THE DELAYED ACTION OF MAGNESIUM ANODES IN PRIMARY BATTERIES
PART II. THEORETICAL STUDIES

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Summary

A physical model for the field-induced breakdown of the passive film on magnesium anodes has been developed based on experimental data on the delayed action of magnesium anodes. The model essentially involves, successively, metal dissolution at the metal–film interface, film-dilatation, and film breakdown. A theoretical analysis of the model has been carried out to obtain an explicit expression for the time dependence of the electrode potential during the delayed action phenomenon. The delay-time curves obtained are compared with experimental data, especially with regard to the effects of film thickness, ageing of the anode in solution, current density, temperature, etc. Finally, possible means of reducing the delayed action of magnesium anodes are predicted from the 'metal dissolution–film dilatation–film breakdown' model.

1. Introduction

One of the inherent shortcomings of the otherwise-promising magnesium dry batteries is the existence of delayed action which manifests itself in a plummeting of the cell voltage on discharge initiation followed by a slow recovery to the normal operating value after the elapse of a certain 'delay time'.

Several theories have been advanced in the literature to clarify the mechanism of delayed action of the magnesium anode. However, a proper theoretical basis to explain the above phenomenon is still lacking in the literature, as discussed earlier [1].

In the present work, an attempt has been made to develop a physical model taking into account all phenomenological components of the delayed action of the magnesium anode in the light of the experimental data presen-

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ted earlier [1] and also to provide a theoretical analysis of the model to obtain explicit expressions for the time dependence of the electrode potential during the above phenomenon.

2. Theoretical study of delayed action of the magnesium anode

The transient behaviour of the Mg anode in contact with magnesium perchlorate solution is examined below theoretically for the time dependence of the electrode potential during galvanostatic polarisation. The choice of galvanostatic rather than the potentiostatic mode is governed by (i) the impossibility of attaining a truly potentiostatic condition due to an unknown large and variable film-resistance at the Mg anode, and (ii) the partial damage of the passive film caused by the surge currents generated during the switching-on and switching-off operations of the potentiostat, as discussed in ref. 1.

2.1. Evolution of the model
Magnesium sustains a small but finite rate of corrosion, suggesting the existence of a few microscopic flaws in the protective film which almost completely covers the metal. Further, the film is significantly resistive, as is evident from the large instantaneous anodic polarisation observed on the oscilloscope. Moreover, the film is only sporadically disrupted during steady-state anodic polarisation, i.e., magnesium sustains a pitting-type dissolution with the metal still largely film-covered and only partly film-free. Based on these observations, a physical picture of the Mg–solution interface could be visualized, as in Fig. 1.
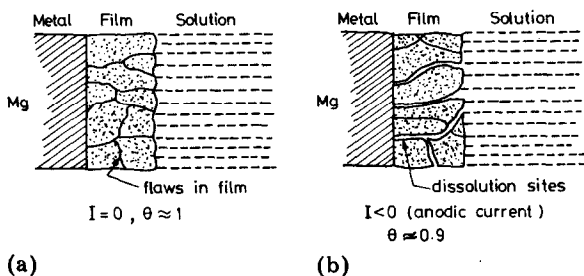

Fig. 1. Schematic view of Mg/film/solution system. (a) Under open-circuit conditions where the film coverage of the metal is almost complete except for flaws in the film; (b) during steady-state anodic dissolution with largely film-covered ($\theta \approx 0.9$) and partly film-free regions.

2.2. Mechanism of film breakdown and anodic current flow

2.2.1. Identification of the reaction zone
The choice of either the Mg–film interface or the film–solution interface as the reaction zone for the occurrence of faradaic and non-faradaic

processes during anodic polarisation is governed by the thickness and resistivity of the film. From the double-layer capacitance value of $1 - 10$ μF cm^{-2} in alkaline solutions [2] the film thickness may be estimated (with the assumption of a parallel-plate capacitor model, which is reasonable in concentrated solutions) as either $10^2 - 10^3$ Å or $10^3 - 10^4$ Å, depending on whether the dielectric constant of the film is one or ten. The probable value of the film thickness may therefore be considered as 10^3 Å to an order of magnitude, which is also close to the experimentally determined thickness of the passive film on Mg [3]. The instantaneous anodic polarisation of magnesium, which is attributed to the *IR* drop across the passive film, is about 1 V at a current density of 10^{-3} A cm^{-2}. The film resistivity may be estimated from the above value of the *IR* drop and from the above film thickness as 10^8 ohm cm, to an order of magnitude.

It therefore follows that magnesium is covered with a thick and resistive passive film which thus sustains no charge-transfer* or electron-tunneling across it. Any charge-transfer involving the ionisation of Mg is therefore likely to be localised at the metal–film interface. Such a conclusion is reasonable also because of a sufficient degree of hydration and porosity of the film, which provides a sufficient supply of water molecules and electrolyte ions at the metal–film interface.

2.2.2. Mechanism of film breakdown on anodic-current flow

On applying a galvanostatic anodic polarisation, magnesium tends to dissolve at the metal–film interface at a constant rate. The transport of hydrated ions so generated across the film into the solution is hindered by the coherent, thick, and resistive passive film on the metal. A dilatation stress is thus necessarily imposed on the film due to a progressive accumulation of $Mg^{2+} \cdot nH_2O$ and/or its hydrolysis product $Mg(OH)_2$ at the Mg–film interface, eventually causing the breakdown of the film at its weak spots (Fig. 2). Subsequently, a sufficient area of the metal is directly exposed to the solution, and the anodic metal dissolution proceeds virtually unhindered in these
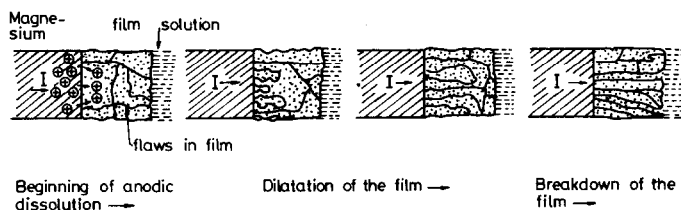

Fig. 2. Schematic representation of the mechanism of breakdown of the passive film on a magnesium anode during galvanostatic polarisation. Ionisation of magnesium and the progressive accumulation of anodic products at the metal–film interface create dilatation stresses in the film, eventually leading to its breakdown at weak spots.

