

# ELECTRO-CHEMICAL DISSOLUTION OF AN ANODE

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## 1. Introduction

In an electro-chemical investigation, an anode in the form of an aluminium cylinder was arranged so that one circular plane end was exposed to a dilute acid electrolyte. A measured electric current was then passed and aluminium from the anode passed into solution. Employing Faraday's laws, the mass of aluminium which was expected to pass into solution as a result of the passage of the known electric charge, was calculated. It was found that, when the current density over the exposed surface of the anode was high (e.g. 100 amp/sq.cm.), the experimental and calculated results were almost in agreement. However, for small current densities (e.g. 0.1 amp/sq.cm.), it was found that the actual loss of aluminium from the anode was about 14 % greater than that predicted by Faraday's laws.

To explain this discrepancy, it was assumed that aluminium atoms at the surface of the anode could react chemically with the water in the electrolyte and in so doing reduced the effective charge on some aluminium ions from three units to one i.e.  $\text{Al}^{+++}$  ions were converted by the reaction into  $\text{AlO}^+$  ions. Clearly, the passage of a given charge would result in the removal of three times as many ions of type  $\text{AlO}^+$  as of the type  $\text{Al}^{+++}$ . This was held to account for the increased rate of dissolution of the anode.

Some experimental data were available relating to the time necessary for an atom to be exposed to the electrolyte before it could be expected to have reacted. To be precise, if a large number of atoms have been exposed to the electrolyte for a period  $\tau$  and  $S(\tau)$  is the proportion which have reacted, the form of  $S(\tau)$  is known approximately. As is to be expected,  $S(\tau) \rightarrow 1$  as  $\tau \rightarrow \infty$ .  $S(\tau)$  can obviously be interpreted as a probability; namely, it is the probability that a given atom has reacted after it has been exposed to the electrolyte for a time  $\tau$ .  $\tau$  will be referred to as the 'age' of an atom.

It is also known that a reacted atom is less likely to pass into solution than an unreacted atom and hence that, as the age  $\tau$  increases, the probability of an atom being removed from the anode decreases. Let  $P(\tau)$  measure this relative probability, i.e. if  $P(\tau_1) : P(\tau_2) = k : 1$ , this implies that an

atom of age  $\tau_1$  is  $k$  times more likely to pass into solution than an atom of age  $\tau_2$ .  $P(\tau)$  is arbitrary to the extent of a numerical multiplier. The approximate form of the function  $P(\tau)$  could also be deduced from experimental data.

## 2. The general theory

Let  $N$  be the number of atoms at the surface of the anode exposed to the action of the electrolyte. We assume that  $N$  remains constant as the dissolution proceeds, i.e. whenever an atom passes into solution, it exposes just one fresh atom to the electrolyte. At any instant  $t$ , let  $n(\tau, t)d\tau$  be the number of surface atoms which have been exposed to the electrolyte for a period lying in the interval  $(\tau, \tau+d\tau)$ . In the steady state,  $n$  will be independent of  $t$ .  $n$  determines the frequency distribution of the surface atoms with respect to their ages  $\tau$ . Clearly, it is necessary that

$$(2.1) \quad \int_0^{\infty} n(\tau, t)d\tau = N.$$

Consider the situation when an atom is about to pass into solution. The probability that it will be an atom having age lying in the interval  $(\tau, \tau+d\tau)$  is

$$(2.2) \quad CP(\tau)n(\tau, t)d\tau,$$

where  $C$  is the multiplier associated with  $P$ . Since some atom certainly passes into solution, it is necessary that

$$(2.3) \quad \int_0^{\infty} CP(\tau)n(\tau, t)d\tau = 1$$

and hence that

$$(2.4) \quad C = C(t) = \left[ \int_0^{\infty} P(\tau)n(\tau, t)d\tau \right]^{-1}.$$

