

THEORY OF ELECTROCHEMICAL PROTECTION. II. DIFFUSION-CONTROLLED REACTIONS

R. R. Dogonadze, V. G. Levich,
and Yu. A. Chizmadzhev

The potential distribution in a system consisting of a metal (cathode) and a protector (anode), for a steady state of spontaneous dissolution, was calculated in the previous paper¹. It was then assumed that the rates of anodic and cathodic processes were determined by the rates of the corresponding electrochemical reactions. Concentration polarisation was completely ignored.

In practice, however, we frequently have to deal with the corrosion of metals in the presence of dissolved oxygen². Here the cathodic process is the electrochemical reduction of oxygen:



the rate of which is given by the polarisation characteristic³:

$$i^{\text{O}_2} = k(c^{\text{O}_2})_s f(\varphi), \quad (2)$$

where i^{O_2} is the rate of the electrode reaction (1) (current density with respect to oxygen), $(c^{\text{O}_2})_s$ the oxygen concentration directly at the metal surface, $f(\varphi)$ a function of the potential of the metal, and k a constant.

In practice conditions of stirring may often be such, and the concentration of oxygen in the solution so low, that the rate of supply of oxygen to the surface is comparable, and sometimes even small in comparison, with the rate of the electrode reaction. In these cases the overall rate of corrosion of metal in a system with a protector is dependent on the rate of supply of oxygen. The purpose of the present paper is to examine systems of this type.

The limiting case of purely diffusion-controlled process was examined recently by Wagner⁴. As boundary condition at the surface of the protected metal, however, he used the requirement

$$i^{\text{O}_2} = \text{const.}$$

With the geometry of the system assumed by Wagner (a flat metal surface having bands of impurities) such a boundary condition does not represent any real conditions for the diffusion transport of oxygen. We shall return to this question later.

Calculation of the rate of a corrosion process in a system with electrochemical protection in the presence of diffusion-controlled reactions is extremely complicated. The geometry of the system must therefore be chosen so that access of oxygen should occur under extremely simple and fully defined conditions. When mixing of the liquid occurs, which is nearly always the case in practice, the supply of oxygen is effected by convective diffusion.

It is simplest to consider convective diffusion to the surface of a rotating disc, which represents the only surface which is uniformly accessible with respect to diffusion, i.e. such that the diffusion flux has the same value at all points on it⁵. In all other cases, in particular in the case of a plane over which liquid is flowing, which was considered by Wagner⁴, the diffusion flux varies from one point to another along the surface. For this reason the boundary condition adopted by Wagner does not correspond to the geometry of his system.

We shall now consider the distribution of potential and current in the following system.

A disc electrode of the main metal, of radius R , contains at its centre a protector (an impurity metal which undergoes the anodic process at a greater rate) in the form of a circle of radius r_0 . The disc is placed in an electrolyte solution containing also dissolved oxygen at concentration c_0 , and rotates with angular velocity ω . We shall neglect edge effects, and regard the disc as being of infinite radius.

The potential of the electric field in the solution satisfies the Laplace equation:

$$\Delta\varphi = 0. \quad (3)$$

In order to find the distribution of potential in the system, appropriate boundary conditions must be specified at the surface of the protector (anode) and the main metal (cathode) as well as at infinity (in the bulk of the solution).

Let us examine first the surface of the anode, i.e. the surface $z = 0$, $r \leq r_0$, where z is the height and r the radius vector in cylindrical coordinates, with the origin at the centre of the disc. We shall assume that the dimensions of the protective anode are sufficiently small to satisfy the condition

$$H = \frac{j_0 r_0^2}{2\kappa RT} \ll 1, \quad (4)$$

where j_0 is the current density at the surface of the anode. As has been shown previously^{4,6}, the boundary condition for the current density at the anode can then be written in the form

$$j_0 = \kappa \left(\frac{\partial \varphi}{\partial n} \right)_{z=0, r \leq r_0} = \text{const.} \quad (5)$$

At the cathode surface (the region $z = 0$, $r_0 \leq r \leq R$) the current density $\kappa(\partial \varphi / \partial n)_{z=0, r_0 \leq r \leq R}$ is equal to the reaction velocity of the electrochemical reduction of oxygen (1) at the electrode.

The function $f(\varphi)$ in the formula for the rate of reaction (1) can be written in the form³

$$f(\varphi) = \exp \left\{ -\frac{F\varphi_0}{2RT} \right\} - \exp \left\{ \frac{F\varphi_0}{2RT} \right\}, \quad (6)$$

where φ_0 is the negative potential at the surface of the metal.