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*This is further confirmed by the steady-state polarisation studies wherein the open-circuit potential of magnesium has been found to be insensitive to the presence of redox systems such as ferrocyanide–ferricyanide, quinone–hydroquinone, etc., in the solution.

areas, thus leading to pitting-type anodic dissolution of magnesium, as observed experimentally.

The above 'metal dissolution–film dilatation' model for film breakdown is indirectly confirmed by the experimental data on the increase of delayed action at a rate proportional to the corrosion of Mg during its ageing in solution and also on the decrease of delayed action with increasing current density as described in ref. 1.

2.3. Equivalent circuit of Mg–film–solution interface

In accordance with the 'dissolution–dilatation' model proposed above, the equivalent circuit for the metal–film–solution interface under anodic polarisation may be represented by Fig. 3.
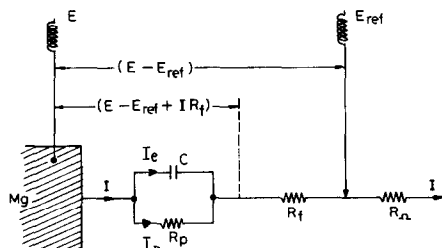

Fig. 3. Equivalent circuit of Mg/film/solution system. The net current, I, flowing through the flaws in the film and the solution consists of a non-faradaic current, I_e required to charge the electrical double layer C and a faradaic current I_p at the metal–film interface. R_p, R_f, and R represent the resistances of the faradaic process, the film, and the solution, respectively. The observed electrode potentials (E measured against E_{ref}) may be corrected for the potential drop across the film as shown in the Figure.

The reaction impedance is purely resistive, owing to an absence of mass-transfer control of the irreversible faradaic processes occurring at the interface under mixed potential conditions, viz., $Mg \rightarrow Mg^{2+} + 2e^-$, and $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, as is evident from the experimentally observed lack of dependence of potential–time transient on the stirring of the solution. The only possible reaction at the highly positive potentials during the course of the transient, viz., ionisation of Mg, is devoid of any mass-transfer control owing to a high density of Mg atoms on the surface. The reaction impedance may therefore be regarded as arising solely from the current–potential dynamic characteristic of the Mg/H$_2$O system under irreversible conditions. The faradaic current during anodic polarisation may therefore be expressed as*

$$I_p \approx -I_{cor} \exp\{\beta f(E_{tr} - E_{cor})\} \tag{1}$$

where I_{cor} is the corrosion current, E_{tr} the true electrode potential devoid of any ohmic drop, E_{cor} the steady-state corrosion potential of the

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*Cathodic current is considered positive. Electrode potentials are consistent with the International convention.

electrode, β the apparent anodic transfer coefficient for the anodic metal dissolution reaction and $f = F/RT$.

In the absence of a potential drop in the solution and also of liquid-junction potentials, the observed electrode potential E may be corrected for ohmic drop across the passive film as

$$E_{tr} = E - E_{ref} + IR_f \tag{2}$$

The non-faradaic impedance is purely capacitive with the capacitive current expressed as

$$I_e = -C \frac{d(E_{tr} - E_{cor})}{dt} \tag{3}$$

where C is the double layer capacitance.

Lastly, the impedance due to the solution is also mainly resistive as shown in Fig. 3.

2.4. Coverage dependence of R_f, C, I_{cor} and E_{cor}

Owing to a breakdown and disruption of the film on anodic polarisation, the film coverage of the metal decreases during the course of the transient, resulting in an increase in the corrosion current and double-layer capacitance and a decrease in the film resistance. The effective values of these parameters at any instant, *i.e.*, at a given degree of film-coverage, θ, may be considered as due to a combination of film-covered and film-free values, the simplest physical situation being a parallel arrangement of film-free and film-covered areas. Accordingly, the equivalent circuit in Fig. 3 may be recast as shown in Fig. 4.
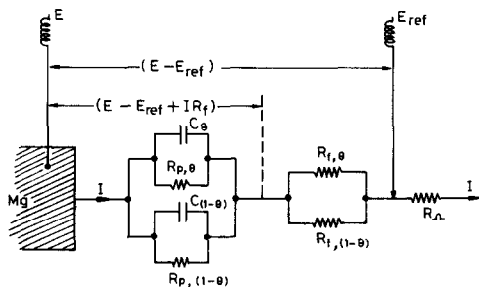

Fig. 4. Equivalent circuit of Mg/film/solution system recast from Fig. 3, taking into account the coverage dependence of C, R_p and R_f (see text).

The film resistance may be expressed as

$$\frac{1}{R_f} = \frac{1}{R_{f,1}} + \frac{1}{R_{f,0}} \tag{4}$$

where

$$R_{f,1} = \frac{\rho_f d}{A\theta} \tag{4.1}$$

and

$$R_{f,0} = \frac{\rho_\Omega d}{A(1-\theta)} \tag{4.2}$$

are the resistances due to the film-covered and film-free regions, respectively. Here, A is the total area of the electrode in contact with the solution, d the average film thickness, ρ_f and ρ_Ω are the specific resistances of the film and solution, respectively.

