

OPEN-CIRCUIT POTENTIAL-TIME TRANSIENT OF THE MAGNESIUM ANODE

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Summary

On interrupting polarisation, the magnesium anode exhibits a negative overshoot in potential followed by a slow recovery to a steady state value. A model has been proposed to explain the open-circuit potential-time transient in terms of a spontaneous passivation of the metal and the consequent changes in the corrosion potential. Theoretical expressions have been derived for the time-dependence of the open-circuit electrode potential. Calculated potential-time curves thus obtained are in qualitative agreement with experimental data. A possible application of this phenomenon to develop non-destructive quality control tests of Mg, Li and Al-based dry cells has been pointed out.

1. Introduction

Open-circuit potential-time transients have been studied for several reactions, such as during the corrosion of stainless steels, anodisation of valve metals and cathodic hydrogen evolution on noble metals (for example, Pt & Pd) [1]. In these cases there is a smooth, asymptotic approach of the open-circuit electrode potential to a final value on terminating polarisation [1]. In the case of magnesium, however, an unusual feature of the open-circuit polarisation transient is exhibited, *viz.*, an initial negative overshoot of the electrode potential (*i.e.*, beyond the final value of the electrode potential) followed by a relatively slow return to the latter (Fig. 1).

Correspondingly, the voltage of a magnesium dry cell, on cessation of discharge, momentarily reaches a value appreciably higher than the normal open-circuit voltage (Fig. 2). An understanding of the mechanism governing the open-circuit transient phenomenon of the magnesium anode is therefore of both theoretical and practical interest.

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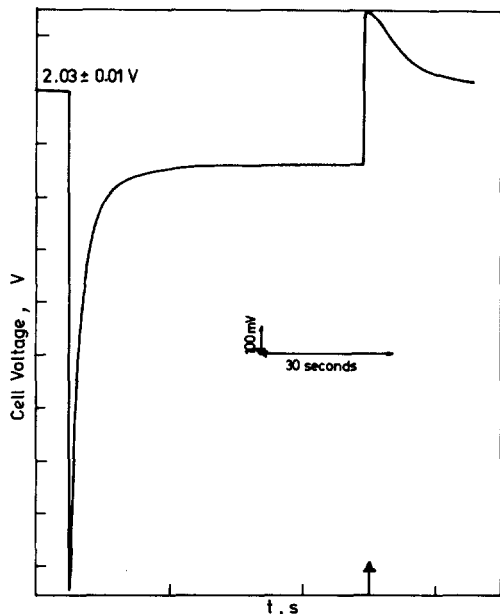


Fig. 1. Open-circuit potential-time transient of a magnesium electrode in contact with $\text{Mg}(\text{ClO}_4)_2$ solution (1N) saturated with $\text{Mg}(\text{OH})_2$ (pH 8.5) on terminating (at an instant $t = 0$) steady state galvanostatic anodic polarisation ($I = -1 \text{ mA/cm}^2$). The arrow indicates the moment of interruption of the galvanostatic current ($t = 0, I = 0$).

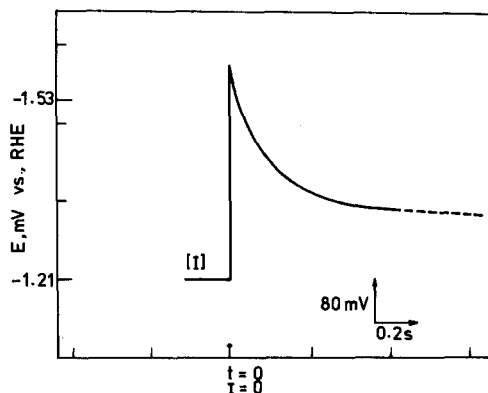


Fig. 2. A typical open-circuit voltage-time transient of a magnesium-manganese dioxide dry cell on termination of the discharge current density of 1 mA/cm^2 (on the magnesium anode).

Robinson and King [2] correctly attributed these unusual features of the open-circuit transient, *viz.*, the initial negative overshoot and the subsequent decay of electrode potential, to a momentary depolarisation and activation of the magnesium anode followed by its spontaneous repassivation.

