 rev/min.

In order to define more accurately the mechanism of anodic dissolution of passive zinc in solutions of alkali not saturated by zincate, let us examine the dependence of the rate of anodic dissolution on the composition of solution during deep passivation, i.e., during passivation in the region of potentials C, in which the stationary rate of dissolution of passive zinc practically is independent of potential. From the data of the potentiostatic measurements on a disc electrode, an example of the results of which is given in Fig. 2, we calculated the concentrations of alkali and zincate at the surface of the disc electrode and determined their dependence on the rate of dissolution of passive zinc.

It was established that, as in other regions of potentials, in the region C, the rate of anodic dissolution i_a of passive zinc in unsaturated solutions is a linear function of the product of the mean activity of ions K^+ and OH^- with the square of the activity of water, and with low concentrations of alkali it is proportional to this product [4]. This type of relation was established also for critical current densities. In addition, in all the regions of passivation, i_a falls linearly with increase in concentration of zincate. Figure 5 shows the dependence of the rate of anodic dissolution of passive zinc and the concentration of zincate in solutions with concentrations of free alkali of 2 and 4 mole/kg.* Parallel to this straight line are the straight lines indicating the linear dependence on the concentration of zincate of the rate of chemical dissolution of the surface oxide formed on the passive zinc with prolonged anodic polarization in the same region of potentials and with the same conditions. The rate of chemical dissolution of the surface oxide was determined by the method of weight loss and from an analysis of the solution.† Saturation in relation to the oxide film is reached in the investigated regions of alkali at concentrations of zincate equal to 0.8 and 1.5 mole/kg respectively, because at these concentrations, the rate of chemical dissolution of the oxide film becomes zero (Fig. 5, curves 3 and 6). It may be assumed that the rate of chemical dissolution i_{chem} of the surface oxide, just as i_a, depends linearly on the product of the mean activity of the ions K^+ and OH^- and the square of the activity of water, and at low concentrations of alkali it is proportional to this product [4]. Then the slow stage of heterogenous reaction of chemical dissolution of the passive film

$$\mathrm{ZnO} + 2\mathrm{OH}^- + 2\mathrm{H_2O} \rightleftarrows \mathrm{Zn(OH)_4}^{2-}, \mathrm{H_2O} \qquad (1)$$

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* This type of relationship was obtained also for a concentration of 8 mole/kg [4].

† The rate of dissolution of the oxide with stirring rate greater than 300 rev/min does not depend on the rate of stirring; therefore, beginning from these rates of stirring, the rate of dissolution is determined by the chemical and not by diffusion kinetics.

is its first stage [2]

$$ZnO + OH^- + 2H_2O \rightleftharpoons Zn(OH)_3^-, H_2O. \qquad (2)$$

The second stage,

$$Zn(OH)_3^- H_2O + OH^- \rightleftharpoons Zn(OH)_4^{2-}, H_2O, \qquad (3)$$

takes place more rapidly than the first.

Reaction (2) in the region of potentials B and partially in the region of potentials C must also be the slow stage for the anodic process of dissolution of zinc, which goes through the stage of electrochemical formation and chemical dissolution of the oxide and which is the basic way in which the anodic process occurs in unsaturated zincate solution. The dependence of i_{chem}—the rate of the reaction of dissolution of oxide film (1) on the concentration of zincate—can be explained by the influence of the reverse reaction, the rate of which $\overleftarrow{i}$ in Eqs. (2) and (3) must be proportional to the activity of the zincate, separated from the activity of the alkali (Fig. 5). Then the rate of the total reaction $i_{chem} = \overrightarrow{i} - \overleftarrow{i}$ with constant concentration of free alkali, is expressed by the equation: $i_{chem} = \text{const} - \overleftarrow{i} = \text{const} - k\,[Zn\,(OH)_4^{2-}]$, because the rate of the direct reaction i in this case is constant. The constant k in this equation must be inversely proportional to the activity of the alkali. In fact, a comparison of the results given in Fig. 5, curve 1, and in [4] confirm this.[*] In saturated solutions of zincate, the rate of the direct ($\overrightarrow{i}$) and reverse reactions ($\overleftarrow{i}$) are obviously equal to one another and determine only the rate of recrystallization of the surface zinc oxide.