Equation (4) may be rewritten as

$$R_f = \frac{\rho_f \rho_\Omega d}{A\{\rho_f + (\rho_\Omega - \rho_f)\theta\}} \tag{5}$$

Similarly, capacitance and corrosion current* may also be expressed in terms of θ as

$$C = C_0(1-\theta) + C_1\theta \tag{6}$$

and

$$I_{cor} = I_0(1-\theta) + I_1\theta \tag{7}$$

where C_0 and I_0 are the specific double-layer capacitance and corrosion current density at film-free regions and C_1 and I_1 are the corresponding values at film-covered regions, respectively.

The corrosion potential of Mg will be substantially different at film-free areas from the value at film-covered areas as mentioned earlier [1]. Owing to the scalar nature of potentials, it may be assumed that E_{cor} is additive of the values at film-covered and film-free areas proportional to the respective areas. Hence, as a first approximation, it may be written

$$E_{cor} = E_0(1-\theta) + E_1\theta \tag{8}$$

where E_0 and E_1 are the corrosion potentials of Mg at the film-free and film-covered regions, respectively.

2.5. Rate of film disruption during anodic polarisation

The film breakdown by dilatation is also accompanied by a spontaneous repassivation of the metal (re-formation of the film) by the anodic product which fills up the voids in the film, especially in neutral or alkaline media. In other words, the onset of anodic polarisation is followed by simultaneous film-disruption and film-repair processes. Assuming a first-order rate law, the net rate of film breakdown may be expressed as

$$-\frac{d\theta}{dt} = K_1V\theta - K_2V(1-\theta) \tag{9}$$

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*More precisely, the reaction resistance R_p is a parallel combination of the value at film-covered and film-free regions as shown in Fig. 3. Nevertheless, since R_p is governed by I_{cor}, β, etc., and since β is characteristic of the reaction and not of the area available for the reaction whereas I_{cor} depends directly on the area exposed, one may write as a first approximation $I_{cor} = I_0(1-\theta) + I_1\theta$, as above.

where K_1 and K_2 are the rate constants* for film-breakdown and film-repair processes, respectively, and V is the volume of the anodic product which has a dual role, *viz.*, film breakdown by the dilatation mechanism and film repair by void-filling process.

After a sufficiently long time of anodic polarisation, the film coverage, θ, reaches a steady-state value, θ_o, which may depend on anodic current density, decreasing with increasing value of the latter. From the observed pitting-type anodic dissolution of magnesium, it may be inferred that θ_o is close to unity.

Under steady state conditions, therefore,

$$-\left(\frac{d\theta}{dt}\right)_{t \to \infty} = 0 = V\{K_1\theta_o - K_2(1 - \theta_o)\}$$

which together with eqn. (9) gives

$$-\frac{d\theta}{dt} = (K_1 + K_2)V(\theta - \theta_o) \tag{10}$$

From Faraday's law $V = WIt/F\delta$** where W is the equivalent weight and δ the density of the anodic product.

Equation (10) therefore gives

$$-\frac{d\theta}{dt} = Kt(\theta - \theta_o) \tag{11}$$

where

$$K = \frac{(K_1 + K_2)WI}{F\delta} \tag{12}$$

Equation (11) on integration leads to

$$\ln(\theta - \theta_o) = -\frac{t^2}{\tau_1^2} + \text{const} \tag{13}$$

where

$$\tau_1 = \left(\frac{2}{K}\right)^{1/2} \tag{14}$$

a characteristic relaxation time for film breakdown.

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*The rate constant K_1 is, in principle, a function of the local electric field, generally decreasing with an increase in the latter because of the faster field-induced processes such as electron injection and the avalanche generation preceding the direct ionic-flux influenced dilatation effect. The rate constant K_2, on the other hand, is independent of the applied field.

**More precisely, $V = WI_pt/F\delta$ where I_p is the current consumed by faradaic processes. The charge density required for even a monolayer formation of anodic product for the dilatation of the film is approximately 200 μC cm^{-2}, assuming an interatomic distance of 3 Å. The double-layer charge density, on the other hand, is 1 - 10 μC cm^{-2}, assuming a capacitance of 1 · 10 μF cm^2 charged to a potential difference of one volt, which is the potential dip in the transient at a current density of 1 mA cm^{-2}. It may therefore be concluded that the film dilatation process consumes nearly the entire quantity of electricity passed, *i.e.*, $I_p \approx I$.

Since the metal is practically stable under open-circuit conditions, it may be assumed that $\theta = 1$ at $t = 0$. Equation (13) then becomes

$$\theta \approx \theta_o + (1 - \theta_o) \exp(-t^2/\tau_1{}^2) \tag{15}$$

2.5.1. Order of magnitude of τ_1

Equation (15) implies that $t = \tau_1$ when θ reaches a value of $\theta_o + (1 - \theta_o)/e$.

The experimental data on the delayed action of magnesium [1] suggest that the attainment of the steady-state electrode potential, which is a consequence of the establishment of steady-state in the film-coverage of the metal, occurs, in most cases, only after about 100 s or more because of the asymptotic variation in the electrode potential. It is therefore likely that the relaxation time for film breakdown will be of the order of 10 - 100 s.

The above relaxation time value for film breakdown is also consistent with the literature. The characteristic relaxation time during electrical breakdown of insulators is of the order of $10^3 - 10^4$ s [4]. The present situation involving field-induced breakdown of a barrier-type film is comparable with the above situation, despite the fact that the primary mechanism postulated in the latter is the injection of electrons into the conduction band of the insulator causing impact ionisation and subsequent avalanche generation. Moreover, the electric field imposed on the passive film on the Mg during anodic polarisation is also of the same order as in ref. 4, i.e., $10^5 - 10^6$ V cm^{-1} with a potential drop of one volt across a film of thickness $10^{-5} - 10^{-6}$ cm. However, due to an additional breakdown mechanism, dilatation by the anodic product, being operative predominantly in the present case, the relaxation time of film breakdown may be expected to be less than with insulators. A value of about 10 - 100 s may thus be assigned, as a first approximation, to the relaxation time of film breakdown, τ_1.

