THE DELAYED ACTION OF MAGNESIUM ANODES IN PRIMARY BATTERIES
PART I. EXPERIMENTAL STUDIES

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Summary

Magnesium exhibits a delayed dissolution on anodic polarisation owing to a slow, field-induced breakdown of the passive film on its surface. The phenomenon depends on several factors such as the pretreatment of the anode, the composition of the solution, etc. In order to clarify the mechanism of the field-induced film-breakdown process, a detailed experimental study of the delayed action and its dependence on several experimental variables such as ageing of the anode in contact with the solution, the nature of the surfactant-coating on the magnesium anode, the anodic current density, etc., has been carried out. The results of the single electrode studies have been verified with improved Mg–MnO$_2$ dry cells. Finally, a probable mechanism based on a 'metal dissolution — film dilatation — film breakdown' model has been proposed in order to explain the delayed action under various experimental conditions.

1. Introduction

The use of magnesium as an anode in different kinds of primary batteries is becoming increasingly widespread. In particular, magnesium–manganese dioxide dry cells exhibit several outstanding features as compared with the conventional zinc–manganese dioxide (Leclanché) dry cells. These beneficial features may be attributed primarily to a more negative standard electrode potential of the Mg^{2+}/Mg reaction (*viz.*, −2.37 V as compared with −0.76 V for Zn^{2+}/Zn), a lower electrochemical equivalent of magnesium (0.45 g/A h for Mg; 1.22 g/A h for Zn), a greater stability of magnesium towards corrosion (which results in a shelf life of about four years for the Mg–MnO$_2$ dry cells as compared with about one year for Zn–MnO$_2$ dry cells), the negligible toxicity of Mg anode products as compared with the toxicity of products from the amalgamated zinc anode, and finally an

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inexhaustible natural resource for magnesium (sea water) as compared with the fast depleting resources for zinc.

The main deterrent factor in the use of the $Mg-MnO_2$ dry cell for several applications is the existence of a significant delay time (of the order of several seconds to minutes), *i.e.*, a time lag between the moment of initiation of cell discharge and the moment of establishment of steady-state or operational cell voltage. During this delay time, there is a steep fall in the terminal voltage of the cell. The delayed action thus reflects the inability of the $Mg-MnO_2$ dry cell to deliver instantaneous power on discharge from an open-circuit condition.

Half-cell studies show that the delayed action is associated with a transient phenomenon at the magnesium–electrolyte interface on anodic polarisation. A typical potential–time transient of a magnesium anode during galvanostatic polarisation (Fig. 1) shows a steep shift in electrode potential in the positive direction followed by a slow recovery to the steady-state value characteristic of the applied current density. The cessation of the anodic polarisation of Mg is also accompanied by a similar transient change in the electrode potential but, in this case, in the opposite direction. Quantitative features of the potential–time transient are strongly influenced by the characteristics of the passive film on the magnesium anode.

A proper understanding of the galvanostatic potential–time transient of the magnesium anode may therefore be expected to throw light on measures which may reduce, if not eliminate, the delayed action of magnesium–manganese dioxide dry cells.

In this paper, we present a variety of experimental data obtained on the transient behaviour of the magnesium anode–electrolyte interface, including the effect of ageing of the electrode, coated with different surfactants, on its delayed-action parameters. Steady-state polarisation data are
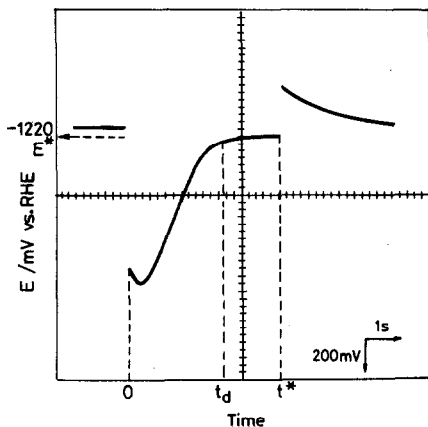

Fig. 1. Typical oscilloscope trace of the potential–time transient of a magnesium anode on initiation ($t = 0$) and interruption ($t = t^*$) of galvanostatic polarisation. The delay time is the time required for the potential to reach a value (to be specified) close to the steady-state potential, E^*.

also presented for typical cases to facilitate a phenomenological interpretation.

