

Fig. 7. Distribution of potential difference:  $\Delta\phi_1$  — fall in potential in surface layer;  $\Delta\phi_2$  — fall in layer of adsorbed dipoles;  $\Delta\phi_3$  — fall in ionic double layer;  $\Delta\phi_4$  — fall in oxide layer.

the transition region. The main portion of the overpotential is localised in this layer (Fig. 7). The ratio of the potential drop in the layer of adsorbed, polarised species to that in the surface layer will depend on the potential and the time during which the barrier layer has been forming. At the start of the transition region, when the curves are obtained under non-stationary conditions, the potential difference in the adsorbed layer will probably be considerable.

Such a view of the structure of the interface shows how the gradual accumulation of oxygen on the  $\text{Ag}_2\text{O}$  surface conditions the latter for the formation of the higher oxide. The part of the overpotential which is localised in the surface layer of the oxide becomes, as the  $\text{Ag}_2\text{O}$  is converted into  $\text{AgO}$ , a part of the potential difference across the double layer.

## SUMMARY

1. A study has been made of the electrochemical and photo-electrochemical behaviour of a silver electrode, in the region of the transition from the lower to the higher oxide, in alkali. Its peculiarities are associated with the semiconductor properties of the system.
2. The measured high resistance and low capacitance and also the high photosensitivity relate to the transition region on the charging curve.
3. The dependence of resistance and capacitance on potential, a.c. frequency, and illumination indicates the presence at the oxide-electrolyte interface of a barrier layer, polarised in the reverse direction. Formation of a barrier layer is due to adsorption on the  $\text{Ag}_2\text{O}$  surface of oxygen, which is an acceptor, and whose concentration increases with the potential.
4. The presence of the barrier layer determines the distribution of the potential drop and the kinetics of the anodic process. Most of the overpotential is localised in the surface layer and in the layer of adsorbed polarised species. The ratio of these overpotential components depends on the potential and the steady-state conditions of the process.

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## THE ANODIC PASSIVATION OF ZINC IN ALKALI. I. MEASUREMENTS AT CONSTANT CURRENT DENSITIES

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The passivation of a zinc electrode in alkali has been studied by many investigators. According to Iofa *et al.*<sup>1</sup> and Nikitina<sup>2</sup>, it is due to the orthorhombic modification of zinc hydroxide. The passivation is associated with the diffusion-controlled saturation of the layer near the electrode with zincate<sup>2</sup>. In sulphate solutions nuclei of the passivating film form by supersaturation of this layer with zinc salt<sup>3</sup>. Flerov<sup>4</sup> explained the rapid passivation of smooth zinc electrodes by "aging" of the hydroxide film on the surface of zinc crystals. Landsberg *et al.*<sup>5,6</sup> determined three passivation regions of zinc dependent on current density. In two regions, which the author called "diffusive", the passivation process is described by the equation  $(i - i_0)\sqrt{t_p} = B$ , where  $t_p$  is the passivation time,  $i$  is the polarising current density, and  $i_0$  and  $B$  are constants independent of the rate of stirring. In the third region of passivation at high current densities the equation  $(i - i_0)t_p = \text{const}$  is applicable. The change in the nature of the relation was explained by supposing that at the low current densities the main anodic process consists of the passage of metal into solution, and at the high current densities of the formation of the passivating film. The work of Sanghi and Wynne-Jones was restricted to low current densities. In dilute borate solutions the quantity of electricity required for the passivation corresponds to the formation of a monolayer of zinc hydroxide on the electrode surface<sup>8</sup>. Some authors<sup>1-3,5,6</sup> explain the relation between  $i$  and  $t$  in terms of diffusion processes near the electrode but none of them considered these processes quantitatively.

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In order to study the mechanism of zinc passivation and the nature of the passivating film, investigations were carried out on the kinetics of passivation of zinc polarised at constant current densities under conditions such that the diffusion processes and composition of the layer of solution near the electrode remained the same over the whole surface and could be fully taken into account.