However, a quantitative treatment of this unusual phenomenon is not available in the literature. Such a treatment is reported in the present work.

2. Theoretical study

2.1. Physical model

At the moment of interruption of anodic polarisation, the magnesium electrode tends to assume an instantaneous corrosion potential corresponding to the prevailing surface characteristics, *viz.*, partly film-free and partly film-covered regions, as pointed out earlier [3]. The mixed potential of such a partly film-covered magnesium electrode is more negative than that of a completely film-covered electrode [3]. Thus, depending on the relative areas of the film-covered and the film-free regions on its surface at the moment of termination of anodic current, the magnesium electrode will exhibit an instantaneous negative overshoot in its potential. The larger the film-free area is at the moment of current interruption, the larger is the negative overshoot in the electrode potential.

Subsequently, a repassivation of the magnesium electrode is initiated spontaneously owing to its reactivity at film-free areas, *i.e.*, the high corrosion rate of bare magnesium. The repassivation is especially favoured in neutral or alkaline solutions where the corrosion products of magnesium are least soluble. Progressively, the metal becomes less reactive owing to repassivation and the electrode potential is shifted to more positive values until it approaches a steady state value.

In other words, the open-circuit transient phenomenon of the magnesium anode is essentially due to a progressive repassivation of an initial, partly film-free, metal surface and the resultant changes in corrosion potential.

To evaluate the instantaneous corrosion potential of the magnesium electrode, it may be reasonable to associate the area effect on the corrosion potential with a linearly-weighted average value, *i.e.*,

$$E_{\text{cor}} = E_0(1 - \theta) + E_1\theta \quad (1)$$

as in ref. 3. Here, E_0 and E_1 are corrosion potentials of film-free and film-covered regions of the magnesium electrode, respectively, which are governed by the kinetics of potential-determining reactions in local cells at the respective regions. E_{cor} refers to the resultant instantaneous corrosion potential and θ is the surface coverage of the magnesium electrode. At a sufficiently long time after the termination of the anodic current, the repassivation of the electrode is complete ($\theta = 1$) and E_{cor} then becomes equal to E_1 , the steady state open-circuit potential.

2.2. Mechanism of repassivation under open-circuit conditions

The film-free areas of the metal sustain a characteristic high rate of corrosion compared with the film-covered regions. A monolayer of

corrosion products may therefore be expected to form almost instantaneously after the termination of current, since the corrosion product is not readily soluble in neutral or alkaline solutions. Moreover, a free dissolution of the corrosion product, which is essentially magnesium hydroxide [4, 5], is prevented to a large extent by the presaturation of the electrolyte with $Mg(OH)_2$ [6], the low solubility of $Mg(OH)_2$ in magnesium perchlorate solution, and the well-known slow rate of dissolution of $Mg(OH)_2$ in neutral or alkaline media. In other words, repassivation of the magnesium electrode under open-circuit conditions is virtually irreversible, involving only film-formation and negligible film-dissolution.

After the formation of the monolayer film, the magnesium electrode will still sustain some corrosion through flaws in the film, leading to a thickening of the film and eventually complete passivation of the electrode. Formally, the open-circuit repassivation may thus be regarded as a 'succession of passive states' with a progressive decrease in the corrosion current and an increase in the open-circuit potential.

2.3. Formulation of the rate equation

The net current in the local cells at the electrode/solution interface under open-circuit conditions is given by

$$0 = -C_d \frac{d(E - E_{cor})}{dt} + I_{cor} [\exp\{-\alpha f(E - E_{cor})\} - \exp\{\beta f(E - E_{cor})\}] \quad (2)$$

where E is the observed electrode potential, I_{cor} is the specific corrosion current, and C_d is the double layer capacitance of the Mg/solution interface at any instant t after the termination of anodic current. α and β are the apparent cathodic and anodic energy transfer coefficients, respectively.