In Part II of this series*, we present a physical model of the magnesium–electrolyte interface, its theoretical analysis, and a comparison of the theory with experiment.

1.1. Earlier work

Several workers have attempted to study and explain the delayed action phenomenon of the magnesium anode as summarised below.

Glicksman and Morehouse [1] ascribed the delayed action of the magnesium anode to the destruction (on polarisation) and reformation (on open-circuit) of the passive film on its surface. Robinson and King [2] as well as Kokoulina and Kabanov [3] advanced a similar explanation with a few modifications, viz., that the initial large polarisation is a normal polarisation of the anode which decreases during film disruption on anodic polarisation due to a decreasing current density. Perrault [4, 5] attributed the delayed action to the slow formation of magnesium hydride as an intermediate — a hypothesis untenable for neutral or alkaline media, as pointed out by the author himself.

These theories are rather qualitative in nature and do not explain the quantitative features of the potential–time transient nor its dependence on several experimental conditions such as ageing of the anode in solution, the nature of the surfactant coating on the anode, etc.

A pioneering attempt to understand quantitatively the delayed action of the magnesium anode was made by Schael [6]. According to his diffusion–pore model, the solution-filled pores in the passive film on the magnesium sustain a boundary which becomes concentrated with respect to Mg^{2+} ions on the metal side of the film during the onset of anodic polarisation. The progressive movement of the boundary inside the pore towards the solution, at a rate linearly dependent on the time of polarisation, causes a corresponding change in the resistance of the solution in the pores, which results in the observed transient change in the electrode potential. This theory is rather oversimplified and incomplete, since the influence of double-layer capacitance which is inevitable during the galvanostatic charging process is completely ignored. Probably, because of this and the other assumptions made, complete delay-time curves could not be calculated by Schael from his theory. Moreover, a model based on pure diffusion control in the film is unlikely to be realistic, since the characteristic time for diffusion through a passive film of even 1000 Å thickness is only a few microseconds**, while the observed delay times are in the range of seconds to minutes.

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*The delayed action of magnesium anodes in primary batteries. Part II: Theoretical studies.

**The thickness of the passive film on magnesium was found to be of the order of 100 Å [7]. Considering the growth of the passive film on Mg in alkaline solutions, a

Swathirajan [8] attributed the initial anodic polarisation of the transient partly to an *IR* drop across the passive film and partly to the activation polarisation of the anodic metal dissolution reaction, both of which decrease due to a gradual film dissolution caused by the time-dependent, diffusion-induced, build-up of hydrogen ions in the film. Based on this 'hydrogen-ion build-up' model, theoretical delay-time curves resembling experimental data were also obtained. This theory also has shortcomings, as in Schael's model, *viz.*, a disregard of double-layer capacitance and also an assumption of diffusion as a rate controlling step for delayed action. The invariance of delay-time curves with the stirring of the solution (*cf.* Section 3.2.1.) refutes any dominant role for diffusion in solution. Moreover, a build-up of hydrogen ion concentration to any significant extent is virtually impossible in buffered neutral or alkaline media, wherein the delay-time curves of magnesium anodes are qualitatively similar to those obtained in acidic media.

In summary, it may be stated that a proper theoretical basis to explain the mechanism governing the delayed action is lacking in the literature. None of the theories developed so far can explain the quantitative features of the galvanostatic potential–time transients, the increase in delayed action during ageing of the anode, the effect of corrosion inhibitors on delayed action, etc., the experimental results for which are presented below.