## EXPERIMENTAL

The anodic behaviour of a zinc electrode in alkali was studied by obtaining the potential-time curves with an oscilloscope for polarisation at constant current density. Measurements were made in a glass apparatus with a disc-shaped zinc electrode (anode) rotated at 60–5000 rev.  $\times$   $\text{min}^{-1}$ , the temperature being  $20^\circ \pm 0.1^\circ$ . The electrode zinc was 99.999% pure. The electrodes were polished with glass powder and subjected to preliminary activation by cathodic polarisation in the appropriate KOH solution for 10 min at a current density of 50–100  $\text{mA cm}^{-2}$ . The second electrode consisted of a platinum wire or plate separated from the main solution by a glass filter. The potential of the zinc electrode was measured with reference to the mercuric oxide electrode, placed in alkali of the same concentration as that of the main solution, and then recalculated with reference to the standard hydrogen electrode. The potentials were measured either with a valve voltmeter or with an oscilloscope with a photographic attachment. The oscilloscope could be used for single-scan measurements at times from  $10^{-4}$  sec to 10 min. The measurements were made in an atmosphere of nitrogen. All the experiments were made with "chemically pure" KOH solutions, purified by prolonged polarisation using a nickel or zinc cathode and a platinum anode. The oscillographic method of determining the charging curves involved the passage of very small quantities of electricity, so that the surface area of the electrode did not change noticeably.

Fig. 1 shows, as an example, the oscillographic potential-time curves for anodic polarisation at constant current density in 0.1, 0.25, and 1  $N$  KOH with the electrode rotating at 16.7 rev.  $\text{sec}^{-1}$ . Lowering the alkali concentration causes a positive shift of the anodic dissolution potential of zinc. The quantity of electricity required for the

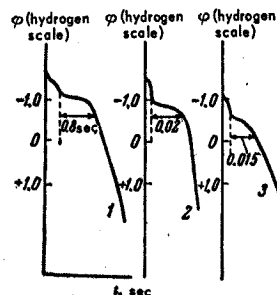


Fig. 1. Oscillographic potential-time curves at  $i = \text{const}$  and a rate of stirring of 16.7 rev.  $\text{sec}^{-1}$ : 1) 1  $N$  KOH ( $20^\circ$ ),  $i = 104 \text{ mA cm}^{-2}$ ; 2) 0.25  $N$  KOH ( $20^\circ$ ),  $i = 200 \text{ mA cm}^{-2}$ ; 3) 0.1  $N$  KOH ( $20^\circ$ ),  $i = 164 \text{ mA cm}^{-2}$ .

passivation of the zinc electrode per unit area was calculated from  $Q_p = it_p$ , where  $i$  is the density of anodic current and  $t_p$  the time that elapses from the moment of switching over to the anodic polarisation up to the abrupt change of potential to a value 0.5 V more positive than that of the active zinc.

Fig. 2a shows the dependence of  $1/Q_p$  on the current density  $i$ , at various rates of stirring, obtained from oscillographic measurements in 0.25  $N$  KOH solution. The curve has three regions. In the central (principal) region, extending from 10 to 200  $\text{mA cm}^{-2}$ , the relation is linear. Variation in the rate of stirring from 1 to 83.5 rev.  $\text{sec}^{-1}$  has practically no effect on  $1/Q_p$ , but the linear relation becomes disturbed both at the higher and lower current densities. At high current densities (above 200  $\text{mA cm}^{-2}$ ) the quantity of electricity required for passivation reaches a limiting value and becomes independent of the density of the polarising anodic current. This limiting value of  $Q_p$  is also independent of the rate of stirring. At low current densities (below 10  $\text{mA cm}^{-2}$ ) with stirring the quantity of electricity  $Q_p$  increases considerably, becoming very much greater than that corresponding to the linear relation

