THEORY OF ZINC PASSIVATION

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A general property of the majority if not of all metals is that anode dissolution is retarded (i.e., passivation) when oxygen is adsorbed. This property is most simply observed when oscillographic measurements are made of the potential change in an electrode when a high density anode current is passed through it. In the proper solution the amount of electricity passed before the passive state is reached may be very small. For example, with iron, it is approximately equal to 1 mcoulomb/cm^2, based on the visible surface. This amount corresponds with one molecular layer of metallic oxide covering the entire surface or even just a part of the surface [1]. It is only when the solution is not activating that this small an amount of electricity is sufficient for passivation. If the solution is activating the current passing will first change the composition of the solution near the electrode and then, after the solution has become right, passivation can occur. Altogether, more electricity is used up than with a nonactivating electrolyte. Accordingly, the quantitative theory of anode passivation must take account of the distribution of the current between dissolution and passivation of the metal. It is easier to find the quantitative relationships in the case where dissolution of the metal in the active state goes without overvoltage and the rate is limited only by diffusion phenomena. For this reason we have tried to set up a quantitative theory by using zinc in KOH solutions, as was studied previously by Popova, Bagotskii and the author [2] as well as by others [3].

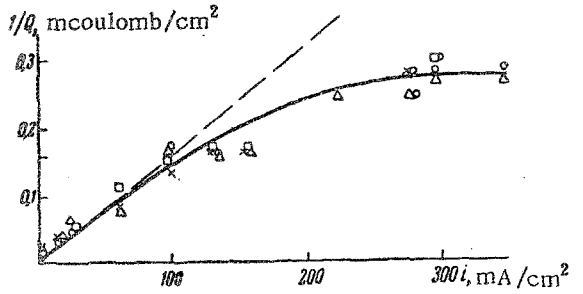

Fig. 1.

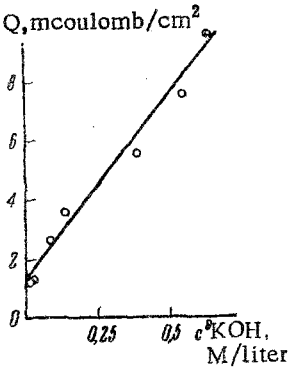

Fig. 2.

If we were going to find what effect the composition of the solution has on the passivation, we obviously had to know the electrolyte concentration at the electrode surface. We used a rotating disc electrode for this purpose, first, because the concentration is the same over the whole electrode surface, and second, because in this case the concentration can be accurately calculated [4]. The relation between the reciprocal of the quantity of passivating electricity and the current density found by means of the oscillograms mentioned above for zinc in 0.25 N KOH solution is shown as an example in Fig. 1 [2]. A calculation of the nonstationary diffusion shows that the quantity of electricity corresponding with the rising (left-hand) part of the curve is sufficient to produce a nonstationary change in alkali and zincate concentration at the electrode surface in the direction of decreasing alkali concentration and increasing zincate concentration, the zincate concentration approaching a value corresponding with a state of saturation. The same thing is observed for other initial concentrations of the solution, as well as at the start of passivation, which was investigated by a potentiostatic method, and which goes under stationary diffusion conditions. Obviously, ZnO adsorption becomes possible when the conditions get close to saturation. A considerable amount of supersaturation is required to form a $Zn(OH)_2$ precipitate phase.

The horizontal part of the curve (Fig. 1) shows the range of current densities in which the quantity of electricity required for passivation is independent of the current density. This limiting quantity of electricity, reduced by the constant quantity Q_p, equal to 1 mcoulomb/cm^2, is proportional to the alkali concentration at the electrode surface (Fig. 2). In dilute solutions this excess above 1 mcoulomb/cm^2 is equal to zero, while for example, in 1 N KOH it is equal to 9 mcoulomb/cm^2. It seems on first glance that it might be concluded from this fact that the thickness of the passivating layer depends on the alkali concentration and can reach thicknesses several times greater than a monolayer. However, if we prevent dissolution of zinc by first adding potassium zincate to the solution, it is found that only 1 mcoulomb/cm^2 goes into passivation at moderate alkali concentrations. In addition, the experiments have shown that after shallow passivation in both dilute and strong alkali the quantity of electricity required for cathode activation corresponds with a single monolayer of zinc oxide. Only after deep* passivation is a significantly larger quantity of electricity required to remove the passivity [2]. Accordingly it must be assumed that in our experiments it is not the thickness of the passivating layer which increases with the concentration of the solution, but rather the amount of zinc dissolved during passivation.

