PASSIVATION AND ACTIVATION OF ZINC ELECTRODES IN ALKALINE SOLUTIONS SUPERSATURATED WITH ZINCATES

I. MEASUREMENTS AT CONSTANT CURRENT DENSITY

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During investigations on rapid anodic passivation of zinc in alkaline solutions [1-3], the following relationship between the current intensity i and passivation time t_p has been determined:

$$(i - i_0)\, t_p^{1/2} = K, \tag{1}$$

where l_0 and K are constants independent of the speed of stirring. Equation (1) was explained by a nonstationary diffusion of reacting particles towards the electrode. At high i, the relationship changes into a linear correlation between i and $1/t_p$ [2, 3].

The aim of the present work was to investigate the kinetics of the passivation and activation of zinc under conditions such that the film forming on the surface of electrode did not dissolve chemically, i.e., in alkaline solutions supersaturated with zincates [4].

EXPERIMENTAL

Anodic and cathodic changing curves (φ–t) were recorded by the oscillographic method at a constant current density using a zinc disc electrode rotating at a speed of 3200 rpm. A special feature of the method was a rapid automatic switching from the anodic polarization, after the passivation of the electrode at a given i and a predetermined potential have been reached, to the cathode polarization at a constant current density of 0.05 A/cm², at which the activation was carried out. The recording of φ–t curves was carried out on loop oscillograph H-700 with vibrogalvanometer M001, connected through a triple-cascade balance amplifier with inlet resistance of 10.2 MΩ. The automatic switching device, which was fed from the second cascade level of the amplifier, comprised a Schmidt trigger and a relay RÉS-9 as an actuating element; the operating time was of the order of 10^{-3} sec.

All the measurements were carried out in a thermostatic glass cell at 25 ± 0.1°C, using an auxiliary platinum electrode, in an atmosphere of purified argon. The potential of the zinc electrode was measured with respect to a mercury oxide electrode in the same solution, and then related to the normal hydrogen electrode. Zinc electrodes were made from a 0.5 mm diam. wire ("high purity"), whose surface was cleaned with moistened glass powder. The solutions used were preliminarily purified by prolonged cathodic polarization. The experiments were carried out in alkaline solutions supersaturated with zincate (Table 1).

RESULTS AND DISCUSSION

Typical anodic curves φ–t are shown in Fig. 1. At the moment when the anodic current is switched on (point a), there is the first ohmic potential drop, whose size is in accordance with calculations, and amounts to 0.1-0.3 V at medium current densities (1.0-2.5 A/cm²). Then, there is a gradual decrease of the potential with stoppages at b, c, and d. The character of the φ–t curves obtained with very strong solutions (Table 1) at relatively small current densities (Fig. 1A) is different. Namely, after the initial sharp change of the potential in the positive direction (a) and a stoppage (a'), there is a reverse change towards more negative values followed by a plateau (b). This effect is apparently caused by anodic activation resulting from a sudden destruction of the originally formed passivating film. Further, there is a drop with delays at (c) and (d). If a correction for the ohmic drop of potential is taken into account, the potential of the plateau (b) corresponds to the active dissolution of zinc in the given solution (−1.15 to −1.2 V). Delays at (c) and (d) correspond to the dissolution to different degrees of the passive zinc in the potential regions of −1.0 V and −0.75 to −0.7 V. On anodic curves obtained with solutions of a low alkali content (e.g., curve D), there is no plateau.

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TABLE 1. Composition of Solutions Investigated

Composition of solution	1	2	3	4	5	6
Free KOH, mole/kg	5,54	3,92	3,41	2,31	1,87	0,61
ZnO, mole/kg	3,85	2,2	1,34	0,965	0,65	0,2

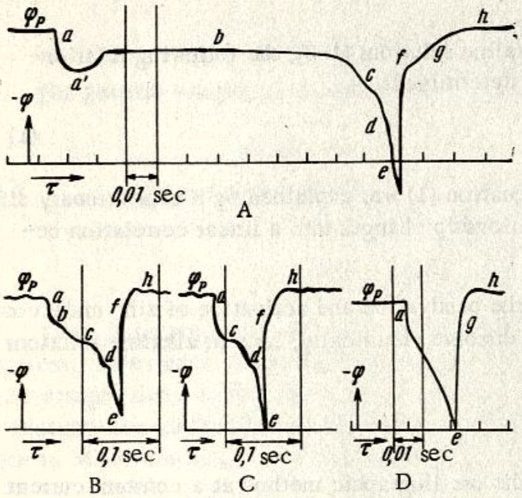

Fig. 1. Typical oscillographic charging curves: section (a–e) is anodic, current density 1.5 A/cm²; section (e–h) is cathodic, current density 0.05 A/cm². Solutions: A) 1–(cf. Table 1); B) 3–(Table 1); C) free alkali 1.9 mole/kg, ZnO 0.94 mole/kg; D 6 (Table 1).

