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Abstract

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ON THE MECHANISM OF THE ANODIC DISSOLUTION OF MAGNESIUM

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It has hitherto not been possible to elucidate the mechanism of a fast stage in the presence of a slower one for the process of anodic oxidation of a metal, owing to experimental and theoretical difficulties. At present this proves possible in the case of metals exhibiting the "negative difference effect," i.e., metals which, during anodic dissolution, form as a transition state an unstable monovalent ion in solution ($^{1,\,2}$).

In the dissolution of magnesium in acid solutions the process may proceed according to the following scheme:

$$\begin{aligned}
&1.\quad Mg \longrightarrow Mg^{+}_{ads} + \theta;\\
&2.\quad Mg^{+}_{ads} \longrightarrow Mg^{++} + \theta;\\
&3.\quad Mg^{+}_{ads} \longrightarrow Mg^{+}_{soln}
\end{aligned}$$

and then

$$4.\quad Mg^{+}_{soln} + H^{+} \longrightarrow Mg^{++} + \frac{1}{2}H_2$$

or, in neutral and weakly alkaline solutions:

$$4'.\quad Mg^{+}_{soln} + H_2O + OH^{-} \longrightarrow Mg(OH_2) + \frac{1}{2}H_2.$$

The oxidation of metallic magnesium to the monovalent state is the slowest of the electrochemical stages of this process, since it is followed by two parallel stages, of which diffusion into the solution is practically always fast because of the instability of the monovalent ions. The electrochemical oxidation of metallic magnesium is very strongly inhibited by adsorption of oxygen on it, i.e., by passivation (^{3}). It might have been expected that the electrochemical process of oxidation of the intermediate compound—the monovalent magnesium ion—to the divalent state (at a constant surface concentration of monovalent magnesium) should not be slowed down upon passivation of magnesium, just as the oxidation of divalent iron to trivalent iron can proceed at a considerable rate on passive iron, on which the oxidation of the metal has practically completely ceased (4). Indeed, the chemical adsorption of oxygen leading to passivation of the metal changes the structure of the metal surface and the structure of the electrical double layer only in that part of it which adjoins the metal surface, and therefore has primary significance for the process of the transition of the metal into the state of a hydrated ion. The process of further oxidation of the hydrated cation occurs without transfer of the ion across the metal-solution boundary; therefore, for the oxidation of the cation, if no change in the ψ_1-potential occurs, the change in the work function

electron should not affect it (for the case of hydrogen evolution, the absence of an effect of the work function was pointed out by A. N. Frumkin as early as 1931 (5)). The reason for this is that, at a constant total electrode potential, a change in the work function of the electron in vacuum or in the contact potential is compensated by an equal change in the potential drop in the ionic double electric layer.

Let us consider the regularities of the oxidation of monovalent magnesium. Assuming that the rate i_2 of the anodic process $\mathrm{Mg}^+ \rightarrow \mathrm{Mg}^{++}$ is determined by the slowness of the electron transfer (accompanied by an increase in hydration), the following expression may be written:

$$i_2 = k_2[\mathrm{Mg}^+]_s \exp\frac{\beta F\varphi}{RT}. \tag{1}$$

We shall take the value of the constant β to be the same as for the oxidation of metallic magnesium to monovalent magnesium, i.e. (according to our data) $\beta = 0.23$. For the parallel process of diffusional transfer of Mg^+ from the electrode surface into the solution, we have:

$$i_3 = FD\frac{dc}{dx} = FD\frac{[\mathrm{Mg}^+]_{x=0}}{\delta} = k_3[\mathrm{Mg}^+]_s, \tag{2}$$

where k_3 depends on the rate of stirring in the case where oxidation of Mg^+ by water does not already end in the part of the diffusion layer immediately adjacent to the electrode. It is assumed that the concentration of magnesium ions in the solution at the surface $[\mathrm{Mg}^+]_{x=0}$ is proportional to their surface concentration $[\mathrm{Mg}^+]_s$, since it is comparatively small.

From comparison of equations (1) and (2) it is seen that the distribution of magnesium between the two parallel processes, i.e. the ratio i_2/i_3, does not depend on the surface concentration of monovalent magnesium $(\mathrm{Mg}^+)_s$, but depends only on the potential:

$$\frac{i_2}{i_3} = \frac{k_2}{k_3}\exp\frac{\beta F\varphi}{RT} = k\exp\frac{\beta F\varphi}{RT}. \tag{3}$$

In order to proceed to a comparison of this theoretical conclusion with the experimental data, it is necessary to find the dependence of the effective valence n_i of the dissolving magnesium (^{1}) on the electrode potential φ. It is easy to show that the effective valence of magnesium is

$$n_i = \frac{1 + 2i_2/i_3}{1 + i_2/i_3}. \tag{4}$$

Comparing equations (3) and (4), we obtain the desired dependence:

$$n_i = \frac{1 + 2k \exp \frac{\beta F \varphi}{RT}}{1 + k \exp \frac{\beta F \varphi}{RT}}. \tag{5}$$