Let  $R(t)$  be the total rate at which atoms are passing into solution at time  $t$ . Thus, during the interval  $(t, t+dt)$ , the number of atoms dissolved will be  $R dt$  and the proportion of these having ages in  $(\tau, \tau+d\tau)$  will be equal to the probability (2.2). The rate of dissolution of atoms having ages in  $(\tau, \tau+d\tau)$  is accordingly

$$(2.5) \quad C(t)R(t)P(\tau)n(\tau, t)d\tau.$$

$n(\tau+\Delta\tau, t)d\tau$  is the number of atoms having ages in  $(\tau+\Delta\tau, \tau+\Delta\tau+d\tau)$  at the instant  $t$ . This must equal the number which had ages in  $(\tau, \tau+d\tau)$  at the instant  $t-\Delta\tau$ , less those passing into solution during the time interval  $(t-\Delta\tau, t)$ . We are thus led to the equation

$$(2.6) \quad n(\tau+\Delta\tau, t)d\tau = n(\tau, t-\Delta\tau)d\tau - C(t)R(t)P(\tau)n(\tau, t)d\tau\Delta\tau,$$

which is correct to the second order of small quantities. Employing Taylor's

theorem and proceeding to a limit, we obtain

$$(2.7) \quad \frac{\partial n}{\partial \tau} + \frac{\partial n}{\partial t} = -CRPn.$$

We are assuming that, when an atom passes into solution, it uncovers a fresh atom having age  $\tau = 0$ . Thus,  $R(t)$  is the rate of production of atoms having zero age and it follows that

$$(2.8) \quad n(0, t) = R(t).$$

It will be assumed that the distribution of ages  $n(\tau, t)$  is known at some initial instant  $t = 0$ . Thus

$$(2.9) \quad n(\tau, 0) = A(\tau),$$

where  $A(\tau)$  is given and must satisfy condition (2.1).

The function  $R(t)$  will be related to the strength of the current flow  $I(t)$ . Defining  $S(\tau)$  (see section 1) to be the proportion of atoms having age  $\tau$  which have reacted, it follows from (2.5) that the rate of dissolution of reacted atoms having ages in  $(\tau, \tau + d\tau)$  is  $CRSPnd\tau$  and hence that the total rate of dissolution of reacted atoms is

$$(2.10) \quad R_r(t) = CR \int_0^\infty SPnd\tau$$

and, hence, that the rate of dissolution of unreacted atoms is

$$(2.11) \quad R_u(t) = R - CR \int_0^\infty SPnd\tau.$$

Let each reacted atom carry a charge  $q$  and each unreacted atom a charge  $3q$ . Then the current flowing is given by

$$(2.12) \quad \begin{aligned} I(t) &= R_r q + 3R_u q, \\ &= 3qR - 2qCR \int_0^\infty SPnd\tau. \end{aligned}$$

This equation relates the functions  $R(t)$  and  $I(t)$ .

The functions  $P(\tau)$ ,  $S(\tau)$ ,  $A(\tau)$ ,  $I(t)$  being given, equations (2.1), (2.4), (2.7), (2.8), (2.9) and (2.12) determine  $n(\tau, t)$ ,  $C(t)$  and  $R(t)$ .

For a current  $I(t)$ , a direct application of Faraday's laws would lead us to expect that the rate of dissolution of atoms should be

$$(2.13) \quad \frac{I}{3q} = R - \frac{2}{3}CR \int_0^\infty SPnd\tau.$$

The excess rate of dissolution is accordingly

$$(2.14) \quad \frac{2}{3}CR \int_0^\infty SPnd\tau.$$

Expressing this as a percentage of the rate of dissolution predicted by Faraday's laws, we obtain

$$(2.15) \quad E(t) = \frac{Q}{3-Q} \times 100 \%,$$

where

$$(2.16) \quad Q = 2C \int_0^\infty SPnd\tau.$$

$E$  will be termed the *percentage excess rate dissolution*; it has been measured experimentally for various steady current strengths. To enable us to compare our mathematical model with the experimental data, therefore, we will first consider the steady state case.