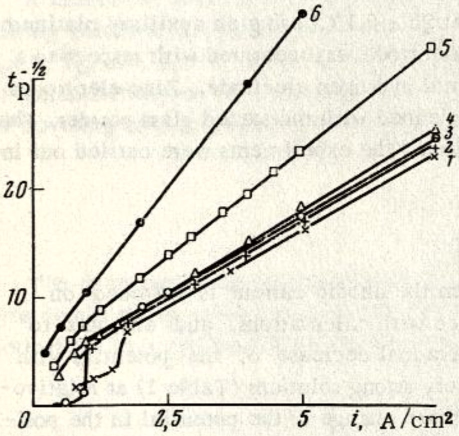

Fig. 2. The relationship between i and $t^{-1/2}$. The numeration of solutions corresponds to Table I.

The total quantity of electricity necessary for the passivation of zinc electrode per unit area of visible surface, $Q_p = it_p$, can be calculated from the current density and passivation time (t_p), i.e., the time between the moment when the anodic polarization is switched on and the sharp change of the potential in the positive direction down to 0.0 V (Fig. 1). It is arbitrarily assumed that at 0.0 V the passivation is complete. For each current density, t_p and Q_p were determined from 10-20 experiments (the deviations did not exceed 5%). The total Q_p can be represented as the sum of different components

$$Q_p = Q_1 + Q_2 + Q_3. \tag{2}$$

Part Q_1 is wasted on active dissolution of zinc with the formation of $Zn(OH)_4^{2-}$ or a loose layer of ZnO crystals, having no direct bearing on the passivation of the electrode. Part Q_2 is usefully spent on the formation of a dense oxide layer containing excess oxygen (ZnO_{1+m}, where $m < 1$), which passivates the electrode. The rate of the reaction of the introduction of excess oxygen into the oxide layer is limited by the electrochemical stage [5] and, as it will be shown hereinafter, does not depend on the composition of the solution. Part Q_3 is again wasted on direct electrochemical dissolution of the passive zinc, without passing through the stage of the formation of zinc oxide [4]. The proportion of Q_3 in the total Q_p is small, as it is consumed only towards the end of the passivation process (delay d, Fig. 1). The proportions of Q_1, Q_2, and Q_3 in the total Q_p vary depending on the intensity of the polarizing current. At relatively low current densities (<1 A/cm²), near the critical value (at which the passivation of the electrode begins), the main process is the active dissolution of the zinc electrode, resulting in large Q_p values of 12-60 mC/cm², for solutions containing 0.61 to 5.5 moles of free alkali per kilogram. At high current densities (5-7 A/cm²), a rapid passivation of the electrode takes place, and the Q_1 term is reduced. In the investigated current density range, in all the solutions, except the dilute alkali solutions, the lower limit of Q_p (Fig. 3a) was not reached, such as can be attained in more dilute alkali solutions, even in the absence of the zincate [3]. In a solution containing only 0.6 mole of free KOH per kilogram, at high current densities, Q_1 approaches to zero, Q_3 can be disregarded, and Q_2 amounts to 3.8 to 4.0 mC/cm², independently on current density. For all the solutions investigated, there was a linear correlation between i and $t^{-1/2}$ (at $t < \tau$) (Fig. 2), which could be represented by the following empirical relationship

$$(i + i_0)(t)^{1/2} = B, \tag{3}$$

where τ is the time of the transition to a stationary state of diffusion, being equal to 0.06 sec at 3000 rpm. Equation (3) differs from relationships (1) occurring in strong solutions [2] by the sign of constant i_0. The relationship

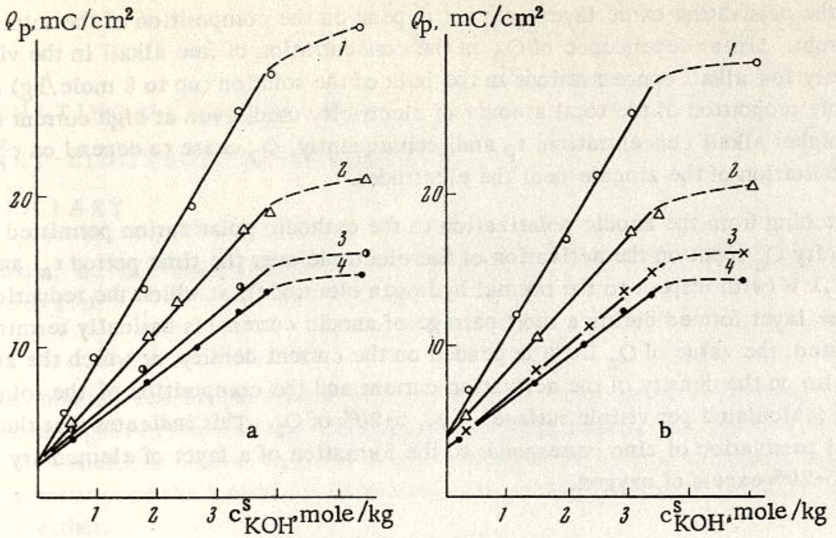

Fig. 3. Dependence of total amount of electricity spent on passivation Q_p, on alkali concentration: a) in the bulk of the solution; current densities: 1) 2 A/cm²; 2) 4 A/cm², 3) 6 A/cm²; 4) 7 A/cm²; b) in the vicinity of the electrode surface; current densities: 1) 2 A/cm²; 2) 4 A/cm²; 3) 6 A/cm²; 4) 7 A/cm².

