Physical Chemistry

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1960

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

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ANODIC PASSIVATION OF ZINC IN ALKALINE SOLUTIONS

(Presented by Academician A. N. Frumkin on 25 I 1960)

In a number of works (^{1}-^{3}) the opinion is expressed that the passivation of zinc is due to the formation of phase films of zinc oxide or hydroxide; the onset of passivation is sometimes associated with diffusion processes in the near-electrode layer. However, the mechanism of formation and the nature of the passivating film are still not clear. In particular, there are no works in which diffusion phenomena have been taken quantitatively into account.

The purpose of the present work was to elucidate the influence of the composition of the near-electrode layer of the solution on the passivation of zinc and to study the character of the passivating layers on zinc in order to clarify the question of the influence of oxygen adsorption and the formation of a phase oxide layer on the passivation of zinc. The anodic behavior of zinc in KOH solutions was studied by us by oscillographically recording potential—time curves (φ—t) at constant current densities on a rotating disk electrode. The quantity of electricity required for passivation, $Q_{\text{pass}} = it_{\text{p}}$ (i is the current density, t_{p} is the passivation time), was determined as a function of the current density, the alkali concentration, and the rate of stirring of the electrolyte. In addition, potentiostatic polarization measurements were carried out, making it possible to determine the dependence of the dissolution rate of active and passivated zinc on the potential and to establish the boundary of potentials at which passivation occurs. Curves of cathodic activation of passivated zinc were also recorded, making it possible to determine the potential at which reduction of the phase film begins.

Fig. 1. Dependence of $1/Q_{\text{pass}}$ on the anodic current density i 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

Figure 1 presents the dependence of $1/Q_{\text{pass}}$ on i, obtained on the basis of oscillographic measurements at constant current densities*. In the region of medium current densities, a linear dependence is observed between $1/Q_{\text{pass}}$ and

Fig. 2

Figure 2: Fig. 2

i, analogous to the dependence observed by other authors (^{2}, ^{3}). It follows from our experiments that Q_{pass}, obtained upon polarization at medium and high current densities, does not depend on the rate of stirring of the electrolyte from 60 to 5000 rpm. At lower current densities the above-mentioned linear dependence is violated, and for the onset of passivation high values of Q_{pass} are required (40-200 μC/cm^2).

* Q_{pass} —average values of the quantity of electricity in μC/cm^2, taken from 10-12 measurements.

With increasing stirring rate in this case an increase in Q_{pass} is observed. At low current densities and especially under vigorous stirring (3000-5000 rpm), in strong 0.5-2.5 N KOH solutions passivation does not occur at all. Calculations showed that, in the region of medium and high current densities, the passivation time is shorter than the time required for establishment of the steady state of diffusion. This can explain the independence of Q_{pass} from stirring, since the effect of stirring on the rate of nonstationary diffusion is initially insignificant. A sharp increase of Q_{pass} with stirring rate is observed at such current densities and stirring rates for which the passivation time is comparable with, or greater than, the time required for establishment of stationary diffusion.

Fig. 2. Anodic polarization curves recorded by the potentiostatic method in KOH solutions:
1 –1 N; 2 –0.5 N; 3 –0.25 N; 4 –0.1 N; 5 –0.03 N

At high current densities (see Fig. 1), Q_{pass} is practically independent of the density of the polarizing current.

Experimental data show that, for passivation to occur, a definite change in the concentration of alkali and zincate in the near-electrode layer is necessary. At low currents and vigorous stirring of the solution, the required concentration changes are not achieved, and even after the stationary state of diffusion has been established zinc passivation does not occur. The experimental results can be explained if it is assumed that, at medium current densities, part of the quantity of electricity required for passivation is spent on dissolution of zinc and the accompanying changes in the concentration of OH$^-$ ions and zincate (Q_1); another part (Q_2), probably not dependent on the current density, is spent on changing the state of the surface of the zinc electrode, causing passivation.

At high current densities Q_1 becomes small, and the measured quantity of electricity required for passivation, Q_{pass}, approaches Q_2. Experimental data show that Q_{pass} for high current densities decreases linearly with decreasing alkali concentration. In very dilute solutions (0.01; 0.03 N KOH, as well as 0.1 N KOH saturated with zincate), Q_{pass} is approximately equal to 1 μC/cm^2. If the

Figure 3

Figure 3: Figure 3

roughness coefficient is taken to be 2.5–3 and it is considered that formation of one monolayer of adsorbed oxygen requires about $0.5\,\mu\mathrm{C/cm}^2$, then it follows from the data presented that, at least in dilute solutions, passivation occurs already with a monolayer or even incomplete coverage of the zinc surface by adsorbed oxygen.