### 3. Steady state conditions

In a steady state  $I$ ,  $R$ ,  $C$  will be constants and  $n$  will be a function of  $\tau$  only. The fundamental equation (2.7) reduces to

$$(3.1) \quad \frac{dn}{d\tau} = -CRPn$$

and this possesses the general solution

$$(3.2) \quad n(\tau) = B \exp\left(-CR \int_0^\tau P(u)du\right).$$

Equation (2.8) shows that  $B = R$  and hence

$$(3.3) \quad n(\tau) = R \exp\left(-CR \int_0^\tau P(u)du\right).$$

Substituting this expression for  $n(\tau)$  in equation (2.3), we obtain the condition

$$(3.4) \quad CR \int_0^\infty P(\tau) \exp\left(-CR \int_0^\tau P(u)du\right) d\tau = 1.$$

Changing the variable of integration from  $\tau$  to  $v$  by the transformation

$$(3.5) \quad v = \int_0^\tau P(u)du,$$

it will be found that this condition reduces to

$$(3.6) \quad CR \int_0^V e^{-CRv} dv = 1,$$

where  $v \rightarrow V$  as  $\tau \rightarrow \infty$ . For this condition to be satisfied, it is clearly necessary that  $V = \infty$  and hence

$$(3.7) \quad \int_0^\infty P(u)du = \infty,$$

if a steady state of this type is to be possible.

Condition (2.1) requires that

$$(3.8) \quad R \int_0^\infty \exp\left(-CR \int_0^\tau P(u)du\right) d\tau = N.$$

Again changing the variable of integration to  $v$ , it will be found that this condition is equivalent to

$$(3.9) \quad \int_0^{\infty} M(v)e^{-CRv} dv = \frac{N}{R},$$

where

$$(3.10) \quad M(v) = 1/P[\tau(v)].$$

This condition determines  $C$ .

$R$  is determined in terms of the current  $I$  by equation (2.12). This equation can be put into the form

$$(3.11) \quad I = qR \left[ 3 - 2CR \int_0^{\infty} S e^{-CRv} dv \right],$$

where it is understood that  $S = S[\tau(v)]$ .

Finally,  $Q$  as given by equation (2.16) may be expressed in the form

$$(3.12) \quad Q = 2CR \int_0^{\infty} S e^{-CRv} dv.$$

Introducing Laplace transforms of functions of  $v$ , these results can be expressed in very simple forms. Thus, if  $\bar{F}(p)$  is the Laplace transform of a function  $F(v)$ , taking

$$(3.13) \quad p = CR,$$

equations (3.9), (3.11) and (3.12) can be written

$$(3.14) \quad R = N/\bar{M}(p),$$

$$(3.15) \quad \begin{aligned} I &= qR[3 - 2p\bar{S}(p)], \\ &= Nq[3 - 2p\bar{S}(p)]/\bar{M}(p), \end{aligned}$$

$$(3.16) \quad Q = 2p\bar{S}(p).$$

Equation (2.16) now yields

$$(3.17) \quad E = \frac{2p\bar{S}(p)}{3 - 2p\bar{S}(p)} \times 100\%.$$

Equations (3.14), (3.15) and (3.17) express the quantities  $R$ ,  $I$  and  $E$  as functions of a parameter  $p$ . The dependence of  $R$  and  $E$  upon  $I$  predicted by our model can accordingly now be ascertained.

#### 4. A special case

It is found that the form of the function  $P(\tau)$  suggested by experiment can be approximated by taking

$$(4.1) \quad P(\tau) = (\tau^2 + \alpha^2)^{-\frac{1}{2}},$$

where  $\alpha > 0$  is constant. In this case, condition (3.7) is satisfied and equation (3.5) shows that

$$(4.2) \quad \tau = \alpha \sinh v.$$

Thus, from equation (3.10), we find that

$$(4.3) \quad M(v) = \alpha \cosh v$$

and hence

$$(4.4) \quad \bar{M}(p) = \frac{\alpha p}{p^2 - 1}.$$

Equation (3.14) now yields

$$(4.5) \quad R = \frac{N}{\alpha} \left( p - \frac{1}{p} \right),$$

from which it is clear that, since  $R \geq 0$ , then  $p \geq 1$ .

The form of  $S(\tau)$  suggested by experiment can be approximated by taking

$$(4.6) \quad S(\tau) = \left[ 1 + \frac{\tau}{\alpha} - \left( 1 + \frac{\tau^2}{\alpha^2} \right)^{\frac{1}{2}} \right]^{\beta},$$

where  $\beta > 0$  (Note:  $S(0) = 0$ ,  $S(\infty) = 1$ ). Employing equation (4.2), this gives

$$(4.7) \quad S[\tau(v)] = (1 - e^{-v})^{\beta},$$

whence

$$(4.8) \quad \bar{S}(p) = \frac{1}{p} - \beta \cdot \frac{1}{p+1} + \frac{\beta(\beta-1)}{2!} \frac{1}{p+2} - \frac{\beta(\beta-1)(\beta-2)}{3!} \frac{1}{p+3} + \dots,$$

the series terminating if  $\beta$  is an integer.