2. Experimental

2.1. Electrolyte

Magnesium perchlorate solution (about 5M) obtained as a battery-grade electrolyte[†] from WIMCO Ltd., India, was diluted to 0.5M and presaturated with $Mg(OH)_2$ by the addition of a small quantity of concentrated sodium hydroxide solution so that the pH of the solution was 8.5 ± 0.1. Under these conditions, there is a significant electrolyte buffer capacity (essential for a proper discharge of the Mg–MnO_2 dry cell) and a reasonable degree of passivity of the magnesium anode (essential for a good shelf life of the Mg–MnO_2 dry cell).

2.2. Surfactants

In a preliminary study of this work, esters of long-chain fatty acids were identified as promising surfactants for the minimisation of delay time and of magnesium anode pitting corrosion susceptibility in Mg–MnO_2 dry

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value of 1000 Å for the film thickness may be a reasonable assumption. The characteristic time for diffusion across such thick films is as low as 50 μs as estimated from Einstein's equation, *viz.*, $t \approx L^2/2D$ where L is the film thickness and D is the diffusion coefficient of the ion (assumed as 10^{-6} cm^2/s which is a reasonable value for a hydrated film in contact with an aqueous solution as in the present case).

[†]A typical analysis of the electrolyte is: Cl^- < 0.004%; SO_4^{2-} < 0.004%; heavy metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}) < 0.001%; $Mg(ClO_4)_2$ ... remainder.

cells. Owing to their ready availability and also the practical success often achieved, oils such as coconut oil (an ester of mainly lauric acid with an iodine value of 8 - 10), olive oil (an ester of mainly oleic acid with an iodine value of 77 - 94) and cottonseed oil (an ester of mainly linoleic acid with an iodine value of 103 - 115) were employed as surfactants. These oils were chosen because of their large surface activity range. All the oils were of food grade purity. In addition to the above oils, chromate ion, which is usually added to the battery electrolyte as a corrosion inhibitor (of magnesium), was also used as a surfactant.

The above oils were found to be ineffective when added directly to the test solution, probably due to their negligible solubility and low density (compared with water), which resulted in their floating on the surface of the solution as a thin layer. The surfactants were therefore coated directly on the magnesium electrode as in ref. 9. Oil-coating was carried out by immersing the cleaned and treated magnesium electrode in a 10 vol.% solution of the oil in benzene, followed by drying at 80 °C for two hours. A second coat was given in a similar fashion to ensure a coherent electrode coating. Chromate passivation was effected in a solution of 20 wt.% CrO_3, 9 vol.% H_3PO_4 and 2 wt.% $Mg(NO_3)_2 \cdot 6H_2O$ for two minutes followed by a thorough cleaning with doubly distilled water and drying of the electrode at 120 °C for two hours.

2.3. Reference electrode

The use of the saturated calomel electrode (SCE) as a reference electrode led to erratic results which could be ascribed to a gradual build-up of the sparingly soluble potassium perchlorate at the flow-barrier in the Luggin capillary causing an increased resistance of the reference electrode arm, and also to a slow diffusion of the Cl^- ion from the SCE into the test solution causing a local passivity breakdown on the magnesium electrode.

In order to overcome these difficulties a "reversible hydrogen electrode" (RHE), i.e., a hydrogen electrode based on platinised platinum, reversible to hydrogen ions in the test solution, was employed for these studies. The potential of the RHE was frequently verified against a carefully prepared fresh calomel electrode in a decinormal HCl solution. The equilibrium potential of the RHE (P_{H_2}: 1 atm; pH: 8.5) is -0.502 V vs. SHE at 25 °C. The use of such an RHE with a Luggin capillary aligned close to the working electrode eliminated liquid-junction potentials as well as errors due to the IR drop in the solution.

2.4. Magnesium electrode

Strips of magnesium alloy anode (alloy AZ 21x, Dow Chemical Co.) were prepared by sectioning impact extruded cans of this alloy. However, graphite powder used as a lubricant in the extrusion process is known to become partly embedded in the magnesium lattice causing localised pitting corrosion of the metal during use.