The parameters E_{cor} , I_{cor} and C_d are linearly dependent on θ [3].

$$E_{cor} = E_0(1 - \theta) + E_1\theta \quad (1)$$

$$I_{cor} = I_0(1 - \theta) + I_1\theta \quad (3)$$

and

$$C_d = C_{d,0}(1 - \theta) + C_{d,1}\theta \quad (4)$$

where I_0 and $C_{d,0}$ are the specific values of corrosion current and double layer capacitance, respectively, of the film-free magnesium electrode, and I_1 and $C_{d,1}$ are the corresponding values of the film-covered magnesium electrode.

The model of 'succession of passive states' evolved above implies that the apparent Tafel slope for the metal dissolution reaction during open-circuit repassivation of the magnesium electrode, *i.e.*, $(\beta f)^{-1}$, is large compared with $(E - E_{cor})^*$. This is also evident from the steady state potentiostatic polarisation curves which show that the passive state of the

*In a passive region, the apparent Tafel slope tends to infinity.

magnesium electrode extends over about 50 mV on either side of the initial steady state (open-circuit) potential. Consequently, eqn. (2) may be simplified as

$$0 \approx -C_d \frac{d(E - E_{\text{cor}})}{dt} + I_{\text{cor}} [\exp\{-\alpha f(E - E_{\text{cor}})\} - 1] \quad (5)$$

2.4. Rate of repassivation

Assuming a first order dependence of the rate of the irreversible passivation process on the quantity of film material causing repassivation and on the film-free area of the electrode,

$$\frac{d\theta}{dt} = KI_{\text{cor}}t(1 - \theta) \quad (6)$$

where K is the specific rate of repassivation under open-circuit conditions. Substituting for I_{cor} from eqn. (3)

$$\frac{d\theta}{dt} = KI_0t(1 - \theta) \left[1 + \frac{I_1 - I_0}{I_0} \theta \right] \quad (7)$$

On integrating eqn. (7),

$$\frac{I_0}{I_1} \ln \left[1 + \frac{I_1}{(I_0 - I_1)(1 - \theta)} \right] = \frac{KI_0t^2}{2} + K^* \quad (8)$$

where K^* is an integration constant which may be evaluated with the boundary conditions that at $t = 0$, $\theta = \theta_0$, the film-coverage of the metal at the moment of anodic current interruption.

Equation (8) thus becomes,

$$1 + \frac{I_1}{(I_0 - I_1)(1 - \theta)} = \left[1 + \frac{I_1}{(I_0 - I_1)(1 - \theta_0)} \right] \exp\left(\frac{KI_1t^2}{2}\right) \quad (9)$$

The open-circuit repassivation of the magnesium electrode in neutral and alkaline solutions has been found to be complete within about ten seconds after the termination of the anodic current as is evident from the cessation of hydrogen evolution on the electrode and the proximity of the electrode potential to the steady state value [6].

Assigning reasonable values* for the parameters involved as in ref. 3, K may be estimated from eqn. (7) to be of the order of $2 \times 10^4 \text{ cm}^2 \text{ A}^{-1} \text{ s}^{-2}$ and $KI_1t^2/2 \ll 1$ over a range of t extending from 0 to about 10 s.

Equation (9) then reduces to

*It has been pointed out earlier [3] that the orders of magnitude of I_0 , I_1 , $C_{d,0}$, $C_{d,1}$ and θ are about $10^{-3} \text{ A cm}^{-2}$, $10^{-6} \text{ A cm}^{-2}$, $50 \mu\text{F cm}^{-2}$, $1 - 10 \mu\text{F cm}^{-2}$ and 0.9, respectively.

$$\theta = \frac{\theta_0 + \frac{t^2}{\tau_0^2}}{1 + \frac{t^2}{\tau_0^2}} \quad (10)$$

where

$$\tau_0 = \left[\frac{2}{K\{(I_0 - I_1)(1 - \theta_0) + I_1\}} \right]^{1/2} \quad (11)$$

τ_0 is a characteristic relaxation time for repassivation under open-circuit conditions. Equation (10) may be further simplified in two limiting cases as shown below.