On the other hand, our experiments showed that in activating solutions ($MgCl_2$, $MgBr_2$, $MgSO_4$) the potential of anodic dissolution of magnesium depends hardly at all on the current density; when the anodic current density is decreased, the passivity of magnesium increases*. The effective valence n_i and the ratio i_2/i_3 (equation (4)) therefore remain constant at different current densities at the same potential, i.e. according to equation (3) the constant k does not depend on the degree of passivity of the metal, although i_2 changes hundreds of times, as does

* This follows from the reversible decrease in the capacitance of the double layer and from the course of the oscillographic curves of the change in electrode potential after a sharp decrease in current density, from which it is seen that the potential gradually returns to its initial value.

i_3. In other words, during passivation of magnesium, the rate of anodic oxidation of Mg^+ ions at constant φ changes only because of the change in $[Mg^+]_s$, as does their diffusion from the electrode (it must be assumed that, when the apparent current density changes, the true current density, determined with allowance for the change in the total true surface and the possible mechanical covering of part of the surface by a phase oxide film, may in time turn out to have changed to a different extent than the apparent one, which is not reflected in our conclusions).

The graphical representation of the theoretical dependence of n_i on φ according to equation (5) gives an S-shaped curve (Fig. 1), generally analogous to the experimental one. As an additional proof one may compare the slopes of the tangents to the curves at $n_i = 1.5$, i.e., at the point of inflection. Differentiating (5) with respect to φ:

$$\frac{dn_i}{d\varphi} = \frac{k\beta F}{RT} \exp\left(\frac{\beta F \varphi}{RT}\right) \left[1 + k \exp\left(\frac{\beta F \varphi}{RT}\right)\right]^{-2},$$

and for the inflection point

Fig. 1

Figure 1: Fig. 1

$$\left(\frac{dn_i}{d\varphi}\right)_{n_i=1.5} = \frac{\beta F}{4RT} = 2.3\,\mathrm{V}^{-1}.$$

Fig. 1. Dependence of the effective initial valence of magnesium on the potential of the magnesium anode. The dashed line is the theoretical curve, the solid line is the experimental curve. Solutions: 1—$MgCl_2$ (1 N); 2—$MgBr_2$ (1 N); 3 —$MgSO_4$ (0.01 N and 1 N); 4—$KClO_3$ (0.5 N).

Within the experimental error at the inflection point, the slopes of the theoretical and experimental curves coincide. The analogous course of the experimental and theoretical curves generally confirms the assumption made about branching of the process into diffusion and a slow discharge.

Thus, it may be assumed that the rate of the second stage of anodic oxidation of magnesium is determined by the rate of electron transfer. Naturally, this rate does not depend appreciably on the passivity of the electrode. However, the experimental curve deviates from the theoretical one when approaching the limiting values. In contrast to the theoretical curve, the experimental curve at large negative values of φ^* tends to the limit $n_i \simeq 1.3$, and not $n_i = 1$. On this basis it may be assumed that either in the given interval of negative values of the potential the rate of oxidation of Mg^+ does not depend on φ, or in this region of potentials the transition into solution of every two Mg^+ ions is always accompanied by the formation of one Mg^{++}. The latter assumption may explain the mechanism of activation and the reason for the stationarity of the anodic potential in "activating" solutions. It may be assumed that in the passivating adsorption layer the state of magnesium is analogous to its state in the bulk oxide of divalent magnesium. If the elementary act of anodic dissolution of magnesium consists in the transition into solution of two monovalent Mg^+ ions structurally bound to one passivating MgO group, then this group will be carried into solution by the monovalent ions, which will lead to activation proportional to the anodic current.

Activation after an increase in current density will continue until the effective surface has increased so much that the true current density decreases to the initial value, which automatically leads to the initial value of the potential, at which there is some stationary number of passivating groups per unit of effective surface.

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* Here the potential φ is measured from the potential of the inflection point, i.e., $k = 1$.

Equation (5) makes it possible to give a general dependence of the rate of hydrogen evolution (in amp/cm^2) on the potential (^{2}):

$$V = V_1 + V_2 = \frac{k' \exp\left(\dfrac{\beta' F\varphi}{RT}\right)}{1 + k \exp\left(\dfrac{\beta F\varphi}{RT}\right)} + k'' \exp\left(-\frac{\alpha F\varphi}{RT}\right),$$

where k' and β' are coefficients for the reaction $Mg \rightarrow Mg^+$ (we have taken $\beta' = \beta$), and k'' is the rate of self-dissolution of magnesium at $\varphi = 0$.

On the basis of the fact of the instability of the Mg^+ ion and the assumptions we have made concerning the sequence of the anodic processes of formation of Mg^+ and Mg^{++}, one may conclude that the normal potential of the Mg^+/Mg^{++} system is substantially more negative than the most negative value of the potential at which formation of Mg^{++} at the anode still occurs, i.e. -1.4 V on the hydrogen scale, and may be estimated at approximately -1.7 V. According to Luther' s rule, the normal electrode potential of the Mg/Mg^+ system in this case should be approximately -3 V, which corresponds to the normal potential of an alkali metal.

By selecting, instead of water, other suitable acceptors for monovalent ions, one may hope to obtain analogous curves $n_i(\varphi)$ for other, more noble metals with the lowest valence state of the ion equal to 2, and to determine the slow stage in these cases as well.

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