In order to remove such graphite inclusions, magnesium strips were subjected to a series of cleaning and etching processes, *viz.*, polishing with emery papers of different grades (up to the fine 600 grade), degreasing in a 20 wt.% sodium hydroxide solution at 80 °C for twenty minutes, pickling in a solution containing 12 vol.% acetic acid and 10 wt.% sodium nitrate for one minute, washing with doubly distilled water, and drying at 120 °C for two hours.

Working electrodes were prepared from the clean, dry strips by press-fitting them into a matching groove cut into a Teflon rod and fastening the two with a heat-shrinkable PVC sleeve. Electrical connection was provided by a copper wire crimped around a hole at the top of the electrode (away from the solution), the entire copper wire being shielded with a PVC sleeve and the intermetallic (Cu–Mg) junction with epoxy resin.

Steady-state polarisation studies were carried out with a stationary magnesium disc electrode as described in ref. 10.

In view of possible variations in the surface characteristics of the solid electrode, four to six specimens were employed for each type of experiment. Results reported in this work are those which were quantitatively reproducible for at least three specimens prepared in a similar fashion.

2.5. Counter electrodes

A large area stainless steel sheet was employed as the counter electrode for transient polarisation studies of the magnesium anode. For steady-state polarisation studies involving both anodic and cathodic polarisation, the counter electrode consisted of two graphite rods arranged symmetrically with the working electrode as in ref. 10.

2.6. Electrochemical cell

The electrochemical cell employed for the transient polarisation studies of magnesium anodes consisted of a 500 ml glass beaker covered with a suitably grooved Perspex lid which contained holes to accommodate the working electrode, the counter electrode and the Luggin capillary of the reference electrode. The solution was stirred by a magnetic stirrer in those experiments in which the effect of mass transfer conditions in the solution on the transient behaviour of the magnesium anode was studied.

The steady-state polarisation of magnesium was carried out in a special form of a three-electrode cell described earlier [10]. Deoxygenation of the test solution in this case was achieved by bubbling purified electrolytic hydrogen.

2.7. Magnesium–manganese dioxide dry cells

Magnesium–manganese dioxide dry cells employing chromate-passivated magnesium anodes also coated with oils such as coconut oil, olive oil and cottonseed oil, were assembled as described in ref. 11 and were kindly supplied by Bharat Electronics Ltd., Bangalore, India.

2.8. Other details

Doubly distilled water was used to prepare the solutions. All the chemicals employed were of analytical grade. Purified hydrogen obtained from electrolysis of water was used for the construction of the RHE and for deoxygenation of the test solution. All studies were carried out at ambient temperature which was 25 ± 5 °C.

2.9. Experimental techniques

2.9.1. Steady-state polarisation studies

Steady-state polarisation studies were carried out with a stationary disc electrode as described in ref. 10. This technique has several advantages over a rotating disc electrode, especially for a passive metal such as magnesium as working electrode. A Wenking potentiostat and a stabilized d.c. power supply in series with a high resistance decade box were used for potentiostatic and galvanostatic polarisation studies, respectively. Electrode potentials were measured to an accuracy of ± 1 mV with a digital voltmeter coupled to the output of an electrometer (Keithley) at unit gain, the input leads of the electrometer being connected to the working and reference electrodes in order to eliminate loading errors in the measured electrode potentials.