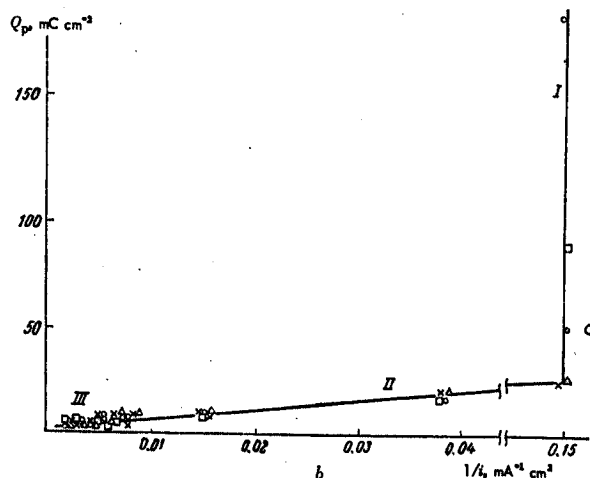
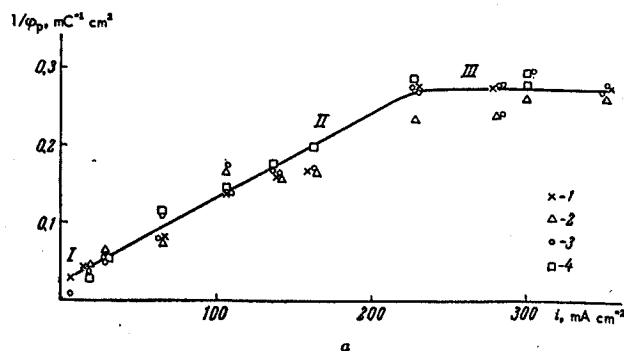


Fig. 2. Relation between  $Q_p$  and  $i$  in 0.25  $N$  KOH at various rates of stirring (rev.  $\text{sec}^{-1}$ ): 1) 1; 2) 5; 3) 16.7; 4) 50; 5) 83.5. a) Relation between  $1/Q_p$  and  $i$ ; b) relation between  $Q_p$  and  $1/i$ ; current density: I) low; II) medium; III) high.

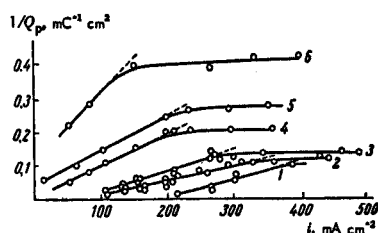


Fig. 3. Relation between  $1/Q_p$  and anodic current density in KOH solutions: 1) 1.5 N; 2) 1 N; 3) 0.75 N; 4) 0.5 N; 5) 0.25 N; 6) 0.1 N.

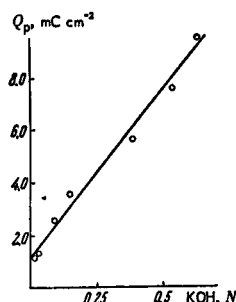


Fig. 4. Relation between  $Q_p$  and the surface  $\text{OH}^-$  ion concentration.

between  $1/Q_p$  and  $i$ . The increase in  $Q_p$  at low current densities can be clearly seen in Fig. 2b, showing the same experimental data as in Fig. 2a but plotted as  $Q_p$  against  $1/i$ . In the region of low current densities a considerable effect of the rate of stirring on  $Q_p$  is observed (see Fig. 2b).

Fig. 3 shows the averaged curves for the relation between  $1/Q_p$  and  $i$  in KOH solutions of various concentrations. Fig. 4 shows the relation between the limiting value of  $Q_p$ , obtained at high current densities, and the KOH concentration at the surface†. The introduction of zincate into alkali had no noticeable effect on the quantity of electricity required for the passivation at the medium and high current densities in 0.25–1.5, 0.01, and 0.03 N KOH. Only in 0.1 N KOH saturating the solution with zincate caused a decrease in the limiting value of  $Q_p$  from 2.5 to 1.2  $\text{mC cm}^{-2}$ . Experiments have shown that preliminary treatment of the zinc electrode affects its subsequent passivation.