The major portion of the transient involving rapid changes in electrode potential is covered within a few seconds (viz., within 1 - 5 s). It is therefore reasonable to assume that $t < \tau_1$ (or $t^2 \ll \tau_1{}^2$) for the present study. Equation (15) then reduces to

$$\theta = 1 - \frac{t^2}{\tau^2} \tag{16}$$

where

$$\tau = \frac{1}{(1 - \theta_o)^{1/2}} = \left\{ \frac{2F\delta}{(1 - \theta_o)(K_1 + K_2)WI} \right\}^{1/2} \tag{17}$$

Here, τ is of the order of $10^2 - 10^3$ s, since θ_o is close to unity.

The dependences of R_f, C, I_{cor} and E_{cor} on time during galvanostatic anodic polarisation may therefore be explicitly written from eqns. (5) - (8) and the above equation as

$$R_f = \frac{\rho_f \rho_\Omega d}{A\left\{\rho_f + (\rho_\Omega - \rho_f)\left(1 - \dfrac{t^2}{\tau^2}\right)\right\}} \tag{18}$$

$$C = C_1\left\{1 + \frac{C_0 - C_1}{C_1} \frac{t^2}{\tau^2}\right\} \tag{19}$$

$$I_{cor} = I_1\left\{1 + \frac{I_0 - I_1}{I_1} \frac{t^2}{\tau^2}\right\} \tag{20}$$

and

$$E_{cor} = E_1\left\{1 + \frac{E_0 - E_1}{E_1} \frac{t^2}{\tau^2}\right\} \tag{21}$$

2.6. Basic differential rate equation for anodic transient

The net current passing through the electrode–solution interface is the sum of the faradaic and the non-faradaic components, i.e.,

$$I = -C\frac{d(E_{tr} - E_{cor})}{dt} - I_{cor} \exp\{\beta f(E_{tr} - E_{cor})\} \tag{22}$$

Substituting for true electrode potential (eqn. (2))

$$I = -C\frac{d(E - E_{cor} + IR_f)}{dt} - I_{cor} \exp\{\beta f(E - E_{cor} + IR_f)\}$$

Rearranging the above equation for the galvanostatic condition (i.e., $I \neq f(t)$), we get

$$\frac{d(E - E_{cor})}{dt} + \frac{I_{cor}}{C} \exp(\beta f IR_f) \exp\{\beta f(E - E_{cor})\} + \left\{\frac{I}{C} + I\frac{dR_f}{dt}\right\} = 0 \tag{23}$$

which is the basic differential equation for galvanostatic anodic polarisation of normally passive metal in contact with electrolyte solution. Here, the parameters R_f, C, I_{cor} and E_{cor} are all time-dependent as expressed by eqns. (18) - (21), respectively.

2.7. Time dependence of electrode potential during delayed action

An explicit expression for the time dependence of electrode potential during galvanostatic potential–time transient obtained* from the above differential rate equation may be expressed as

$$E = E_1 - (E_1 - E_0)\frac{t^2}{\tau^2} - \frac{\rho_\Omega I d}{A\left\{1 - \left(1 - \dfrac{\rho_\Omega}{\rho_f}\right)\left(1 - \dfrac{t^2}{\tau^2}\right)\right\}} - \frac{1}{\beta f} \ln\left\{-\frac{I_1}{I} + \right.$$

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*The details of solution of the rate equation (eqn. (23)) for the time dependence of the electrode potential are given under Appendix 1.

$$+ \left(1 + \frac{I_1}{I}\right) \exp\left(\frac{\beta f I t}{C_1}\right)\Big\}\Big\} \tag{24}$$

Typical E vs. time curves obtained from the above equation with reasonable values of the parameters involved (see Appendix 1) are represented in Fig. 5.

2.8. Comparison of the theoretical potential–time curves with experimental data

The delay-time curves obtained theoretically (from eqn. (24)) are characterized by a continuous and smooth decrease in the slope of the potential-recovery portion (Fig. 5), while the experimental data often show two or more distinct slopes in the recovery portion (Fig. 6). This suggests that the variation of film-coverage with time may not be continuous as assumed in the above theory, but discrete. In other words, mechanical breakdown of the film caused by dilatation stresses imparted by the anodic product occurs not continuously but in a few discrete steps. Nevertheless, considering the complexity of the resulting theoretical problem, a simpler, continuous function of θ in time has been expected to unravel the basic features of the theoretical model.
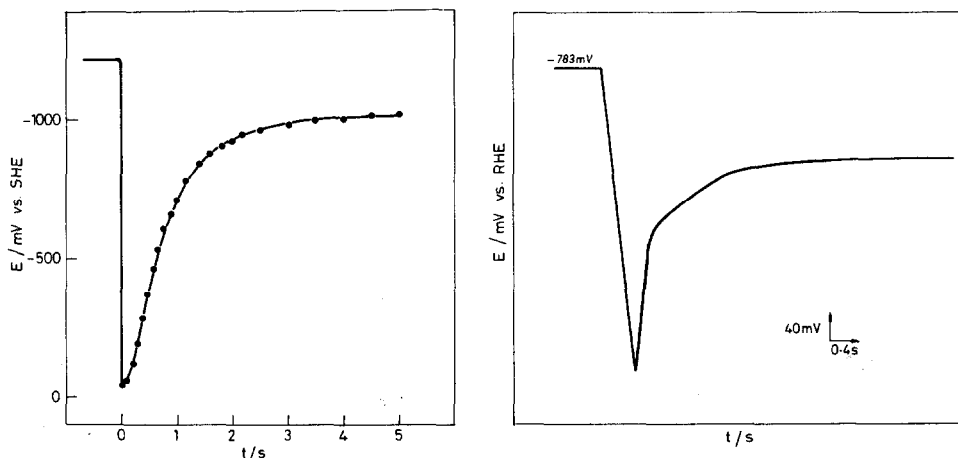