Figure 2 presents anodic polarization curves recorded by the potentiostatic method in various KOH solutions. The curves have the form characteristic of many passivating metals ([4,5]).*

Under anodic polarization, at first an active region of zinc dissolution is observed (for example, Fig. 2, curve 5, segment *ab*). Passivation of zinc upon shifting its potential in the positive direction manifests itself in a decrease in the dissolution rate (segment *bc*), by approximately two orders of magnitude compared with the dissolution rate of active zinc polarized up to this potential, and in a slowing of the growth of the dissolution rate with further increase of the potential (segment *cd*). At sufficiently positive potentials, the dissolution rate of zinc almost ceases to depend on the potential (segment *de*). The shape of the curves and calculation show that this "limiting" current in the passivation region is not an ordinary diffusion limiting current. It may be assumed that the magnitude of the "limiting" current is determined by the rate of chemical dissolution of the phase film, the thickness of which remains unchanged (⁀4). Experiments showed that after the onset of passivation and a strong shift of the potential in the positive direction, upon switching off the anodic current, as well as under weak cathodic polarization, there is at first a rapid return of the potential in the negative direction, and then at −0.7-−0.9 V a delay appears (see Fig. 3). The appearance of the delay is associated with partial reduction of the thin phase film formed during anodic polarization. The value of the potential at which reduction of the phase film begins shows that, besides zinc oxide, the film also contains a more positive compound than ZnO—for example, zinc peroxide.

Fig. 3. Curves of potential increase at a cathodic current density of $0.017\ \mathrm{mA/cm}^2$ after passivation for 60 min at various constant potentials: 1—(−1.1 V) and (−0.9 V); 2–(−0.7 V); 3–(−0.3 V); 4—0.1 V; 5—0.5 V; 6—1.3 V; 7—2.1 V.

The dissolution of zinc at the "limiting" current is apparently determined by the rate of the chemical reaction of dissolution of zinc oxide (and also peroxide):

$$\mathrm{ZnO} + 2\mathrm{OH}^- \rightarrow \mathrm{ZnO}_2^{2-} + \mathrm{H_2O}.$$

* Quite recently, similar anodic curves have also been obtained for zinc ([6]).

Figure 4

Figure 4: Figure 4

This can explain the observed strong dependence of the "limiting" current on the alkali concentration (Fig. 2). The dependence we established of the "limiting" current on the concentration of zincate ions in the near-electrode layer of the solution* is explained by the inhibiting effect of zincate ions on the rate of film dissolution. This also explains the dependence of the rate of zinc dissolution on stirring of the electrolyte (Fig. 4).

Fig. 4. Dependence of the dissolution rate of the passive zinc electrode on the angular rotation velocity (ω) in solutions of 0.5 N KOH: 1—+0.6 V; 2—(−1.1 V); in saturated zincate solution 0.5 N KOH: 3—+0.6 V; in 0.25 N KOH: 4—+0.6 V; 5—(−1.1 V).

The phase film that forms and the zinc peroxide arising in it are not necessary for passivation of the zinc electrode. This is evident from the fact that passivation already occurs at a potential of −1.1 or −1.0 V (Fig. 2), i.e., at potentials more negative than the reduction potential of zinc peroxide in the phase film. Moreover, as described above, the amount of electricity Q_2 going to passivation under the corresponding conditions is less than that sufficient for the formation of a phase layer on the electrode surface. Formation of zinc peroxide in the phase layer is a consequence of passivation of the electrode, not its cause; without preliminary passivation it is impossible to bring the potential of the zinc electrode to the value at which formation of this compound begins.

It follows from the experiments described above that the passivation of a zinc electrode during its anodic polarization is affected by concentration changes near the electrode surface, which promote a change in the state of the surface, leading to inhibition of the zinc-dissolution process. As in the case of the passivation of iron in alkalis (7), the passivation of zinc in alkali is caused by the adsorption of oxygen or hydroxide in an amount insufficient to cover the entire surface with a monatomic layer. The formation of films that are phase-like in nature and contain zinc peroxide is a secondary process.

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Received
11 I 1960

* For example, at a zincate concentration of $3.5 \cdot 10^{-2}$ N, the dissolution rate is 2-2.5 times lower than at $1.7 \cdot 10^{-2}$ N.

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Note: Figure translations are in progress. See original paper for figures.