$I$  and  $E$  now follow from equations (3.15) and (3.17). It will be observed that  $I = 0$  when  $p = 1$ ; for this value of  $p$  it follows from equation (4.8) that  $\bar{S} = 1/(\beta+1)$ ; hence

$$(4.9) \quad E_0 = \frac{200}{3\beta+1} \%,$$

where  $E_0$  is the percentage excess rate of dissolution for very small current densities.

The frequency distribution for ages can be found from equation (3.3); the result proves to be

$$(4.10) \quad n = \frac{N}{\alpha} \left( p - \frac{1}{p} \right) \left[ \frac{\tau}{\alpha} + \left( 1 + \frac{\tau^2}{\alpha^2} \right)^{\frac{1}{2}} \right]^{-p}.$$

For large current densities, i.e. for large values of  $p$ , this equation shows that the distribution will be concentrated in the neighbourhood of  $n = 0$ , i.e. most atoms will have small ages.

### 5. Comparison with experimental results

Appropriate values of  $\alpha$  and  $\beta$  were determined by experiment. These proved to be,  $\alpha = 2.5 \times 10^{-5}$  sec,  $\beta = 4.5$ . The functions  $P$  and  $S$  being known, the dependence of  $E$  upon  $I$  can be predicted. This relationship has been plotted in the Figure and experimentally determined values have been marked by crosses for comparison.

The agreement is reasonably satisfactory.

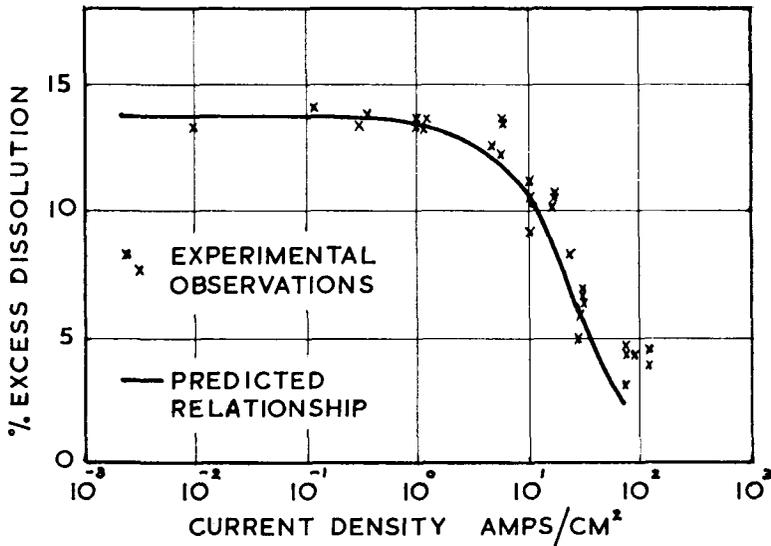


Fig. 1. Percentage excess dissolution  $E$  as a function of current density  $I$ .

### 6. Transient conditions

The partial differential equation (2.7) can be solved by standard techniques. Its general solution proves to be

$$(6.1) \quad n = \exp \left[ f(\tau - t) - \int_0^t C(x)R(x)P(x + \tau - t)dx \right],$$

where  $f$  is an arbitrary function and  $P(\tau)$  may be defined arbitrarily for negative values of its argument. Condition (2.9) requires that

$$(6.2) \quad f(\tau) = \log A(\tau), \quad \tau > 0.$$

This equation determines  $f$  for positive values of its argument. Condition (2.8) requires that

$$(6.3) \quad f(-t) = \log R(t) + \int_0^t C(x)R(x)P(x - t)dt, \quad t > 0.$$

This equation determines  $f$  for negative values of its argument. It now follows that

$$(6.4) \quad n = \begin{cases} R(t-\tau) \exp \left[ - \int_{t-\tau}^t C(x)R(x)P(x+\tau-t)dx \right], & \tau < t, \\ A(\tau-t) \exp \left[ - \int_0^t C(x)R(x)P(x+\tau-t)dx \right], & \tau > t. \end{cases}$$