Passivation does not occur instantaneously, and the dissolution continues for some time while passivation is going on. Thus, the total quantity of electricity going into passivation and dissolution is equal to

$$Q = it_a + (i - i_p)\, t_p + i_p t_p \tag{1}$$

Here t_a is the length of time dissolution goes on up to the start of passivation, t_p is the length of time required for passivation, i is the total current strength, and i_p is the part of the current going into passivation; $i_p t_p = Q_p$.

If the current density is large enough, the first term in Eq. (1) may be neglected. Then Q is equal to it_p. As we have seen from Fig. 2, $Q - Q_p = b\,[OH^-]$, where $[OH^-]$ is the concentration of alkali at the electrode surface. Then

$$(i - i_p)\, t_p = b\,[OH^-]. \tag{2}$$

Since it was assumed that $Q_p = i_p t_p = \text{const}$, it is found that the experiment ought to give

$$\frac{i - i_p}{i_p} = b'[OH^-], \tag{2'}$$

and for constant alkali concentration and varying potential

$$\frac{i - i_p}{i_p} = \text{const}. \tag{3}$$

The over-all reaction for the anode dissolution of active zinc, $Zn + 4OH^- = Zn(OH)_4^{2-} + 2\theta$, as shown by the experiments of T. I. Popova in a solution free of zincate approximately obeys the following kinetic equation

$$\varphi = 0{,}03 \log_{10} i_a - 0{,}1 \lg [OH^-] + \text{const}. \tag{4}$$

Equation (4) can apparently be interpreted to show that the dissolution reaction goes without overvoltage** right up to the formation of $Zn(OH)_3^-$, and that only the last stage, the union of OH^- to $Zn(OH)_3^-$, is retarded and occurs in solution. Actually, under this assumption the reaction occurring at the electrode surface is $Zn + 3OH^- = Zn(OH)_3^- + 2\theta$. The rate of this reaction is

$$i_a = k\,[OH^-]^3 \cdot e^{\frac{2F\varphi}{RT}},$$

which corresponds approximately with Eq. (4). We assume that the union of OH^- to $Zn(OH)_3^-$ is enough retarded so that the $Zn(OH)_3^-$ ion can go into solution, but at the same time fast enough so that, without any current, equili-

* Deep passivation is understood to mean passivation produced by means of strong anode polarization.

** This fact, under the present conditions, allows us to eliminate the possibility of monovalent zinc being formed in the dissolution and liberation processes.

brium is established practically immediately in the system $Zn/Zn(OH)_4^{2-}$, OH^- [5]. The idea that there is no retardation in the discharge during anode dissolution of zinc in this range of current densities is supported by the fact that, as the experiments have shown, anode polarization of zinc in dilute solutions is independent of whether or not an excess of neutral salt (Na_2SO_4)* is present.

The experimental Eq. (2) can be explained if we assume that a ZnO molecule passivates the zinc. This assumption is in accord with the fact that passivation occurs on approaching a state of saturation of the solution with zincate. The slow stage of this process can be dehydration of the $Zn(OH)_2$ molecule. With these assumptions the passivation kinetics takes on the following form

$$i_p = k\,[OH^-]^2\, e^{\frac{2F\varphi}{RT}}. \tag{5}$$

If we write Eq. (4) as

$$i_a = i - i_p = k\,[OH^-]^3 \cdot e^{\frac{2F\varphi}{RT}}$$

and divide it by Eq. (5) we get Eqs. (2') and (2).

Accordingly to what we have been saying, formation of a passivating phase layer can only start if an adsorptive passivating layer has been formed and dissolution has suddenly been rendered difficult, which at constant current density allows the potential shift to occur which is necessary for the diffusion of ions in the oxide layer, which in its turn is required to increase the thickness of the continuous oxide layer up to the values known to occur. The rate at which the passivating film is thickened isorders of magnitude less than the rate at which an adsorptive passivating film is formed. The stationary dissolution rate of the passive metal can, according to Bonhöffer [6], be determined by the chemical dissolution rate of the continuous oxide layer.

SUMMARY

1. Passivation can occur in an activating solution only after the composition of the solution at the electrode has been changed.

2. A theoretical interpretation is given of the kinetic equationobtained experimentally for the dissolution of zinc in alkali.

3. Theoretical considerations as to the kinetics of dissolution and passivation of a metal have been used to derive an equation giving the quantity of electricity required for anode passivation of a metal as a function of the concentration of the solution, which agrees with experiment.

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* Anode polarization of zinc and alkali is caused by an increase in zincate concentration at the electrode. The zincate concentration at the electrode cannot be greater than the alkali concentration in the middle of the solution. Since the mobility of hydroxyl ion is greater than the mobility of the zincate ion, adding an extraneous (third) electrolyte has practically no effect on the anode concentration polarization of the zinc.