## DISCUSSION

According to the laws of non-steady-state diffusion<sup>9</sup>, the variation in the concentration  $\Delta c$  of the reacting species in the layer of solution near the electrode is proportional to

† In calculating the alkali concentration at the electrode surface it was arbitrarily assumed that at high current densities all the current is expended on the passivation and that one electron is required for each reacting  $\text{OH}^-$  ion.

$i\sqrt{t}$  when the electrode is polarised at constant current density:

$$\Delta c = \frac{i}{nF} \sqrt{\frac{4t}{\pi D}}, \quad (1)$$

where  $D$  is the diffusion coefficient. This equation is applicable for an unstirred electrolyte in the absence of convection, which tends to suppress the changes in concentration. With a rotating disc electrode after a long time the following expression is applicable:

$$\Delta c = \frac{i}{nF} \left[ \sqrt{\frac{4t}{\pi D}} - \frac{0.08\omega^{1/2}t^{1/4}}{\nu^{1/4}} \right], \quad (2)$$

where  $\omega$  is the angular velocity of rotation and  $\nu$  is the kinematic viscosity. In the presence of convection a steady state becomes established at the electrode after some time and  $\Delta c$  is no longer time dependent:

$$\Delta c = \frac{i}{nF} \frac{1.62\nu^{1/4}}{D^{1/2}(\omega)^{1/4}}. \quad (3)$$

Fig. 5 shows the variation of concentration with time calculated from Eqns. (1)–(3) for two speeds of rotation, 5 and 50  $\text{rev. sec}^{-1}$ , taking  $\nu = 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$ ,  $D = 10^{-5} \text{ cm}^2 \times \text{sec}^{-1}$ ,  $n = 1$  and  $i = 0.1 \text{ A cm}^{-2}$ . At higher rates of stirring (higher speeds of rotation of the electrode) the suppression of  $\Delta c$  is more pronounced and the steady state is reached more rapidly. Analysis of Eqns. (2) and (3) shows that with each speed of rotation of the electrode the suppression of  $\Delta c$  and attainment of the steady state occur after a time of the order of  $3/Z$  sec (where  $Z = \omega/2\pi$  is the number of revolutions of the electrode per sec). After  $t = 3/Z$ , the stirring should have no effect on non-steady diffusion. Table 1 gives the calculated values of  $3/Z$  and the experimental passivation times ( $t_p$ ) of zinc at various rates of stirring and three different current densities in 1 N KOH. The passivation time is considerably shorter than  $3/Z$  at medium and high current densities, in particular at the low rates of stirring. At these current densities the passivation time is practically independent of the rates of stirring. At low current densities and high rates of stirring, when  $3/Z$  is comparable to or smaller than the passivation time, a more rapid increase in  $t_p$  is observed when  $i$  is reduced and the effect of the rate of stirring on  $t_p$  becomes greater.

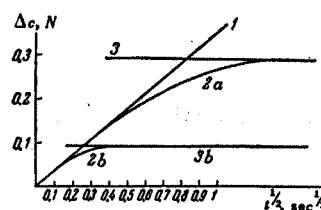


Fig. 5. Changes in the concentration of the reacting components in the layer of solution near the disc electrode: 1) non-steady-state concentration polarisation without convection; 2) non-steady-state concentration polarisation in the presence of convection; 3) steady-state value of concentration change in the presence of convection. Speed of rotation  $Z$  of the electrode: a) 5  $\text{rev. sec}^{-1}$ ; b) 50  $\text{rev. sec}^{-1}$ .