The boundary condition at the cathode surface means that

$$\kappa \left(\frac{\partial \varphi}{\partial n} \right)_{z=0, r_0 \leq r \leq R} = k(c^{\text{O}_2})_s f(\varphi_0), \quad (7)$$

where $f(\varphi_0)$ is defined by (6).

The last equation contains the oxygen concentration at the surface, $(c^{\text{O}_2})_s$. It is determined from the requirement that under steady-state conditions the velocity of the electrode reaction (1) should be equal to the diffusion flux of oxygen to the electrode surface. This has been found previously⁴ to be

$$i^{\text{O}_2}_{\text{diff}} = 4FD_0 \frac{c_0^{\text{O}_2} - c_s^{\text{O}_2}}{\delta'}, \quad (8)$$

where δ' , the thickness of the boundary diffusion layer, which is constant over the whole surface of the disc, is given by

$$\delta' = 1.61 D_0^{1/2} \omega^{-1/2}, \quad (9)$$

D_{O_2} being the coefficient of diffusion of oxygen molecules, and ν the viscosity of the liquid.

On equating $i_{diff}^{O_2}$ and i^{O_2} , we find the surface concentration of oxygen (c^{O_2})_s under steady-state conditions:

$$(c^{O_2})_s = \frac{c_0}{1 + \frac{k\delta'}{4FD_{O_2}} f(\varphi_0)} \quad (10)$$

Substitution of (10) in (7) gives the final boundary condition at the cathode (protected metal):

$$\kappa \left(\frac{\partial \varphi}{\partial n} \right)_{z=0, r_0 \leq r \leq R} = \frac{k f(\varphi_0) c_0}{\delta' + \frac{4FD_{O_2}}{k} f(\varphi_0)} = \frac{i^{O_2}}{1 + \frac{i^{O_2}}{i_{lim}^{O_2}}}, \quad (11)$$

where $i_{lim}^{O_2} = Dc_0/\delta'$.

Finally, at a great distance from the disc, as $z \rightarrow \infty$, we have the condition

$$\varphi \rightarrow 0 \text{ as } z \rightarrow \infty. \quad (12)$$

Eqn. (3) together with the boundary conditions (5), (11), and (12) forms, from a mathematical point of view, a completely defined system. In view of the extreme complexity of the boundary condition (11), however, it is not possible to obtain an exact solution. It is therefore necessary to simplify condition (11) by utilising the fact that different stages of the process — diffusion and chemical — may be of decisive significance at different, spatially separate portions of the protected metal.

The whole surface of the protected metal (cathode) can be roughly divided into two regions — region 1, in which the rate of the electrode reaction i^{O_2} is much greater than the diffusion current $i_{lim}^{O_2}$,

$$i^{O_2} \gg i_{lim}^{O_2}, \quad (13)$$

and region 2, in which the opposite inequality holds.

Clearly, in the first region the overall velocity of the electrode process is determined by the diffusion stage. Indeed, when $i^{O_2} \gg i_{lim}^{O_2}$, Eqn. (11) becomes

$$\kappa \left(\frac{\partial \varphi}{\partial n} \right)_{z=0, r_0 \leq r \leq R} = i_{lim}^{O_2} = j_1, \quad (14)$$

where j_1 is a constant independent of r .

The velocity of the electrode reaction is especially high in the vicinity of the protector, where the shift in potential and the current density are high. In this region, therefore, the supply of oxygen, whose concentration in the aqueous solution is low, may limit the overall rate of the cathodic process.

The potential φ , and hence also the rate of the electrode reaction, fall with increase in distance from the protector. Therefore condition (14) can be regarded as satisfied only up to some radius R_1 , whose value will be determined below.

The second region is located at great distances from the protector, and in it the boundary condition is of the form

$$\kappa \frac{\partial \varphi}{\partial n} = i^{O_2}. \quad (15)$$

The boundary condition can be further simplified if it is supposed that in the range $r \gg R_1$ the shift in potential is small. The function $f(\varphi)$ can then be expanded as a power series in $F\varphi/2RT$, and we have, approximately, for i^{O_2}

$$i^{O_2} \approx k(c^{O_2})_s \frac{F}{RT} \varphi_0 \approx k c_0^{O_2} \frac{F}{RT} \varphi_0, \quad (16)$$

since changes in concentration can be neglected in the second region.

