

3. Certain non-steady-state concentration changes near the electrode surface promote changes in the state of the zinc surface causing retardation of the dissolution process. The linear dependence of $1/Q_p$ upon the current density is explained in terms of non-steady-state diffusion.
4. At high current densities the total quantity of electricity Q_p expended on passivation is independent of the anodic current density. It diminishes with decrease in alkali concentration.
5. In dilute solutions the quantity of electricity Q_2 expended on passivation at high current densities reaches a limiting value of 1 mC cm^{-2} . This quantity is equivalent to an amount of oxygen or oxide incompletely covering the zinc surface with a monolayer.

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THE ANODIC PASSIVATION OF ZINC IN ALKALI. II. POTENTIOSTATIC AND ALTERNATING CURRENT MEASUREMENTS; DETERMINATION OF CHARGING CURVES

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and B. N. Kabanov

The potentiostatic method has been widely used in studies of anodic behaviour of metals^{1,2}. Sanghi and Fleischman³ obtained potentiostatic curves for zinc in alkali. They suggested that at the start of passivation an insoluble film of zinc oxide forms on zinc which later passes into a soluble form.

The purpose of this work was to study the nature of the passivating films on zinc in alkali. The potentiostatic method of obtaining polarisation curves made it possible to

investigate the relation between the steady-state dissolution rate of the passivated zinc and the composition of the solution at various potentials. The activation curves were also obtained for zinc previously passivated under known conditions. In addition, the impedance of the zinc electrode was measured under the conditions employed in the determination of the polarisation curves.

EXPERIMENTAL

The measurements were made in a glass apparatus either with a rotating disc electrode ($S = 0.3 \text{ cm}^2$) or with a fixed zinc wire ($d = 0.5 \text{ cm}$ and $S = 0.5 \text{ cm}^2$) in 0.03 to 2.5 N KOH in an atmosphere of pure nitrogen. The experimental conditions and the electrode material were the same as those described previously⁴.

Alternating current was passed between a zinc wire ($d = 0.05 \text{ cm}$ and $S = 0.03 \text{ cm}^2$) and a cylindrical platinum electrode ($d = 0.75 \text{ cm}$ and $l = 1.1 \text{ cm}$). The zinc electrode to be investigated was placed coaxially with the platinum cylinder. This ensured a sufficiently uniform distribution of the alternating current over the electrode surface. The capacitance and resistance were measured by a balanced bridge system using a.c. of frequencies from 100 to 50 000 c/s. The impedance of the electrode was balanced by resistance R_1 and capacitance C_1 connected in series. The resistance of the cell was calculated from

$$R_0 = \frac{1}{\kappa} \frac{S}{2\pi l} 2.3 \log \frac{r_1}{r_2},$$

where κ is the conductivity of the solution, S the surface area of the test electrode, l its length, and r_1 and r_2 are the radii of the test and auxiliary electrodes. In addition R_0 was determined from $R'_0 = (\kappa/\kappa')R_0$, where R'_0 was obtained from the measurements of the conductivity κ' at high frequencies in 0.01 N KOH solution. The resistance R_0 thus found was deducted from R_1 . The results were then recalculated for a system consisting of the capacitance C_2 and the resistance R_2 connected in parallel. In the presence of concentration polarisation the calculations were made by Kruger's equation. All the potentials are referred to the standard hydrogen electrode. Variations of the current with time on passing from one constant potential to another over the intervals of about 100 mV were recorded with a loop oscillograph.

Fig. 1 shows the steady-state anodic polarisation curve obtained from the potentiostatic measurements. With anodic polarisation up to -1.1 V (hydrogen scale) dissolution of the

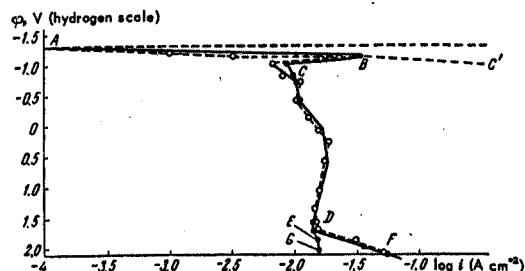


Fig. 1. Anodic polarisation curve determined by the potentiostatic method in 1 N KOH.

active zinc electrode is observed (section AB). At -1.0 V the dissolution rate (point C) is approximately 1% of that of the active zinc obtained by extrapolation to the same potential (point C'). On further change of potential in the positive direction, the rate of dissolution of zinc remains practically constant (section CD). When the potential becomes more positive than 1.7 V, evolution of oxygen begins (section DF). In this region the dissolution rate of the zinc electrode, determined from the concentration of zincate ions in the solution, remains the same as in the passivation region (section CD). Points E and G correspond to the dissolution rates determined in the region of oxygen evolution from changes in the composition of the solution. When the anodic polarisation curve is obtained in the reverse order with zinc already passivated, complete activation of the passivated zinc surface is observed at -1.1 V (broken curve).