Case when $t \ll \tau_0$:

In the first few moments of the open-circuit polarisation transient (*i.e.*, when $t \ll \tau_0$) the rate of repassivation may be expressed (from eqn. (10)) as

$$\theta \approx \theta_0 + \frac{t^2}{\tau_1^2} \quad (12)$$

where

$$\tau_1 = \frac{\tau_0}{(1 - \theta_0)^{1/2}} \quad (13)$$

τ_1 is a characteristic time for repassivation in the initial stages.

Case when $t \gg \tau_0$:

In the penultimate phase of the open-circuit transient (*i.e.*, when $t \gg \tau_0$), the rate of repassivation may be expressed (from eqn. (10)) as

$$\theta \approx 1 - \frac{\tau_2^2}{t^2} \quad (14)$$

where

$$\tau_2 = \tau_0(1 - \theta_0)^{1/2} \quad (15)$$

τ_2 is a characteristic relaxation time for repassivation in the penultimate phase of the transient.

2.5. Time dependence of E_{cor} , I_{cor} and C_d

From eqns. (1), (3), (4) and (12) the variations of E_{cor} , I_{cor} and C_d with time during the initial moments of open-circuit repassivation may be expressed as

$$E_{\text{cor}} = E_2 \left(1 - \frac{E_0 - E_1}{E_2} \frac{t^2}{\tau_1^2} \right) \quad (16)$$

$$I_{\text{cor}} = I_2 \left(1 - \frac{I_0 - I_1}{I_2} \frac{t^2}{\tau_1^2} \right) \quad (17)$$

and

$$C_d = C_{d,2} \left(1 - \frac{C_{d,0} - C_{d,1}}{C_{d,2}} \frac{t^2}{\tau_1^2} \right) \quad (18)$$

where

$$E_2 = E_0 + (E_1 - E_0)\theta_0 \quad (16a)$$

$$I_2 = I_0 + (I_1 - I_0)\theta_0 \quad (17a)$$

and

$$C_{d,2} = C_{d,0} + (C_{d,1} - C_{d,0})\theta_0 \quad (18a)$$

E_2 , I_2 and $C_{d,2}$ are the respective values at the moment of current interruption.

Similarly, the dependence of E_{cor} , I_{cor} and C_d on time in the penultimate phase of repassivation may be expressed from eqns. (1), (3), (4) and (14) as

$$E_{\text{cor}} = E_1 + (E_0 - E_1) \frac{\tau_2^2}{t^2} \quad (19)$$

$$I_{\text{cor}} = I_1 + (I_0 - I_1) \frac{\tau_2^2}{t^2} \quad (20)$$

and

$$C_d = C_{d,1} + (C_{d,0} - C_{d,1}) \frac{\tau_2^2}{t^2} \quad (21)$$

2.6. Time dependence of the electrode potential

Rearranging eqn. (5)

$$\frac{d(E - E_{\text{cor}})}{dt} - \frac{I_{\text{cor}}}{C_d} \exp\{-\alpha f(E - E_{\text{cor}})\} + \frac{I_{\text{cor}}}{C_d} = 0 \quad (22)$$

Introducing a new variable

$$Y = -\exp\{\alpha f(E - E_{\text{cor}})\} \quad (23)$$

the above equation becomes

$$\frac{dY}{dt} + \frac{\alpha f}{C_d} I_{\text{cor}} (Y + 1) = 0 \quad (24)$$

On integration

$$\ln(Y + 1) = -\int \alpha f \frac{I_{\text{cor}}}{C_d} dt + \text{constant} \quad (25)$$

Case when $t < \tau_0$, i.e., initial moments of repassivation:

On substituting for I_{cor} and C_d from eqns. (17) and (18) in the above equation

$$\ln(Y + 1) = -\alpha f \int \frac{I_2}{C_{d,2}} \left(\frac{1 + \frac{I_0 - I_1}{I_2} \frac{t^2}{\tau_1^2}}{1 - \frac{C_{d,0} - C_{d,1}}{C_{d,2}} \frac{t^2}{\tau_1^2}} \right) dt + \text{constant} \quad (26)$$