Fig. 5. Theoretical galvanostatic potential–time transient of a magnesium anode in contact with 1N $(MgClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) obtained from eqn. (24) with reasonable values of the parameters as given below. $\rho_f \approx 10^8$ ohm cm; $\rho_\Omega \approx 10$ ohm cm; $\theta_0 \approx 0.8$; $I_1 = 10^{-6}$ A cm^{-2}; $I_0 \approx 10^{-3}$ A cm^{-2}; $\beta f \approx 39$; $E_0 \approx -2.37$ V vs. SHE; $E_1 = -1.22$ V vs. SHE; $A = 1$ cm^2; $C_1 = 10$ μF cm^{-2}; $d = 10^{-5}$ cm; $\tau_1 = 10^3$ s (or $\tau = 2.236 \times 10^3$ s) and $I = 10^{-3}$ A cm^{-2}.

Fig. 6. A typical galvanostatic potential–time transient, of an oil-coated (coconut oil) magnesium anode in contact with 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 1 mA cm^{-2} and after an ageing of the anode for 24 h in the solution, exhibiting distinct regions of different slopes in the potential-recovery portion of the transient (unlike a smooth recovery predicted by theory).

3. Implications of the 'dissolution–dilatation' model

3.1. Delay-time parameters

The characteristic time constants of the galvanostatic potential–time transient obtained from eqn. (24) as reciprocal coefficients of t are

$$\tau_{d,_1} = \frac{C_1}{\beta fI} \tag{25}$$

$$\tau_{d,_2} = \tau = \left\{ \frac{2F\delta}{(1 - \theta_o)(K_1 + K_2)WI} \right\}^{1/2} \tag{26}$$

and

$$\tau_{d,_3} = \left\{ \frac{\rho_f}{\rho_f - \rho_\Omega} \right\}^{1/2} = \left\{ \frac{2F\delta\rho_f}{(1 - \theta_o)(K_1 + K_2)(\rho_f - \rho_\Omega)WI} \right\}^{1/2} \tag{27}$$

The delay time of a battery during discharge, t_d, may be assumed to be made up of the above time constants, viz., $\tau_{d,_1}$, $\tau_{d,_2}$ and $\tau_{d,_3}$ as

$$t_d = m_1\tau_{d,_1} + m_2\tau_{d,_2} + m_3\tau_{d,_3} \tag{28}$$

where m_1, m_2, and m_3 are the appropriate weightage factors.

It is evident from the relative orders of magnitude of t_d, $\tau_{d,_1}$, $\tau_{d,_2}$ and $\tau_{d,_3}$ that $\tau_{d,_1}$ does not contribute significantly to the delay time. At times greater than $C_1/\beta fI$ ($\approx 10^{-2}$ s; cf. Appendix 1), the metal exhibits Tafel-like behaviour characterised by the equation (from eqn. (24))

$$E - E_{cor} \approx -IR_f - \frac{1}{\beta f} \ln \left\{ -\frac{I_1}{I} \right\} \tag{29}$$

wherein the electrode potential E is time-dependent due to a change of R_f and E_{cor} with time.

It therefore follows from the above discussion that $\tau_{d,_1}$ may contribute to the initiation of the charge-transfer process and, hence, of the film breakdown process, whereas film disruption by dilatation is governed by the characteristic times $\tau_{d,_2}$ and $\tau_{d,_3}$.

Equation (28) then reduces to

$$t_d = m_2\tau_{d,_2} + m_3\tau_{d,_3} \tag{30}$$

3.2. Effect of film thickness on the delayed action parameters

The increase in film thickness is accompanied by an increase in the potential dip as well as in the delay time, the former increasing due to an increased IR drop and the latter due to larger relaxation times $\tau_{d,_2}$ and $\tau_{d,_3}$, as demonstrated by a set of theoretical potential–time transients (eqn. (24)) in Fig. 7.
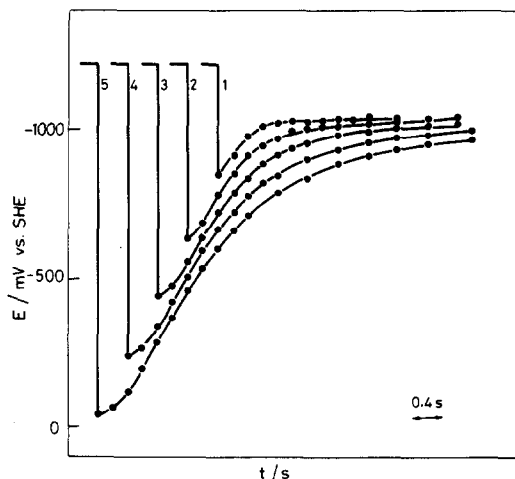
Fig. 7. Theoretical galvanostatic potential–time transients of a magnesium anode in contact with 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) obtained from eqn. (24) for a film thickness of: 1, 10^{-6} cm ($\tau_1 = 10^2$ s); 2, 2×10^{-6} cm ($\tau_1 = 2 \times 10^2$ s); 3, 4×10^{-6} cm ($\tau_1 = 4 \times 10^2$ s); 4, 6×10^{-6} cm ($\tau_1 = 6 \times 10^2$ s); 5, 8×10^{-6} cm ($\tau_1 = 8 \times 10^2$ s); with the same values of other parameters as in Fig. 5. The relaxation time for film breakdown, τ_1, varies proportionally with the film thickness through the rate constant K_1 as also pointed out in the text.