TABLE 1.

| No. of rev. per sec, Z | 3/Z (calc.), sec | Passivation time $t_p$ , sec     |                                  |                                  | No. of rev. per sec, Z | 3/Z (calc.), sec | Passivation time $t_p$ , sec     |                                  |                                  |
|------------------------|------------------|----------------------------------|----------------------------------|----------------------------------|------------------------|------------------|----------------------------------|----------------------------------|----------------------------------|
|                        |                  | $i = 104$<br>mA cm <sup>-2</sup> | $i = 260$<br>mA cm <sup>-2</sup> | $i = 340$<br>mA cm <sup>-2</sup> |                        |                  | $i = 104$<br>mA cm <sup>-2</sup> | $i = 260$<br>mA cm <sup>-2</sup> | $i = 340$<br>mA cm <sup>-2</sup> |
| 1.0                    | 3                | 0.44                             | 0.06                             | 0.028                            | 50.0                   | 0.06             | 4.4                              | 0.053                            | 0.021                            |
| 5.0                    | 0.6              | 0.4                              | 0.053                            | 0.021                            | 83.5                   | 0.04             | >50.0                            | 0.04                             | 0.022                            |
| 16.7                   | 0.2              | 1.0                              | 0.05                             | 0.026                            |                        |                  |                                  |                                  |                                  |

From the experimental data (see below), it follows that in the region of medium current densities the passivation time corresponds to the time required to attain definite changes in the concentration of the reacting ions at the electrode surface (a reduction in the hydroxide ion concentration and a corresponding increase in the zincate ion concentration). These concentration changes give rise to the passive state. At low current densities and high rates of stirring the concentration changes necessary for passivation cannot be attained even after the steady state has been reached, and the electrode remains in the active state for a long time. Evidently a part  $Q_1$  of the total quantity of electricity  $Q_p$  passing through the electrode is expended on the dissolution of zinc and the corresponding changes in the concentration of the solution. The remaining part  $Q_2$  (where  $Q_p = Q_1 + Q_2$ ) is expended on changing the state of the surface of the zinc electrode, leading to passivation without increasing the zinc concentration in the solution. It may be assumed that this part of electricity is independent of current density. At high current densities, because of the rapid changes in concentration (at least at low alkali concentrations),  $Q_1$  becomes small and the total observed quantity of electricity  $Q_p$  required for the passivation approximates to  $Q_2$ . This explains why at high current densities  $Q_p$  reaches a lower limit and becomes practically independent of current density (Fig. 3). At medium current densities when  $Q_1 > Q_2$  the relation between  $Q_p$  and  $i$  practically corresponds to that between  $Q_1$  and  $i$ .

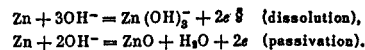
The value of  $Q_p$  depends greatly on the concentration of alkali solution. Table 2 gives the surface concentrations of hydroxide and zincate ions attained at medium current densities at the moment of reaching passivation in different initial solutions. The  $OH^-$  concentrations have been calculated from  $i$  and  $t_p$  corresponding to  $Q_p$ , obtained at medium current densities, and the  $Zn(OH)_4^{2-}$  ion concentrations from  $i$  and  $t_p$  corresponding to  $Q_1$  ( $Q_1 = Q_p - Q_2$ , where  $Q_2$  was arbitrarily taken as 1 mC cm<sup>-2</sup>, which is the limiting value of  $Q_p$  in dilute solutions). The following values were employed in the calculations by Eqn. (1):  $n = \frac{1}{2}$ ,  $D = 3 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup> for  $OH^-$  ions and  $n = 2$ ,  $D = 0.9 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup> for  $Zn(OH)_4^{2-}$  ions. At the moment of attaining the passive state the ratio of the molar concentrations of zincate and hydroxide ions becomes about 0.16 (see Table 2). This concentration ratio is considerably higher than that corresponding to the dissolution of zinc oxide in alkali<sup>10</sup> and can be explained by considerable supersaturation of the solution. The approximate constancy of this ratio shows that diffusion controls the passivation of zinc and that the process is to some extent reversible.