Introducing the dimensionless variable $N = n/R_1$ and the dimensionless potential $\Phi = \varphi F/RT$, we can rewrite (16) in the form

$$\frac{\partial \Phi}{\partial N} = \frac{R_1 k c_0 F}{\kappa RT} \Phi. \quad (17)$$

As in the previous paper¹, we shall assume that the dimensionless quantity

$$K = \frac{R_1 k c_0 F}{\kappa RT} \gg 1. \quad (18)$$

Then instead of (17) we can write finally

$$\varphi \approx 0 \text{ when } \infty \gg r \gg R_1. \quad (19)$$

The physical significance of (19) is that polarisation of the protected metal is quite small at a distance from the protector. Condition (19) is satisfied at those points on the surface at which the current density is sufficiently small for the chemical resistance to be less than the ohmic resistance.

It is self-evident, of course, that division of the protected metal into two zones is schematic and can represent the actual behaviour of the system in only a simplified form. Nevertheless, such a separation reflects the fundamental tendencies in the behaviour of the system. With sufficiently vigorous stirring, the transition zone, within which condition (16) is satisfied but the approximation (17) is still inadmissible, will evidently be quite narrow.

As a result of the simplifications which have been made, we arrive at the boundary problem:

$$\begin{aligned} \Delta \varphi &= 0, \\ \left(\frac{\partial \varphi}{\partial n} \right) &= i_0 \text{ when } 0 \leq r \leq r_0, \quad z = 0, \\ \left(\frac{\partial \varphi}{\partial n} \right) &= i_1 \text{ when } r_0 \leq r \leq R_1, \quad z = 0, \\ \varphi &= 0 \text{ when } R_1 \leq r < \infty, \quad z = 0, \\ \varphi &= 0 \text{ when } z \rightarrow \infty. \end{aligned} \quad (20)$$

The value of the constant i_1 is determined from (8). Solution of this problem, given below, gives the required distribution of potential and current within the system. Here we quote only the main results of the calculation.

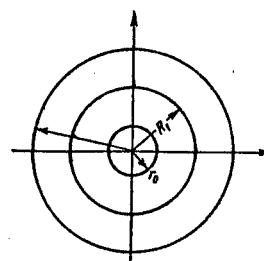


Fig. 1.

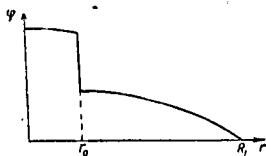


Fig. 2.

The potential distribution at the surface of a protected metal is given to a first approximation by the formula

$$\begin{aligned}\varphi &= \frac{i_0 R_1}{2\kappa} \sqrt{1 - (r/R_1)^2}, \quad r < r_0, \\ \varphi &= \frac{i_1 R_1}{2\kappa} \sqrt{1 - (r/R_1)^2}, \quad r > r_0,\end{aligned}\quad (21)$$

where for R_1 we can write, approximately,

$$R_1 \approx r_0 \sqrt{i_0/i_1}.$$

This estimate of R_1 assumes that a great proportion of the current of the protector i_0 is associated with the diffusion-controlled region of the disc, satisfying the condition $r < R_1$. More exact agreement with experiment can be obtained by calculating R_1 from Eqn. (21) after measuring the potential at a single point r^* . Fig. 2 shows the change in potential as a function of the radius vector at the surface of the disc.

The conditions for the applicability of the model can be formulated as follows. At a distance δ from the point R_1 the potential φ is so low that the condition

$$i_{\text{diff}} < i_{\text{chem}}$$

breaks down. The magnitude of δ can be found by equating the currents:

$$\begin{aligned}i_{\text{diff}} &= i_{\text{chem}} \\ i_{\text{diff}} &= K' c_0 \varphi = \frac{K' c_0 \sqrt{\delta R_1}}{\kappa} i_{\text{diff}}, \quad K' = \frac{kF}{RT}, \\ \delta &= \frac{\kappa^2}{K' c_0^2 R_1}.\end{aligned}$$

The requirement that δ should be small compared with R_0 yields

$$R_1 \gg \frac{\kappa}{K' c_0}.$$

Since $R_1 \leq r_0 (i_0/i_{\text{diff}})^{1/2}$, we have

$$r_0 \sqrt{i_0/i_1} \gg \frac{\kappa}{K' c_0},$$

which is the criterion for applicability of the model. It follows from these estimates that at large R_1 the quantity $\delta \sim 1/R_1$ is extremely small.

In deriving the boundary conditions it was assumed that even close to the protector the potentials do not become so negative that the evolution of hydrogen at a finite rate becomes possible.

Allowance for this last reaction would considerably complicate the problem, since it would be necessary to introduce kinetic boundary conditions at both great and small

distances from the protector — the reduction of oxygen and the evolution of hydrogen respectively.