With an increase in the film thickness d, both the rate constants K_1 and K_2 decrease, the former due to a higher film pressure and a lower electric field [5, 6] and the latter due to a larger void volume to be covered. Consequently, the relaxation times $\tau_{d_{,2}}$ and $\tau_{d_{,3}}$ increase with increasing film thickness d, at a rate proportional to $d^{1/2}$. The relaxation time $\tau_{d_{,1}}$ on the other hand, becomes lower for thicker films due to an increase in capacitance. Nevertheless, $\tau_{d_{,1}}$ does not contribute significantly to the delay time t_d, as pointed out above.

The effect of film thickness on the delay time has been experimentally verified in Mg [7] and Li [8] batteries where the growth of the passive film on the anode is accompanied by the severity of the delayed action.

3.3. Effect of anodic (discharge) current density on delayed action

The potential–time transients obtained theoretically (Fig. 8) exhibit shorter delay times at higher anodic current densities*, as also observed experimentally [1], owing to a decrease in all the relaxation times $\tau_{d_{,1}}$, $\tau_{d_{,2}}$, and $\tau_{d_{,3}}$ (eqns. (25) - (27)).

An effective method to minimise the delay time is therefore to perform a 'conditioning discharge', i.e., to draw momentarily a heavy discharge

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*The decrease in potential dip observed experimentally [1] with increasing anodic current density may also be a consequence of the decrease in the relaxation time $\tau_{d_{,1}}$ which characterises the initiation of the charge-transfer process across the film.
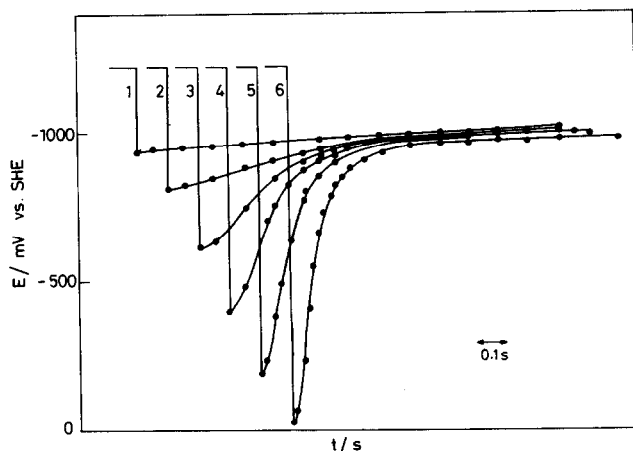
Fig. 8. Theoretical galvanostatic potential–time transients of a magnesium anode in contact with 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) obtained from eqn. (24) for current densities of: 1, 1 mA/cm^2 ($\tau_1 = 10^3$ s; $\theta_o = 0.88$); 2, 2 mA/cm^2 ($\tau_1 = 5 \times 10^2$ s; $\theta_o = 0.864$); 3, 4 mA/cm^2 ($\tau_1 = 2.5 \times 10^2$ s; $\theta_o = 0.848$); 4, 6 mA/cm^2 ($\tau_1 = 1.667 \times 10^2$ s; $\theta_o = 0.832$); 5, 8 mA/cm^2 ($\tau_1 = 1.25 \times 10^2$ s; $\theta_o = 0.816$); 6, 10 mA/cm^2 ($\tau_1 = 10^2$ s; $\theta_o = 0.8$) for a film thickness of 10^{-6} cm and with the same values of other parameters as in Fig. 5. The value of τ_1 as well as that of θ_o decreases with an increase in anodic current density as also pointed out in the text.

current to break down the film, the duration required for such a conditioning discharge being determined by the freshness of the cell, the ambient temperature, the anode pretreatment, etc.

3.4. Effect of ageing of electrode on delayed action

The higher the corrosion rate of magnesium, the faster will be the growth of the passive film of corrosion products on Mg over a given period of ageing (or the longer the ageing period of the electrode in solution, the more will the passive film grow) since the film material (essentially magnesium hydroxide) is insoluble in the electrolyte, which is also presaturated with $Mg(OH)_2$. From the 'dissolution–dilatation' model (cf. Section 3.1.), the rate constants K_1 and K_2 decrease, with an increase in film thickness resulting in longer delay times, as also observed experimentally [1].

3.5. Effect of anode-film characteristics on delayed action

It follows from eqns. (25) - (27) that the most obvious characteristic of the film influencing the delay time is the capacitance, C_1, of the film-covered metal and that a decrease in the latter will decrease the delay time. This conclusion may be explained as being due to a decrease of the dielectric constant which increases the local electric field intensity, and thus decreases the rate constant K_1 as well as the delay time. Consequently, impregnation of the micropores in the anode-film with low dielectric constant materials may be expected to shorten the delay time, especially in the initial stages of the transient. In other words, such materials accelerate the initiation of

the charge-transfer process for film breakdown by decreasing the relaxation time $\tau_{d_{,1}}$, as also observed experimentally with electrodes coated with esters of long-chain fatty acids [1].

3.6. Effect of K_1 and K_2

Both the rate constants K_1 and K_2 decrease at higher temperature, for example, according to the Arrhenius-type equation for a rate process. An increase, almost exponentially, in the delay time during discharge of the battery at lower battery temperatures, as normally experienced, may thus be understood as above. This increase in delay time may be suppressed with a "conditioning discharge cycle" of sufficient duration as to cause an internal cell heat-up and also high-field initiation of film breakdown, as mentioned above (cf. Section 3.3.).

4. Conclusions

Magnesium exhibits delayed anodic dissolution due to a time-dependent breakdown of the passive film on its surface. Based on the experimental data on the delayed action of the Mg anode presented earlier, a physical model for the field-induced breakdown of the passive film has been developed as outlined below.

Magnesium being covered with a thick and resistive passive film sustains ionisation on anodic polarisation preferably at the metal–film interface. The hydrated magnesium ions or their hydrolysis product, unable to diffuse across the film, impose a progressively increasing dilatation stress on the film, eventually breaking down the latter at its weak spots.