Fig. 2 shows anodic polarisation curves obtained by the potentiostatic method in alkali solutions ranging from 0.03 to 1 N KOH. The dissolution rate of zinc in the passivation region varies considerably with alkali concentration. Fig. 3 shows the anodic curves obtained by the potentiostatic method in 0.5 N KOH solution (pure and saturated with zincate) with a rotating zinc electrode at various rates of stirring of the electrolyte. An increase in the rate of stirring from 6 to 83.5 rev. sec $^{-1}$ caused a 2- to 3-fold increase in the rate of dissolution without a substantial effect on the shape of the curve. In the presence of zincate ions in 0.5 N KOH the dissolution rate decreased about 2.5 times. Similar curves were obtained with 0.25 and 1 N KOH. Saturating these solutions with zinc ions also caused a 2- to 2.5-fold reduction in the rate of dissolution. In Fig. 4 the dissolution rate of the passivated zinc electrode is plotted against the square root of the angular velocity of stirring. The relation is linear at each potential, the lines not passing through the origin.

The conditions of activation of the passivated zinc electrode were investigated. The zinc electrode was passivated for a definite time at a constant potential and then the potential-time curves were determined without current or with a weak cathodic polarisation. Fig. 5 shows the cathodic activation curves for a zinc electrode passivated at various potentials. Similar curves were obtained with spontaneous activation of the electrode without current.

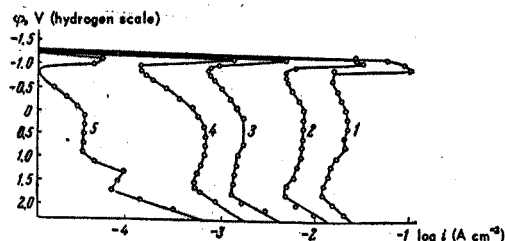


Fig. 2. Anodic polarisation curves determined by the potentiostatic method in KOH solutions stirred with a stream of nitrogen: 1) 1 N; 2) 0.5 N; 3) 0.25 N; 4) 0.1 N; 5) 0.03 N.

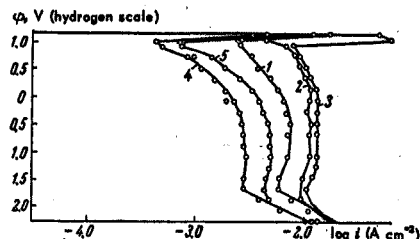


Fig. 3. Anodic polarisation curves determined by the potentiostatic method at various rates of stirring in 0.5 N KOH: 1) 1 rev. sec $^{-1}$; 2) 50 rev. sec $^{-1}$; 3) 83.5 rev. sec $^{-1}$. In 0.5 N KOH + 2.7×10^{-2} N Zn (saturated solution): 4) 1 rev. sec $^{-1}$; 5) 50 rev. sec $^{-1}$.

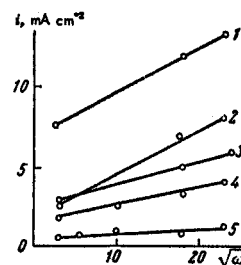


Fig. 4. Dependence of the dissolution rate of a passivated zinc electrode on the square root of the angular velocity of stirring ($\sqrt{\omega}$) in 0.5 N KOH: 1) at 0.6 V; 2) at -1.1 V. In 0.5 N KOH saturated with zincate: 3) at 0.6 V. In 0.25 N KOH: 4) at 0.6 V; 5) at -1.1 V.

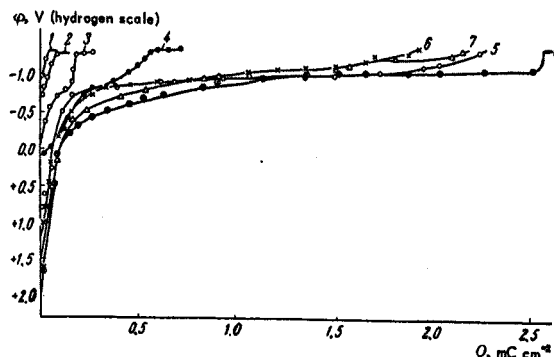


Fig. 5. Increase in the potential of zinc in 0.25 N KOH at a cathodic current density of 0.017 mA cm $^{-2}$ after passivation for 60 min at various constant potentials: 1) -1.0 V; 2) -0.7 V; 3) -0.1 V; 4) 0.1 V; 5) 0.9 V; 6) 1.1 V; 7) 1.5 V; 8) 2.0 V.