Solution of the Boundary Problem

The boundary problem which has been formulated can be conveniently solved by the method applied by Levich and Frumkin⁶. Let us introduce the elliptic coordinates ξ, η, ζ , related to the Cartesian coordinates by

$$z = R_1 \eta \zeta; \quad x = r \cos \zeta; \quad y = r \sin \zeta,$$

where r is the radius vector:

$$r = R_1 \sqrt{(1 + \xi^2)(1 - \eta^2)}.$$

The surfaces $\xi = \text{const.}$ represent the surfaces of rotation of confocal ellipses. The surfaces $\eta = \text{const.}$ represent surfaces of rotation of confocal hyperbolas. The surface $\xi = 0$ corresponds to $r \leq R_1$, and the surface $\eta = 0$ to $r > R_1$.

In the new variables the Laplace equation assumes the form

$$\frac{1}{r_0 (\xi^2 + \eta^2)} \frac{\partial}{\partial \xi} \left[(1 + \xi^2) \frac{\partial \varphi}{\partial \xi} \right] + \frac{1}{r_0 (\xi^2 + \eta^2)} \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial \varphi}{\partial \eta} \right] + \frac{1}{r_0 (1 + \xi^2)(1 - \eta^2)} \frac{\partial^2 \varphi}{\partial \zeta^2} = 0,$$

and hence the boundary conditions become

$$\begin{aligned}\kappa \left(\frac{\partial \varphi}{\partial n} \right)_{\xi=0} &= \Phi(\eta) = \begin{cases} i_0, & \eta_0 \leq \eta \leq 1, \\ i_1, & 0 \leq \eta \leq \eta_0, \end{cases} \quad r \leq R_0, \\ \varphi &= 0, \quad r \geq R_1, \\ \eta_0 &= \sqrt{1 - (r_0/R_1)^2}.\end{aligned}$$

where

Elliptic coordinates were chosen because of the simple form of the boundary conditions expressed in these variables. In virtue of the axial symmetry of the problem, the field potential φ cannot depend on the angular coordinate ζ .

We shall seek a solution of the boundary problem in the form of a series:

$$\varphi = \sum_l A_l P_l(\eta) Q_l(i\xi),$$

where P_l and Q_l are Legendre polynomials of the first and second degree respectively.

Legendre functions of the first degree with the argument $i\xi$ increase indefinitely with increase in ξ and do not satisfy the boundary condition $\varphi_\infty = 0$. The boundary condition (20) gives

$$\varphi_{\eta=0} = \sum_l A_l P_l(0) Q_l(i\xi) = 0.$$

It follows from the properties of Legendre polynomials that $l = 2k + 1$. Hence

$$\varphi = \sum_k A_{2k+1} P_{2k+1}(\eta) Q_{2k+1}(i\xi).$$

The boundary condition (20) gives

$$\left. \frac{\partial \varphi}{\partial n} \right|_{\xi=0} = \frac{1}{\eta R_1} \sum_k A_{2k+1} P_{2k+1}(\eta) \left[\frac{dQ_{2k+1}(i\xi)}{d\xi} \right]_{\xi=0}$$

or

$$\frac{\kappa i}{l_1 \eta} \sum_k A_{2k+1} P_{2k+1}(\eta) Q_{2k}(0) = \Phi(\eta),$$

since

$$\frac{dQ_{2k+1}(\xi)}{d\xi} \Big|_{\xi=0} = iQ_{2k}(0).$$

Introducing the notation

$$\frac{\kappa i}{R_1} = a, \quad A_{2k+1} Q_{2k}(0) = B_{2k+1},$$

where $i = (-1)^{1/2}$, we have

$$\sum_k B_{2k+1} P_{2k+1}(\eta) = \frac{1}{a} \eta \Phi(\eta). \quad (22)$$

Utilising the orthogonality of Legendre polynomials, we obtain

$$\begin{aligned} B_{2m+1} &= \frac{4m+3}{2a} \int_{-1}^1 \eta \Phi(\eta) P_{2m+1}(\eta) d\eta = \\ &= \frac{4m+3}{a} \left[i_1 \int_0^{\eta_0} \eta P_{2m+1} d\eta + i_0 \int_{\eta_0}^1 \eta P_{2m+1}(\eta) d\eta \right]. \end{aligned}$$

The following relationships are useful for calculating the integrals:

$$\begin{aligned} x P_n(x) &= \frac{n+1}{2n+1} P_{n+1}(x) + \frac{n}{2n+1} P_{n-1}(x), \\ (2n+1) P_n(x) &= \frac{d}{dx} P_{n+1}(x) - \frac{d}{dx} P_{n-1}(x). \end{aligned}$$