Since $\frac{C_{d,0} - C_{d,1}}{C_{d,2}} \approx 1 - 10$, and $t \ll \tau_1$, it follows that

$$\ln(Y + 1) \approx -\alpha f \frac{I_2}{C_{d,2}} \int \left\{ 1 - \left(\frac{I_0 - I_1}{I_2} - \frac{C_{d,0} - C_{d,1}}{C_{d,2}} \right) \frac{t^2}{\tau_1^2} \right\} dt + \text{constant}$$

On integrating the above equation and substituting for Y from eqn. (23)

$$\begin{aligned} \ln[1 - \exp\{\alpha f(E - E_{\text{cor}})\}] \\ = -\frac{\alpha f I_2}{C_{d,2}} \left[t - \left(\frac{I_0 - I_1}{I_2} - \frac{C_{d,0} - C_{d,1}}{C_{d,2}} \right) \frac{t^2}{3\tau_1^2} \right] + \text{constant} \end{aligned} \quad (27)$$

The integration constant is evaluated with the boundary conditions: when $t = 0$, $E_{\text{cor}} = E_2$ and $E = E^*$, the electrode potential during steady state anodic polarisation. Thus,

$$\begin{aligned} E = E_2 - (E_0 - E_1) \frac{t^2}{\tau_1^2} + \frac{1}{\alpha f} \ln \left[1 - \{1 - \exp(\alpha f[E^* - E_2])\} \right] \cdot \\ \exp \left\{ -\alpha f \frac{I_2}{C_{d,2}} \left(t - \frac{t^3}{3\tau_1^2} \left[\frac{I_0 - I_1}{I_2} - \frac{C_{d,0} - C_{d,1}}{C_{d,2}} \right] \right) \right\} \end{aligned} \quad (28)$$

Since $t < \tau_1$

$$\begin{aligned} E = E_2 - (E_0 - E_1) \frac{t^2}{\tau_1^2} + \frac{1}{\alpha f} \ln \left[1 - \exp \left(-\frac{\alpha f I_2 t}{C_{d,2}} \right) \right] + \\ + \exp \left\{ \alpha f \left(E^* - E_2 - \frac{I_2 t}{C_{d,2}} \right) \right\} \end{aligned} \quad (29)$$

Case when $t \geq \tau_0$, i.e., penultimate phase of repassivation:

On substituting for I_{cor} and C_d from eqns. (20) and (21) and solving for the electrode potential as above,

$$\ln[1 - \exp\{\alpha f(E - E_{\text{cor}})\}] = -\frac{\alpha f I_1}{C_{d,1}} \left\{ t - \left(\frac{I_0 - I_1}{I_1} - \frac{C_{d,0} - C_{d,1}}{C_{d,2}} \right) \frac{\tau_2^2}{t^2} \right\} + \text{constant} \quad (30)$$

However, it is not possible to evaluate the integration constant in the above equation without a knowledge of the electrode potential at some instant t such that

$$t > \tau_2 \left(\frac{C_{d,0} - C_{d,1}}{C_{d,1}} \right)^{1/2}$$

Alternatively, it may be reasonable to neglect the nonfaradaic (capacitive) current in this case, owing to a low capacitance of film-covered metal as well as the small rate of change of the electrode potential with time. The rate equation then reduces to

$$I_{\text{cor}} [\exp\{-\alpha f(E - E_{\text{cor}})\} - 1] = 0$$

Or,

$$E = E_{\text{cor}} \text{ since } I_{\text{cor}} \neq 0 \quad (31)$$

Thus from eqns. (19) and (31)

$$E \approx E_1 + (E_0 - E_1) \frac{\tau_2^2}{t^2} \quad (32)$$

2.7. Comparison with experimental data

Shape of the potential-time curves:

The theoretical potential-time curves during open-circuit repassivation of the magnesium electrode obtained from eqn. (29) for $t \ll \tau_0$ and eqn. (32) for $t \geq \tau_0$ are shown in Fig. 3. These curves show agreement with the experimental trend, viz., an instantaneous negative overshoot followed by, initially, a rapid, and finally an asymptotic decay of the electrode potential.