The unknown function  $C(t)$  is determined by the conditions (2.1) and (2.4). These conditions are not independent for, differentiating equation (2.1) with respect to  $t$ , we find that

$$(6.5) \quad \begin{aligned} 0 &= \int_0^\infty \frac{\partial n}{\partial t} d\tau, \\ &= - \int_0^\infty \left( \frac{\partial n}{\partial \tau} + CRPn \right) d\tau, \text{ by equation (2.7),} \\ &= n(0, t) - n(\infty, t) - CR \int_0^\infty Pnd\tau, \\ &= R \left( 1 - C \int_0^\infty Pnd\tau \right), \end{aligned}$$

where we have assumed  $n(\tau, t) \rightarrow 0$  as  $\tau \rightarrow \infty$  (for otherwise the integral in equation (2.1) does not converge) and have employed equation (2.8). Equation (2.4) now follows.

$R(t)$  is determined in terms of  $I(t)$  by equation (2.12).

As an illustrative special case, suppose  $P(\tau) = P$  (a constant). Then

$$(6.6) \quad C = \left[ \int_0^\infty Pnd\tau \right]^{-1} = 1/PN$$

and the equations (6.4) give

$$(6.7) \quad n = \begin{cases} R(t-\tau) \exp \left[ - \frac{1}{N} \int_{t-\tau}^t R(x)dx \right], & \tau < t, \\ A(\tau-t) \exp \left[ - \frac{1}{N} \int_0^t R(x)dx \right], & \tau > t. \end{cases}$$

The second of these equations shows that, after a time  $t$  has elapsed, as would be expected the initial age distribution  $A(\tau)$  has shifted a distance  $t$  along the  $\tau$ -axis and has been attenuated by a factor which approaches zero as  $t \rightarrow \infty$  (assuming  $R \geq R_0 > 0$ ). The first equation shows that the 'gap' extending over the interval  $(0, \tau)$  so created, is filled by a distribution function which is determined entirely by the form of  $R(t)$ ; this also is to be expected, since the rate at which fresh atoms are appearing on the surface of the anode is exactly  $R(t)$ .

Taking  $R$  to be constant and

$$(6.8) \quad A(\tau) = N\delta(\tau),$$

where  $\delta(\tau)$  is the unit impulse function (i.e. at the initial instant, all atoms

are supposed to be fresh), we find that

$$(6.9) \quad n = \begin{cases} Re^{-R\tau/N}, & \tau < t, \\ N\delta(\tau-t)e^{-Rt/N}, & \tau > t. \end{cases}$$

Fixing the form of the function  $S(\tau)$  to be

$$(6.10) \quad S(\tau) = 1 - e^{-\alpha\tau}$$

(which is reasonable), we then calculate from equation (2.12) that

$$(6.11) \quad I(t) = \frac{q\gamma\alpha N}{1+\gamma} [1 + 3\gamma + 2e^{-\alpha(1+\gamma)t}].$$

This shows that the current decreases exponentially, approaching a steady value as  $t \rightarrow \infty$ . Initially, only fresh  $\text{Al}^{+++}$  atoms pass into solution and the current is comparatively high; however, after some time has elapsed, reacted  $\text{AlO}^+$  atoms also contribute to the flux of atoms passing into solution and the current is consequently reduced.

## 7. Acknowledgements

The practical investigation of this problem was conducted by Dr. Hagyard and Mr. Kirkpatrick of the Chemical Engineering Department, University of Canterbury, New Zealand and the graph appearing in the Figure has been drawn from experimental data supplied by them. The form for the function  $S(\tau)$  appearing in equation (4.6) was found by Mr. Kirkpatrick. The author wishes to thank Dr. Hagyard and Mr. Kirkpatrick for introducing him to the problem and for helpful discussions.

## Reference

- K. J. Kirkpatrick, *The Anodic Behaviour of Aluminium in Aqueous Solution*. Ph.D. Thesis, University of Canterbury, 1967.

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