Simple calculations lead to the following formula for the coefficients in the series:

$$\begin{aligned} B_1 &= \frac{i_0}{a} + \frac{i_1 - i_0}{a} \eta_0^3, \\ B_{2m+1} &= \frac{i_1 - i_0}{a} \left\{ \frac{2m+2}{4m+5} P_{2m+3}(\eta_0) + \right. \\ &\quad \left. + \frac{4m+3}{(4m+1)(4m+5)} P_{2m+1}(\eta_0) - \frac{2m+1}{4m+1} P_{2m-1}(\eta_0) \right\}, \end{aligned} \quad (23)$$

where $m > 0$.

The greatest interest attaches to a solution in the plane:

$$\Phi(\xi, \eta) \Big|_{z=0} = \sum_k \frac{Q_{2k+1}(0)}{Q_{2k}(0)} B_{2k+1} P_{2k+1}(\eta), \quad (24)$$

where

$$Q_{2k+1}(0) = (-1)^{(k+1)} \frac{2k!!}{(2k+1)!!}, \quad Q_{2k}(0) = i\pi (-1)^{k+1} \frac{(2k-1)!!}{2k!!}.$$

Let us calculate the limit of the ratio

$$I_k = \frac{Q_{2k+1}(0)}{Q_{2k}(0)} = \frac{2^k (k!)^4}{i\pi 2k! (2k+1)!} \text{ as } k \rightarrow \infty.$$

Using Stirling's formula

$$n! = n^n e^{-n} \sqrt{2\pi n},$$

we have

$$\lim_{k \rightarrow \infty} I_k = \frac{1}{2}.$$

Since the lower limit of the ratio $iQ_{2k+1}(0)/Q_{2k}(0)$ is $\frac{1}{2}$, the series

$$S = \frac{1}{2i} \sum_k B_{2k+1} P_{2k+1}(\eta)$$

is a majorant for the series (22). At the same time, the series S converges to the function

$$\frac{1}{2ia} \eta \Phi(\eta).$$

Thus a solution to the boundary problem has been obtained in the form of a series, its convergence has been proved, and expressions have been obtained for the coefficients.

SUMMARY

The potential distribution has been obtained at a rotating disc electrode with an impurity at the centre which acts as an anode. It is assumed that cathodic reduction of oxygen occurs on the metal, its rate being limited by diffusion in the region around the impurity, and by the electrochemical reaction at the peripheral part of the disc. The conditions under which the disc can be legitimately divided into diffusion and kinetic regions have been investigated.

1. R. R. Dogonadze, V. G. Levich, and Yu. A. Chizmadzhev, Zhur. Fiz. Khim., **33**, 1111 (1959) [Rus. J. Phys. Chem., Abs., **24** (1959)].
2. N. D. Tomashov, "Korroziya Metallov s Kislorodnoi Depolyarizatsiei" (Corrosion of Metals with Oxygen Depolarisation), Izd. Akad. Nauk SSSR, 1947.
3. A. N. Frumkin, V. S. Bagotskii, A. Z. Iofa, and B. N. Kabanov, "Kinetika Elektrodnykh Protssessov" (Kinetics of Electrode Processes), Izd. Moskov. Gos. Univ., 1952.
4. C. Wagner, J. Electrochem. Soc., **24**, 380 (1957).
5. V. G. Levich, "Fiziko-Khimicheskaya Gidrodinamika" (Physicochemical Hydrodynamics), Izd. Akad. Nauk SSSR, 1954.
6. V. G. Levich and A. N. Frumkin, Zhur. Fiz. Khim., **15**, 748 (1941).

Institute of Electrochemistry,
Academy of Sciences of the USSR

Received 5th February 1959

EQUILIBRIUM IN THE ZIRCONIUM-NITROGEN SYSTEM AT HIGH TEMPERATURES

E. I. Smagina, V. S. Kutsev,
and B. F. Ormont

A study of the interaction of zirconium with nitrogen at high temperatures is of considerable interest because at present zirconium is being used increasingly as a constructional material in modern engineering. Even in the most modern thermodynamic studies¹, the nitrides of this and similar metals are treated, in accordance with the principles of classical chemistry, as phases of constant composition, and equations of the type



are used to describe the decomposition of these nitrides, or their synthesis from simple compounds.

In actual fact, these nitrides are phases of variable composition with a wide region of homogeneity, and their thermodynamic parameters must vary greatly with composition within the limits of the homogeneous region.