The electrical equivalent circuit for the above model is represented by a double-layer capacitance with a parallel charge-transfer resistance and the film resistance in series with the capacitance. All the above parameters are functions of the film coverage of the metal which itself is time-dependent. An explicit relation for the time-dependence of the electrode potential during a galvanostatic potential–time transient has been derived from the above model. The results show that there are several relaxation times governing the 'delayed action' phenomenon.

The theoretical potential–time transients are in qualitative agreement with the experimental data, especially with regard to their shape and their dependence on the film thickness, ageing duration of the anode in solution, film capacitance, anodic current density, ambient temperature, etc. The directions in which the experimental conditions and the film characteristics such as those above should be altered to minimise the 'delayed action' of the magnesium anode have thus been predicted from the above 'metal dissolution–film dilatation–film breakdown' model.

List of symbols

A	Area of the electrode
B	Integration constant in eqn. (A6)
β	Apparent anodic energy transfer coefficient
C	Specific double-layer capacitance of metal–solution interface at any instant t
C_0	Specific double-layer capacitance of film-free metal
C_1	Specific double-layer capacitance of film-covered metal
d	Average thickness of passive film on magnesium electrode
δ	Density of the anodic product generated at the metal–film interface and causing dilatation of the film
E_{tr}	True electrode potential at any instant t
E	Observed electrode potential at any instant t different from the true value E_{tr} due to IR drop
E_{cor}	Corrosion potential of the electrode at any instant t
E_1	Corrosion potential of film-covered metal
E_0	Corrosion potential of film-free metal
f	F/RT
I	Galvanostatic (anodic) current density
I_p	Current due to charge-transfer process
I_e	Current due to double-layer charging
I_{cor}	Specific corrosion current at any instant t
I_0	Specific corrosion current of film-free metal
I_1	Specific corrosion current of film-covered metal
K_1	Rate constant for film-disruption process (eqn. (9))
K_2	Rate constant for film-reformation process (eqn. (9))
K	Rate constant for film-disruption process (eqn. (12))
m_1, m_2, m_3	Weightage factors of individual relaxation times for the delay time (eqn. (29))
N	$\dfrac{I_0 - I_1}{I_1} - \dfrac{C_0 - C_1}{C_1}$
P	Variable defined by eqn. (A4)
Q	Variable defined by eqn. (A5)
t	Time after initiation of galvanostatic anodic polarisation
t_d	Delay time during battery discharge
τ_1	Relaxation time for film breakdown defined by eqn. (14)
τ	Relaxation time for film breakdown defined by eqn. (17)
θ	Degree of film coverage of the metal at any instant t
θ_o	Degree of film coverage of the metal during steady-state galvanostatic anodic polarisation
W	Equivalent of the anodic product generated at metal–film interface and dilating the film
V	Volume of the anodic product, at any instant t, generated at the metal–film interface and dilating the film.
Z	A function of $(E - E_{cor})$; eqn. (A2)

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Appendix 1

The differential rate equation for galvanostatic anodic polarisation,

$$\frac{d(E - E_{cor})}{dt} + \frac{I_{cor}}{C} \exp(\beta f I R_f) \exp\{\beta f(E - E_{cor})\} + \left(\frac{I}{C} + I\frac{dR_f}{dt}\right) = 0 \qquad (A1)$$

may be solved for the time dependence of electrode potential as shown below.

On introducing a new variable

$$Z = \exp\{-\beta f(E - E_{cor})\} \qquad (A2)$$

eqn. (A1) may be recast as

$$\frac{dz}{dt} + Pz + Q = 0 \qquad (A3)$$

where

$$P = -\beta f I \left\{\frac{1}{C} + \frac{dR_f}{dt}\right\} \qquad (A4)$$

and

$$Q = -\frac{\beta f}{C} \{I_{cor} \exp(\beta f I R_f)\} \qquad (A5)$$

Equation (A3) is a standard form of linear differential equation with the solution

$$Z = \exp\left(-\int p\,dt\right)\left\{-\int Q \exp\left(\int p\,dt\right)\,dt + B\right\} \qquad (A6)$$

where B is an integration constant.

(a) Evaluation of $\int pdt$

$$\int pdt = -\beta f IR_f - \beta f I \int \frac{dt}{C} \tag{A7}$$

From eqn. (19) in the text

$$C = C_1 \left\{ 1 + \frac{C_0 - C_1}{C_1} \frac{t^2}{\tau^2} \right\}$$

Since t is of the order of one second, τ of the order of 10^3 s, C_1 of the order of 10^{-5} F cm^{-2}, and C_0 of the order of 10^{-4} F cm^{-2} (assuming a roughness factor of two and a film-free capacitance of about 50 μF cm^{-2}), it follows* that

$$t^2 \ll \frac{\tau^2 C_1}{C_0 - C_1}$$

Equation (A7) therefore reduces to

$$\int pdt \approx -\beta f IR_f - \frac{\beta f I}{C_1} \int \left(1 - \frac{C_0 - C_1}{C_1} \frac{t^2}{\tau^2} \right) dt$$

or

$$\int pdt \approx -\beta f IR_f - \frac{\beta f I}{C_1} \left\{ t - \frac{C_0 - C_1}{C_1} \frac{t^3}{3\tau^2} \right\} \tag{A8}$$

(b) Evaluation of $\int Q \exp(\int pdt) \, dt$

Substituting for I_{cor} and C (eqns. (19) and (20) in the text) in eqn. (A5)

$$Q = -\frac{\beta f I_1}{C_1} \exp(\beta f IR_f) \left\{ \frac{1 + \dfrac{I_0 - I_1}{I_1} \dfrac{t^2}{\tau^2}}{1 + \dfrac{C_0 - C_1}{C_1} \dfrac{t^2}{\tau^2}} \right\}$$