2.9.2. Transient polarisation studies

It was experimentally observed in this work that switching-on and switching-off operations of the potentiostat resulted in a current transient even at a potential corresponding to the steady-state open-circuit value (*i.e.*, without any polarisation). Further, the experimental data on the transient behaviour of Mg during potentiostatic polarisation were found to be highly irreproducible. These were eventually attributed to a finite potentiostat response time which resulted in a momentary build-up (or decay) of current through the passive film and, hence, in overshoots and undershoots of potential. The passive film characteristics are therefore altered by the switching transients introduced by the potentiostat itself. Lastly, a truly potentiostatic polarisation of the Mg electrode is hardly possible due to an unknown large and variable (because of a progressive breakdown of the film) potential drop across the passive film. For these reasons, it was concluded that the potentiostatic polarisation mode is not a suitable technique for transient polarisation studies of the magnesium anode.

The study of the magnesium anode transient behaviour therefore consisted of recording potential — time transients both on initiation as well as on interruption of galvanostatic polarisation. The transient response of the electrode potential was initially monitored with a Tektronix storage oscilloscope. Final quantitative studies were carried out with a Hewlett-Packard strip chart recorder or an Endim-2200 X–Y recorder coupled with a time base. The X–Y recorder had, however, a low pen speed (max. 20 cm/s) which caused a slight distortion of the potential–time transients, especially at the moment of current injection or current interruption.

In view of the susceptibility to breakdown of the passive film on the magnesium electrode even at low current densities, and especially on the anodic side, a Keithley electrometer was used at unit gain to interface between the working electrode–reference electrode combination and the input of the recorder.

2.9.3. Discharge transients of Mg–MnO$_2$ dry cells

The conventional discharge of Mg–MnO$_2$ dry cells across a constant resistance is inadvisable for a quantitative study of the delayed action parameters because of significant changes in the cell voltage during this phenomenon. In the present work, therefore, the cells were force-discharged in a galvanostatic mode using a stabilized d.c. power supply in series with a high resistance decade box.

3. Results and discussion

3.1. Steady-state polarisation characteristics of Mg

3.1.1. Polarisation curves

Steady-state polarisation curves were obtained for magnesium electrodes coated with various surfactants both potentiostatically and galvanostatically. The two sets of curves were found to be virtually identical for cathodic polarisation but substantially different for anodic polarisation. Typical current–potential curves* are presented in Figs. 2 and 3. Since the open-circuit potential is a mixed potential of corrosion for magnesium, the corrosion currents were evaluated as 41, 6, 4, 3 and 26 μA/cm^2 for curves 1 - 5 (Fig. 2), respectively.

The general features of these steady-state polarisation curves were found to be virtually unaffected, except for a small decrease in corrosion current density (from 41 μA/cm^2 to 36 μA/cm^2 for uncoated Mg) on ageing of the electrodes in the solution for eight days. Since any corrosion products, essentially Mg(OH)$_2$ in alkaline solutions [12, 13], may be expected to be precipitated on the metal surface from the high pH solution which is also presaturated with Mg(OH)$_2$, the above observation leads to the conclusion that ageing of the electrode in solution causes a film thickening with only a marginal healing of the flaws in the film.