However, the rate of anodic dissolution of zinc in saturated and supersaturated solutions of zincate is not zero [4], and, in the region of potentials C, it has a constant value, depending neither on the degree of supersaturation nor on the concentration of free alkali in the solution (for example, Fig. 5, lines 2 and 5). It was proposed earlier [4] that in supersaturated solutions of zincate, the basic anodic process is the direct electrochemical dissolution of metallic zinc (escaping the stage of formation of zinc oxide). New data, obtained for other concentrations of alkali, confirm this hypothesis. In unsaturated solutions of zincate, the dependence of the rate of anodic dissolution of passive zinc and the chemical dissolution of the surface oxide on the concentration of zincate is expressed by parallel straight lines. The difference between these rates agrees for different alkali solutions and is equal to the rate of anodic dissolution of passive zinc in supersaturated solutions of zincate (Fig. 5, lines 2 and 5). The same value for the rate of dissolution was obtained on zinc passivated at potentials of 0.0, 0.4, and 0.6 V, i.e., the given data are true for the whole region of potentials C (Fig. 2).

The independence of the direct electrochemical constituent of the stationary rate of dissolution on composition of solution is observed also in the potential region B and also in the potential region A (Fig. 2). From this, it follows that the rate of stationary anodic dissolution of zinc in unsaturated solutions of zincate is determined by the occurrence of two parallel processes: 1) direct electrochemical dissolution of metallic zinc, in all the conditions, not depending on concentration of alkali, i.e., obviously taking place by the reaction $Zn \rightarrow Zn^{2+} \rightleftharpoons Zn(OH)_4^{2-}$ [4],[†] and 2) the electrochemical formation of oxide on the surface of the electrode and its chemical dissolution ("chemical component"). The chemical component of the rate of anodic dissolution of passive zinc consists (at constant stirring rate) of a lower percentage of the total anodic current, the greater the concentration of zincate in the solution.

In supersaturated solutions, with prolonged passivation of zinc (1-2 h at 0.2, 0.4, or 0.6 V), 80-90% of the total stationary anodic current passing through the electrode is consumed in the direct electrochemical dissolution of zinc. The remaining 10-20% is consumed in the electrochemical process of the formation or thickening of the oxide film. However, even with more prolonged passivation (4-6 h), the phase films on the zinc do not achieve the thickness at which, because of difficulties for diffusion of the metal through the film, the dissolution or oxidation of zinc is stopped. The rate of direct electrochemical dissolution of metallic zinc remains constant. In supersaturated zincate solutions, with prolonged passivation (4-6 h), in the region of potentials C, the film breaks from

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[*] The deviation in the case of 2 N alkali (Fig. 5) should be explained by the special behavior of relatively dilute solutions of alkali (see Fig. 3 in [4]).

[†] At high concentrations of oxygen on the surface (see below), the ion Zn^{2+} may not go into solution, and after diffusion along the surface forms ZnO : $Zn^{2+} + O^{2-} = ZnO$.

the electrode and its mean thickness decreases by about 2 times, down to 3×10^{-4} cm. We take this thickness of film as the maximum thickness of a dense layer.

In [4, 9], it was shown that the oxide passivating films on the zinc electrode contain excess oxygen above the stoichiometric ratio in zinc oxide. From the cathodic curves for activation, recorded on zinc passivated at various constant potentials, the quantity of excess oxygen in the oxide films was determined after passivation in supersaturated solutions for 1 h* at each potential (Fig. 3). The content of excess oxygen in the thick films is given, as a percentage, of the total quantity of zinc oxide (Fig. 3). The excess oxygen is formed in the anodic process by:

$$1/m\mathrm{ZnO} + 2\mathrm{OH}^- \rightleftharpoons 1/m\mathrm{ZnO}_{1+m} + \mathrm{H_2O} + 2e^-, \qquad (4)$$

where $1 > m > 0$. This excess oxygen obviously also determined the passivating properties of the film. For short passivation times, thinner oxide films are obtained with a greater content of oxygen. The direct electrochemical dissolution of the metal (not passing through the formation and dissolution of the metal oxide) in the presence of excess oxygen in the surface layer of oxide above the stoichiometric composition permits a certain inhomogeneity of the oxide layer.

From a balance of the material and the consumed electricity, we determined that passive zinc is dissolved in the form of the bivalent ion.

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* With this passivation time, oxide films thick enough for spalling from the electrode are not formed.