Effect of anodic current density prior to current interruption:

The open-circuit polarisation transient becomes more pronounced with an increase in the anodic current density prior to the current interruption, i.e., there is a larger negative overshoot of the electrode potential and a longer time required for repassivation [6]. This may be attributed to an increase in the film-free area fraction at high anodic current densities which, in turn, makes the instantaneous corrosion potential more negative than at lower current densities.

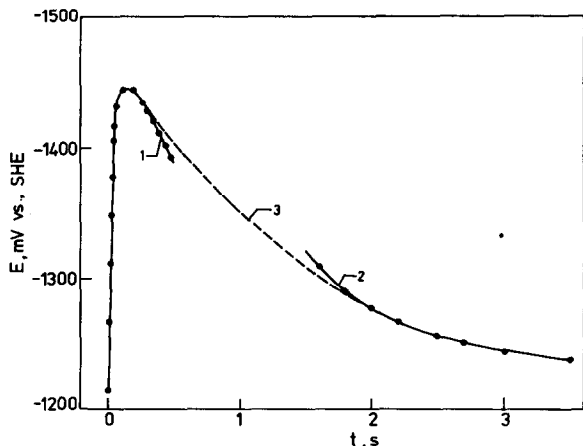


Fig. 3. Theoretical open-circuit potential-time transient of a magnesium electrode in contact with $\text{Mg}(\text{ClO}_4)_2$ solution (1N) saturated with $\text{Mg}(\text{OH})_2$ (pH 8.5) on the interruption of an anodic current density of 1 mA cm^{-2} with reasonable values of the parameters involved as given below: $\rho_f \approx 10^8 \text{ ohm cm}$; $\rho_{\text{SL}} \approx 10 \text{ ohm cm}$; $\theta_0 \approx 0.8$; $I_1 = 10^{-6} \text{ A cm}^{-2}$; $I_0 \approx 10^{-3} \text{ A cm}^{-2}$; $E_1 = -1.22 \text{ V vs. SHE}$; $\beta_f \approx 39$ ($\beta_m \approx 0.5$); $E_0 \approx -2.37 \text{ V vs. SHE}$; $A = 1 \text{ cm}^2$; $C_{d,1} = 10 \mu\text{F cm}^{-2}$; $d = 10^{-5} \text{ cm}$; $\tau_1 = 10^3 \text{ s}$ (or $\tau = 2.336 \times 10^3 \text{ s}$) and $I = 10^{-3} \text{ A cm}^{-2}$. Curve 1 (eqn. (29)) corresponds to the initial phase of the transient, i.e., when $t < \tau_0$, τ_0 being the relaxation time of open-circuit repassivation; Curve 2 corresponds to the final phase of the transient (i.e., when $t > \tau_0$) (eqn. (32)) and curve 3 is obtained by interpolation; ($\alpha = 0.37$; $E^* = -1.215 \text{ V vs. SHE}$; $C_{d,0} = 100 \mu\text{F cm}^{-2}$ and $\tau_0 \approx 1 \text{ s}$).

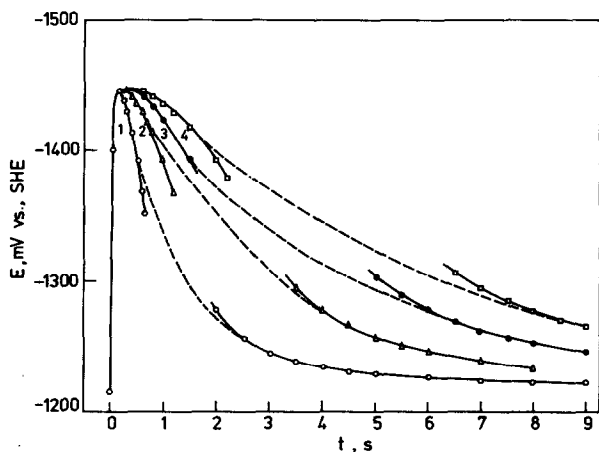


Fig. 4. Theoretical potential-time transients, on interruption of an anodic current density of 1 mA cm^{-2} , of a magnesium electrode in contact with $\text{Mg}(\text{ClO}_4)_2$ solution (1N) saturated with $\text{Mg}(\text{OH})_2$ (pH 8.5) obtained from eqns. (29) and (32) with a relaxation time τ_0 of (1) 1 s, (2) 2 s, (3) 3 s and (4) 4 s and with values of other parameters as in Fig. 3. These curves have been obtained by interpolation of the curves at $t < \tau_0$ and $t > \tau_0$ as in Fig. 3.