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*Figures 2 and 3 were obtained with increasing polarisation from the rest potential of the electrode. When the curves were retraced with decreasing polarisation after reaching the final values shown, a hysteresis was noticeable in most cases, i.e., forward and reverse scanning of polarisation curves point by point did not give identical results. Such a hysteresis may be expected for potentiostatic anodic polarisation curves of passive metals such as magnesium because of a substantial difference in the film-breakdown and film-formation (repassivation) potentials. The hysteresis for cathodic polarisation curves, however, suggests that there are potential-dependent slow steps (e.g., desorption of electrolyte ions at large cathodic polarisation and their slow readsorption on reverse polarisation) even on undamaged films. Potentiodynamic scanning or cyclic voltammetric studies are therefore likely to lead to erroneous results in such cases.
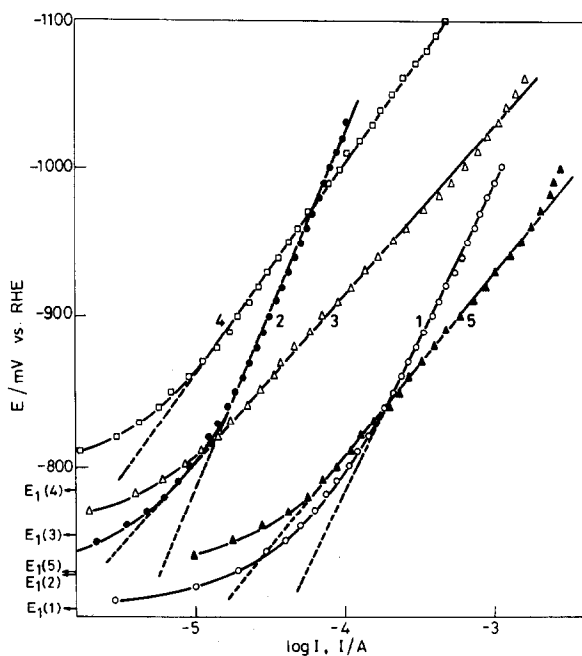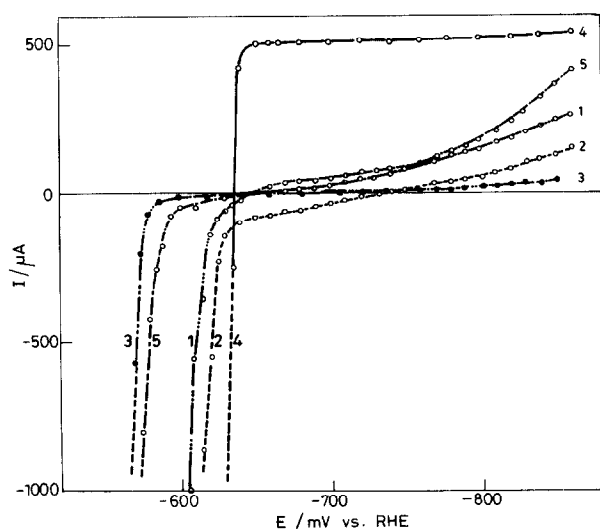
Fig. 2. Tafel plots recast from steady-state potentiostatic cathodic polarisation curves of (1) uncoated, (2) coconut oil-coated, (3) olive oil-coated, (4) cottonseed oil-coated, and (5) chromate-passivated magnesium electrodes (area: 0.9 cm^2) in contact with a de-oxygenated 1N Mg(ClO$_4$)$_2$ solution saturated with Mg(OH)$_2$ (pH: 8.5). $E_1(1)$, $E_1(2)$, etc., are the steady-state open-circuit potentials of the corresponding magnesium electrodes. Curve 4 has been shifted vertically (upwards) by 40 mV.

Fig. 3. Steady-state potentiostatic anodic polarisation curves of (1) uncoated, (2) coconut oil-coated, (3) olive oil-coated, (4) cottonseed oil-coated, and (5) chromate-passivated magnesium electrodes (area: 0.9 cm^2) in a deoxygenated 1N Mg(ClO$_4$)$_2$ solution saturated with Mg(OH)$_2$ (pH: 8.5). Curve 4 has been shifted vertically (upwards) by 500 mV.

3.1.2. Inhibition of Mg corrosion

The corrosion of magnesium is inhibited by about an order of magnitude with any of the above ester coatings. Further, these coatings also reduce the cathodic reaction* exchange current conjugate to the metal dissolution reaction in local galvanic cells.

Chromate film is a poor magnesium corrosion inhibitor compared with any of the oil coatings.