In dilute solutions about 1 mC cm<sup>-2</sup> is expended on passivation. Assuming that the coefficient of roughness is equal to 3 and remembering that 0.5 mC cm<sup>-2</sup> is required

TABLE 2.

| Initial KOH concn., M | Surface concn., M |                      | Initial KOH concn., M | Surface concn., M |                      |
|-----------------------|-------------------|----------------------|-----------------------|-------------------|----------------------|
|                       | $OH^-$ ions       | $Zn(OH)_4^{2-}$ ions |                       | $OH^-$ ions       | $Zn(OH)_4^{2-}$ ions |
| 1.0                   | 0.63              | 0.1                  | 0.25                  | 0.14              | 0.03                 |
| 0.75                  | 0.54              | 0.08                 | 0.1                   | 0.07              | 0.015                |
| 0.5                   | 0.39              | 0.05                 | 0.03                  | 0.008             |                      |

to form a monolayer of adsorbed oxygen or zinc oxide, it follows from the results given above that in dilute solutions passivation occurs before the zinc surface becomes completely covered with a monolayer of oxygen or oxide<sup>11</sup>. With more concentrated solutions it is not clear whether practically all the limiting quantity of electricity is expended on passivation or whether it is partly expended to form a monolayer that is sufficient for passivation, the remainder of the electricity being involved in the dissolution of the passivating oxides or the dissolution of zinc that takes place after a definite concentration ratio of zincate to hydroxide ions is reached and after commencement of the passivation process, which may proceed slowly. In fact, the higher the alkali concentration, the greater should be the dissolution rate by comparison with the passivation rate, because the specific expenditure of hydroxide ions is greater in the dissolution of zinc than in the passivation:



Consequently

$$i_{\text{diss}} = K_1 [OH^-]^3 e^{k\phi}; \quad i_p = K_2 [OH^-]^3 e^{k\phi}, \quad i_{\text{diss}}/i_p = K_3 [OH^-].$$

Assuming that

$$t_{\text{diss}} = t_p,$$

we obtain

$$i_{\text{diss}} t_p = Q_1, \quad i_p t_p = Q_2 \quad \text{and} \quad Q_1 / Q_2 = K_3 [OH^-].$$

Assuming further that  $Q_2$  is independent not only of  $i$  but also of the alkali concentration the relation  $Q_p = K[OH^-] + Q_2$  should hold, because  $Q_1 = Q_p - Q_2$ ; experiments have shown (Fig. 4) that this is approximately the case.

## SUMMARY

1. The passivation of zinc has been studied by the oscillographic potential-time curve method at constant current density.
2. At medium and high current densities the passivation time for the zinc electrode is shorter than the time required to attain steady-state diffusion in the layer of solution near the electrode. This explains why under these conditions the quantity of electricity required for passivation is independent of the rate of stirring of the electrolyte.  $Q_p$  depends on the rate of stirring only when the passivation time is equal to or greater than that required to attain steady-state diffusion. This holds at low current densities and high rates of stirring.

† In the case of dilute solutions allowance was made for the fact that  $n = 1$  in the passivation process.

§ According to this assumption, the final stage of the dissolution  $Zn(OH)_3^- + OH^- = Zn(OH)_4^{2-}$  proceeds in solution.

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  $1 \text{ mC cm}^{-2}$ . 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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The potentiostatic method has been widely used in studies of anodic behaviour of metals<sup>1,2</sup>. Sanghi and Fleischman<sup>3</sup> 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 previously<sup>4</sup>.

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  $\kappa$  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  $\kappa'$  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

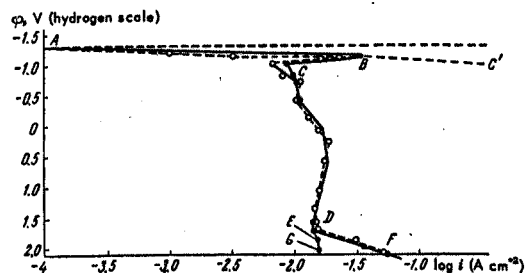


Fig. 1. Anodic polarisation curve determined by the potentiostatic method in 1 N KOH.