Similarly, the open-circuit transient becomes more pronounced the larger the fraction of anodic transient completed before interrupting the current [2], due to an increase in the film-free area fraction.

Effect of pH of the solution:

The observed fast recovery of the open-circuit electrode potential in alkaline media [6] and its slow recovery in acidic media [7] may be explained on the above basis. In alkaline media wherein the corrosion product of the magnesium electrode (essentially $\text{Mg}(\text{OH})_2$) is insoluble, the repassivation kinetics is fast, whereas in acidic media it is slow. The theoretical curves calculated with appropriate values for relaxation times of repassivation (Fig. 4) agree with the above trend.

3. Conclusions

The theoretical analysis developed in this work for the open-circuit potential-time transient observed with the magnesium anode is consistent with the physical model of a succession of passive states governing the transient behaviour. Thus, the theory satisfactorily predicts the time dependence of the open-circuit potential following a current interruption, especially in the initial and final stages of the transient. The effects of a change in the pH of the solution, as well as of the current density applied to the anode prior to current interruption, on the shape of the transient are also explained by the model proposed.

Since the magnitude of the overshoot of the electrode potential on terminating anodic polarisation is directly determined by the fraction of the film-free surface on the electrode at the moment of current interruption, this part of the open-circuit polarisation transient may be used to control the on-load current permissible for momentary test discharges of magnesium-based dry cells and thereby check their quality nondestructively, *i.e.*, with negligible anodic film-breakdown.

Finally, the open-circuit transient behaviour of lithium [8] and aluminium electrodes [9] which are similar to that of magnesium, may also be expected to be governed by an analogous mechanism to that described here.

List of symbols

A	Area of the electrode
α	Apparent cathodic energy transfer coefficient
β	Apparent anodic energy transfer coefficient
C_d	Capacitance of the metal-solution interface at any instant t
$C_{d,0}$	Capacitance of the film-free metal in contact with solution
$C_{d,1}$	Capacitance of film-covered metal in contact with solution

$C_{d,2}$	Capacitance of metal–film interface at the moment of opening the circuit
d	Average thickness of passive film on magnesium electrode
E	Electrode potential at any instant t
E^*	Electrode potential during steady state anodic dissolution (prior to current interruption)
E_{cor}	Corrosion potential of metal–solution interface at any instant t
E_0	Corrosion potential of film-free metal surface in contact with solution
E_1	Corrosion potential of film-covered metal surface in contact with solution
E_2	Corrosion potential of metal–solution interface at the moment of opening the circuit
f	F/RT , F being the Faraday constant, R the universal gas constant and T the absolute temperature
I_{cor}	Corrosion current density of metal–solution interface at any instant t
I	Galvanostatic anodic current density
I_0	Corrosion current density of film-free metal in contact with solution at any instant t
I_1	Corrosion current density of film-covered metal in contact with solution at any instant t
I_2	Corrosion current density of metal–solution interface at the moment of opening the circuit
K	Specific rate of repassivation of the metal under open-circuit conditions; <i>cf.</i> eqn. (6)
K^*	Integration constant in eqn. (8)
t	Time after terminating anodic polarisation of the metal
τ_0	Relaxation time for repassivation under open-circuit conditions
τ_1	Relaxation time for repassivation during the initial stages
τ_2	Relaxation time for repassivation in the penultimate stage
θ	Fraction of the area of the metal covered by film at any instant t
θ_0	Coverage of the metal by the film at the moment of opening the circuit
Y	A function of electrode potential given by eqn. (26)
RHE	Reversible hydrogen electrode
SHE	Standard hydrogen electrode
ρ_f	Specific resistance of the film
ρ_Ω	Specific resistance of the solution

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