corresponding to equation (3) can be feasibly represented in the following manner:

$$(i - i_{\text{diss.}} + i_{\text{cryst.}})\, t_p^{1/2} = B, \tag{4}$$

where $i_{\text{diss.}}$ denotes the rate of dissolution of a metal layer, depending on the composition of the solution; and $i_{\text{cryst.}}$ characterizes the precipitation of a solid phase in supersaturated zincate solutions. In alkaline solutions, in which the surface film dissolves, $i_{\text{cryst.}} = 0$, and Eq. (4) assumes the form (1). In alkaline solutions supersaturated with zincates, or in dilute alkaline solutions slightly supersaturated with zincates, anodic dissolution of zinc is accompanied by precipitation of the solid phase of zinc oxide, because under these conditions $i_{\text{diss.}} < i_{\text{cryst.}}$, and the process conforms to Eq. (3).

In fact, calculations according to the nonstationary diffusion equation for a rotating disc electrode show that the anodic dissolution in sufficiently concentrated alkali solutions results in a rapid increase in the relative concentration of the zincate in the vicinity of the electrode surface c^s_{ZnO}/c^s_{KOH} at the expense of OH^- ions into the solution. This increase in the degree of supersaturation should lead to a prompt precipitation of zinc oxide from the solution. At low concentrations of free alkali, the degree of zincate supersaturation of the solution layer adjacent the electrode is mainly determined by the delayed convection diffusion of OH^- ions to the electrode, as follows from the decrease in t_p when the alkali concentration is lowered (Fig. 2, lines 6 and 5). During anodic dissolution in more concentrated alkali solutions, the change in concentration during the passivation time t_p is relatively small, and the degree of supersaturation depends mainly on the transfer of zinc ions into the solution and their diffusion away from the electrode. Figure 3b shows the dependence of Q_p on the concentration of free alkali at the surface of zinc electrode* for current densities of 2-7 A/cm². With the increasing current density, the slopes of straight sections of curves in Fig. 3 decrease. Extrapolation of straight sections of the Q_p vs c^s_{KOH} curves (Fig. 3b) to intersection with the ordinate axis is practically independent of anodic current densities (at $i > i_{\text{cryst.}}$) and gives $Q_2 = 3.5\text{-}4.0$ mC/cm² (equal to Q_p determined by us earlier [3] in dilute alkali solutions and in a solution containing 0.6 mole of free alkali per kilogram), corresponding to the coating of the electrode surface with a single elementary layer of crystalline lattice of zinc oxide containing a small excess of oxygen (if the roughness factor is assumed to be 3-4). Apparently, this is in fact the amount of oxygen sufficient to passivate the zinc surface. During further anodic polarization of the passive zinc, the phase layer may gradually thicken. It follows that the quantity of electricity spent on

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* The alkali concentration in the vicinity of the electrode surface was considered on the basis of the nonstationary diffusion equation for a rotating disc electrode, because in this current density range $t_p < \tau$. Approximation was made that all the current was spent on the formation of ZnO, i.e., the number of electrons was equal to the number of OH^- ions.

the formation of the passivating oxide layer does not depend on the composition of the solution and on the density of the anodic current. Linear dependence of Q_p on the concentration of free alkali in the vicinity of the electrode surface at relatively low alkali concentrations in the bulk of the solution (up to 3 mole/kg) indicates that Q_1 represents a considerable proportion of the total amount of electricity used, even at high current densities. As it has been shown above, at higher alkali concentration, t_p and, consequently, Q_p cease to depend on c^s_{KOH}, and depend only on the relative concentration of the zincate near the electrodes.

A rapid switching from the anodic polarization to the cathodic polarization permitted the determination of the amount of electricity Q_a spent on the activation of the electrode over the time period t_a, and corresponding to a potential shift to −1.1 V (with respect to the normal hydrogen electrode), at which the reduction of excess oxygen (included in the phase layer formed during a short passage of anodic current) is basically terminated [4]. For all the solutions investigated, the value of Q_a little depended on the current density, at which the anodic polarization was carried out, and also on the density of the activation current and the composition of the solution. Q_a amounted to 0.17-0.7 mC/cm^2 (calculated per visible surface), i.e., 5-20% of Q_2. This indicates that the amount of electricity used for the initial passivation of zinc corresponds to the formation of a layer of elementary crystalline cells of zinc oxide containing 5-20% excess of oxygen.

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