When the passivation had been carried out at potentials more positive than -0.3 V, an arrest was observed on the activation curve between -0.7 and -0.9 V. The length of the arrest depended on the potential at which the electrode had been passivated, increasing as the passivation potential rose from -0.3 to 0.9 V. Further change of the potential above 0.9 V had no effect on the length of the arrest. The arrest depends on the passivation time. The longer the time at a given potential, the larger the quantity of electricity required for the activation. If the electrode had been passivated for 60 min at -0.2 and $+0.4$ V then 0.2 and 1.4 mC cm $^{-2}$ respectively were required for the activation with a current of 0.03 mA cm $^{-2}$. But these quantities of electricity required for the activation probably amount to only a fraction of those necessary for the complete removal of the oxide film. The time required for self-activation of the zinc electrode (without current) is nearly three times as long as that for activation with a constant current density of 0.03 mA cm $^{-2}$, and 12 times as long as that with a current density of 0.07 mA cm $^{-2}$.

Fig. 6 shows the variation of the capacitance of the double layer C_2 and the resistance R_2 with potential in 1 N KOH. The values of the resistance R_2 are given only up to 10 kc/s because at higher frequencies the measurements were not sufficiently accurate. At a potential of about -1.1 V, corresponding to the dissolution of active zinc, a maximum in the capacitance is observed, which is particularly pronounced at low frequencies. The maximum

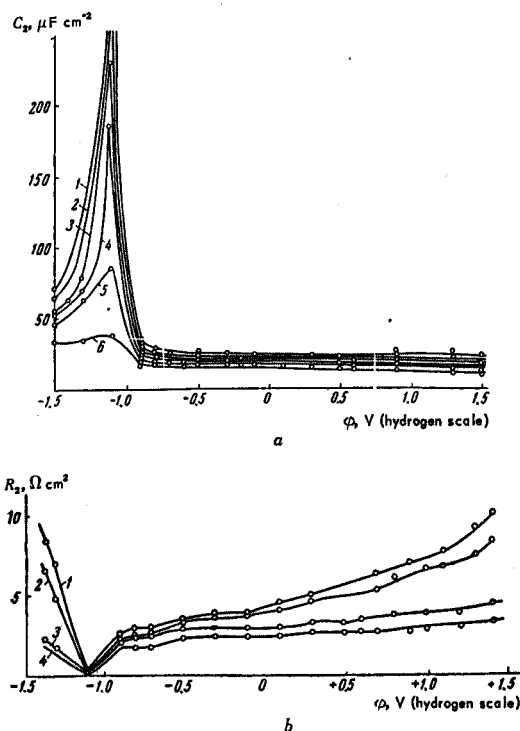


Fig. 6. Variation of (a) capacity C_2 and (b) resistance R_2 with potential in 1 N KOH at various frequencies (kc/s): 1) 0.5; 2) 1.0; 3) 5; 4) 10; 5) 20; 6) 50.

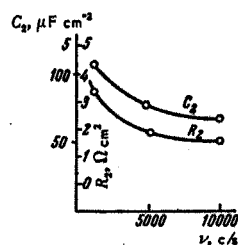


Fig. 7. Variation of double layer capacitance (C_2) and resistance (R_2) with frequency in 1 N KOH (at -1.3 V).

in the capacitance and the minimum in the resistance result from the concentration pseudocapacitance due to zinc ions, according to reaction $\text{Zn} + 4\text{OH}^- - 2e = \text{Zn}(\text{OH})_4^{2-}$. This is confirmed by the polarisation measurements and the phase shift which is close to 45° in the frequency range 0.5 – 50 kc/s and also by the parallel course of the C_2 and R_2 curves at moderate frequencies (Fig. 7). The lowering of the maximum at higher frequencies is also due to the concentration polarisation.

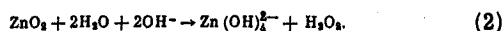
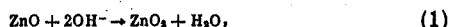
At about -1.0 V, corresponding to the passivation potential of zinc on the anodic curves (see Fig. 2), a drop in the capacitance C_2 and an increase in the resistance R_2 are observed. The capacitance of the double layer measured at 50 kc/s is then about half that observed at -1.5 V, i.e. at the potential of hydrogen evolution (Fig. 6a, curve 6). After passivation the reaction resistance R_2 becomes greater than that in the region of the active dissolution of zinc by ~ 1.5 powers of ten. On further positive change of potential in the passivation region from -1.0 V, the capacitance of the double layer C_2 and the reaction resistance R_2 remain practically constant at high frequencies. In the passivation region C_2 and R_2 vary with frequency in the way usually found with solid electrodes.