Since $t^2 \ll \dfrac{\tau^2 C_1}{C_0 - C_1}$ as mentioned above,

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*The values of other parameters involved in the analysis are $I_1 = 10^{-6}$ A cm^{-2} [1] and $I_0 = 10^{-3}$ A cm^{-2}. I_0 has been assumed to be 10^{-3} A cm^{-2}, since the corrosion rate of Mg in slightly acidic solutions (pH: 6), where the metal will be devoid of a passive film, is about 1 mA cm^{-2} [9].

$$Q \approx - \frac{\beta f I_1}{C_1} \exp(\beta f I R_f) \left\{ 1 + \frac{I_0 - I_1}{I_1} \frac{t^2}{\tau^2} \right\} \left\{ 1 - \frac{C_0 - C_1}{C_1} \frac{t^2}{\tau^2} \right\}$$

Ignoring terms of higher order than t^2/τ^2

$$Q \approx - \frac{\beta f I_1}{C_1} \exp(\beta f I R_f) \left(1 + N \frac{t^2}{\tau^2} \right)$$

where

$$N = \frac{I_0 - I_1}{I_1} - \frac{C_0 - C_1}{C_1}$$

Hence

$$\int - Q \exp\left(\int p dt \right) dt = \int \frac{\beta f I_1}{C_1} \left(1 + N \frac{t^2}{\tau^2} \right) \exp\left\{ - \frac{\beta f I}{C_1} \left(t - \frac{C_0 - C_1}{3 C_1} \frac{t^3}{\tau^2} \right) \right\} dt$$

From the orders of magnitude given above for different parameters, it follows that

$$\frac{\beta f I}{3 C_1^2} (C_0 - C_1) \frac{t^3}{\tau^2} \ll 1$$

Accordingly

$$\int - Q \exp\left(\int p dt \right) dt =$$

$$= \frac{\beta f I_1}{C_1} \int \left(1 + N \frac{t^2}{\tau^2} \right) \left(1 + \frac{\beta f I}{3 C_1^2} (C_0 - C_1) \frac{t^3}{\tau^2} \right) \exp\left(- \frac{\beta f I t}{C_1} \right) dt =$$

$$= - \exp\left(- \frac{\beta f I t}{C_1} \right) \left\{ \frac{I_1}{I} + \frac{I_0 - I_1}{I \tau^2} \left(\frac{2 C_1^2}{\beta^2 f^2 I^2} + \frac{2 C_1 t}{\beta f I} + t^2 \right) + \beta f I_1 \frac{C_0 - C_1}{3 C_1^2} \frac{t^3}{\tau^2} \right\} \quad (A9)$$

(c) Time dependence of electrode potential

On combining eqns. (A2), (A6), (A8) and (A9) we get

$$\exp\{ - \beta f(E - E_{cor}) \} =$$

$$= \exp(\beta f I R_f) \exp\left\{ - \frac{\beta f I}{3 C_1^2} (C_0 - C_1) \frac{t^3}{\tau^2} \right\} \left[- \frac{I_1}{I} - \frac{I_0 - I_1}{\tau^2 I} \left\{ \frac{2 C_1^2}{\beta^2 f^2 I^2} + \right. \right.$$

$$\left. \left. + \frac{2 C_1 t}{\beta f I t} + t^2 \right\} - \frac{C_0 - C_1}{3 \tau^2 C_1^2} \beta f I_1 t^3 + B \exp\left(\frac{\beta f I t}{C_1} \right) \right] \quad (A10)$$

The integration constant B may be evaluated from the boundary condition, viz., at $t = 0$ and $I = I$ (i.e., immediately after the application of galvanostatic anodic polarisation), $E - E_{cor} = -IR_f$, as

$$B = 1 + \frac{I_1}{I} + \frac{2C_1{}^2(I_0 - I_1)}{\beta^2 f^2 \tau^2 I^3}$$

Substitution of the above equation in eqn. (A10) gives

$$E = E_{cor} - IR_f + \frac{I(C_0 - C_1)}{3C_1{}^2\tau^2} t^3 - \frac{1}{\beta f} \ln\left[-\frac{I_1}{I} - \frac{C_0 - C_1}{3C_1{}^2\tau^2} \beta f I_1 t^3 - \right.$$

$$\left. - \frac{I_0 - I_1}{\tau^2 I}\left(\frac{2C_1{}^2}{\beta^2 f^2 I^2} + \frac{2C_1 t}{\beta f I} + t^2 \right) + \left\{ 1 + \frac{I_1}{I} + \frac{2C_1{}^2(I_0 - I_1)}{\beta^2 f^2 I^3 \tau^2} \right\} \exp\left(\frac{\beta f I t}{C_1} \right) \right]$$

$$(A11)$$

It is possible to simplify the above equation by neglecting terms containing τ^{-2} as mentioned above, i.e.,

$$E = E_{cor} - IR_f - \frac{1}{\beta f} \ln\left\{ -\frac{I_1}{I} + \left(1 + \frac{I_1}{I} \right) \exp\left(\frac{\beta f I t}{C_1} \right) \right\} \qquad (A12)$$

On introducing the time-dependences of E_{cor} and R_f (eqns. (18) and (21) in the text) explicitly, the time dependence of electrode potential during the galvanostatic potential–time transient may be expressed as

$$E = E_1 - (E_1 - E_0)\frac{t^2}{\tau^2} - \frac{\rho_\Omega I d}{A\left\{ 1 - \left(1 - \frac{\rho_\Omega}{\rho_f} \right)\left(1 - \frac{t^2}{\tau^2} \right) \right\}} - \frac{1}{\beta f} \ln\left\{ -\frac{I_1}{I} + \right.$$

$$\left. + \left(1 + \frac{I_1}{I} \right) \exp\left(\frac{\beta f I t}{C_1} \right) \right\} \qquad (A13)$$