DISCUSSION

The passivation of zinc already occurs at a potential of ~ -1.0 V. If the electrode is polarised at a potential of -0.3 V or above, plateaus appear on the cathodic activation curves between -0.7 and -0.9 V (Fig. 5). These plateaus are absent when the electrodes are polarised at more negative potentials. The arrest of the potential is probably due to the reduction of the oxide layer formed at the potentials more positive than -0.3 V. The magnitude of the reduction potential of the oxide layer (-0.7 to -0.9 V) shows that the layer consists of a more electropositive compound than zinc oxide or hydroxide, such as, for example, zinc peroxide. The presence of peroxide in the layers covering zinc was suggested by Fischer and Budiloff⁵. However, this was denied by Thomson⁶, who explained the excess of oxygen in the layer by its adsorption on zinc oxide. However, this explanation conforms with our reduction potentials only if it is assumed that the adsorbed oxygen is bonded with the film just as strongly as in metal peroxides. These and other results⁴ show that the passivation is caused not by the relatively dense oxide layers formed at the more

positive potentials but by changes in the state of the surface occurring at about -1.0 V. These changes are due to the presence on the surface of a small quantity of oxygen or oxide (in the limit less than a monolayer), *i.e.* due to the effect of chemisorbed oxygen on the kinetics of the dissolution of metal. Only after the passivation has occurred do other processes begin to take place, such as, for example, the formation of layers containing zinc peroxide.

Calculations and the shape of the anodic polarisation curves show that the observed so-called "limiting" current in the passivation region is not the limiting current due to the OH⁻ ions. Dissolution with the "limiting" current may proceed according to the reactions



It may be assumed that the magnitude of the limiting current is determined by the rate of the chemical stage of the dissolution process [Eqn. (2)] of the passivating layer, the thickness of which remains constant.

The dependence of the dissolution rate of the film on the equilibrium solubility of the film material may be explained by the strong dependence of the "limiting" current on the alkali concentration. The observed dependence of the limiting current on the zincate ion concentration in the layer of solution near the electrode may also be explained by the effect of zincate ions on the solubility of the film. This also explains the linear dependence of the rate of dissolution to zincate on the square root of the angular velocity of the electrode. Measurements of the resistance R_2 showed that, in accordance with the potentiostatic measurements, the reaction rate slows down by about 1.5 powers of ten at a passivation potential of ~ -1.0 V. The double layer capacitance falls to a half, evidently due to adsorption of oxygen.

The value of the resistance R_2 outside the equilibrium region is related to the reaction rate by the following expression:

$$i_{\text{diss}} = \frac{b}{2.3R_2}, \quad (3)$$

where i_{diss} is the dissolution rate (A cm^{-2}), R_2 the resistance ($\Omega \text{ cm}^2$), and b the slope of the semi-logarithmic overpotential curve (V).

In the passive region, because of the rapid changes in the state of the surface[†], it has not been possible to determine the true slope by the method employed by other authors². Therefore the slope b was calculated from Eqn. (3) and was found to be 0.06 V, which according to published work² also confirms the absence of the passivating layer. The negligible variation of R_2 and C_2 with potential in the passivation region shows that the film formed at positive potentials has a fairly high electronic conductivity.

SUMMARY

1. The passivation of a zinc electrode in KOH solutions of various concentrations has been investigated by a potentiostatic method and by measuring the impedance components using alternating current.

[†] Using a loop oscillograph a clearly overestimated value of the slope of the overpotential curve, equal to 0.25 V, has been obtained.

2. The presence of a "limiting" current in the passivation region and its strong dependence on the alkali concentration may be explained by the limited solubility of the dense passivating film.
3. The observed dependence of the "limiting" current on the concentration of zincate ions in alkali solution and on the square root of the stirring rate is explained by the effect of the zincate ions on the solubility of the film material.
4. The cathodic activation curves show that formation of layers, apparently containing zinc peroxide, occurs at more positive potentials than the minimum passivation potential, *i.e.* on already passivated zinc.

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THE ELECTRODEPOSITION OF CHROMIUM-MOLYBDENUM ALLOYS

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Simultaneous deposition of chromium and other metals is difficult because the electrolysis proceeds under specific conditions, where the usual laws for the simultaneous discharge of metal ions are not applicable.

In the electrodeposition of chromium from the usual chromic acid electrolytes containing ions of other metals (Cu^{2+} , Zn^{2+} , Ni^{2+} , Fe^{2+}), whose reduction potentials are more positive than that of the chromium ions, only metallic chromium is deposited, the ions of the other metals not being reduced¹. This anomaly makes it difficult to select the conditions for simultaneous deposition of chromium with other metals.

Early attempts at preparation of chromium alloys were based on empirical methods. Difficulties of deposition of chromium together with other metals present in the form of simple ions led to investigations with various compounds of these metals. Thus a Cr-W alloy was obtained by adding tungstic anhydride to the usual electrolyte²; a Cr-Mo alloy of satisfactory quality containing 1.7% of molybdenum was prepared by using molybdic acid as an additive³.