3.1.3. Mechanism of corrosion inhibition by ester coatings

As seen above, the effect of the ester coating of magnesium is to decrease both the corrosion current of Mg as well as the exchange current for the hydrogen evolution reaction on Mg. Moreover, the extent of corrosion inhibition achieved with the ester coatings is independent of the degree of unsaturation present in the hydrocarbon chain of the ester. All these observations point to the fact that a parallel orientation of ester molecules on the surface of the Mg is unlikely, since such a parallel orientation would have led to an interaction of the metal with delocalised electrons in the hydrocarbon chain, resulting in an increased corrosion inhibition with an increase in the iodine value of the ester coating. On the other hand, adsorption with a perpendicular orientation of the ester molecule, with its glyceride group located near the magnesium surface, is compatible both with the hydrophilicity of the oxide or hydroxide film invariably present on the magnesium surface, and with the near invariance of corrosion inhibition with the various ester coatings of widely differing iodine value.

The ester molecules may therefore be visualized as forming a hydrophobic layer on the metal surface with the hydrocarbon ends directed towards the solution. The thickness of this layer depends on the length of the hydrocarbon chain of the ester. In other words, oil-coated electrodes are covered with films which are relatively impervious and repellant to the ions and molecules of the solution and, hence, are more corrosion resistant than uncoated or even chromate-passivated magnesium electrodes**. The decrease in the exchange current for hydrogen evolution by the ester coatings may also be understood as a consequence of the reduced accessibility of water, which is the source of hydrogen ions to the metal surface. On this basis, more effective corrosion inhibitors may be developed in the future from water repellent compounds coated directly on the electrode surface.

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*The most probable cathodic reaction conjugate to the metal dissolution reaction in local cells would be the hydrogen evolution reaction ($H_2O + e^- \rightarrow 1/2 H_2 + OH^-$) owing to: (i) the observed evolution of hydrogen over the Mg surface on cathodic polarisation, and (ii) a lack of dependence of the cathodic polarisation curves on the extent of deoxygenation of the solution as well as on the mass-transfer conditions in the solution, which rules out the possibility of the oxygen depolarisation reaction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) being the cathodic reaction.

**The relatively high corrosion rate of the chromate-passivated Mg electrode points to the existence of a significant number of flaws or pores in the passive film. Moreover, these flaws in the film are not physically screened from the solution by any water-repellent layer as is the case for ester-coated electrodes.

In other words, the mechanism of corrosion inhibition by the ester coatings is by an indirect ohmic control of the corrosion reactions *via* an exclusion of water in the reaction zone.

3.1.4. Breakdown of passivity on anodic polarisation

It follows from Fig. 3 that the magnesium electrode exhibits a passive behaviour up to about 40 mV of anodic polarisation, beyond which a vigorous localised* dissolution of the metal occurs in a transpassive state. Owing to a time-dependent, non-uniform, localised breakdown of the passive film on the anode, kinetic parameters such as the anodic Tafel slope and the exchange current for the metal dissolution reaction cannot be evaluated from the anodic polarisation curves.

The wider passivity range as well as the lower passive currents exhibited by oil-coated electrodes (Fig. 3) as compared with the uncoated or chromate-passivated electrodes are in accordance with their corrosion currents (*cf.* Section 3.1.2.).

The ester-coated electrodes exhibit a larger breakdown voltage (on anodic polarisation) as compared with the uncoated electrodes, probably due to solution depletion in the film on the surface of the ester-coated electrodes. Chromate-passivated electrodes exhibit a lower breakdown voltage as compared with ester-coated electrodes (and almost the same as uncoated electrodes) owing to the porosity and hydrophilicity of chromate films.

3.2. Transient behaviour of the magnesium anode on initiation of galvano-static polarisation

3.2.1. Oscilloscopic studies

A typical galvanostatic potential–time transient of a Mg anode (Fig. 1) consists of three distinct regions corresponding to (i) an instantaneous, large anodic shift (potential-dip or initial anodic polarisation) in potential, (ii) a rapid decrease in the anodic polarisation after the maximum anodic potential is reached, and (iii) an asymptotic approach of the potential to the steady-state value. A large time delay (of the order of several seconds) is observed before the potential reaches the steady-state value from the moment of applying the current.

The large, instantaneous anodic shift may be ascribed to an *IR* drop at the electrode surface and, in particular, across the passive film on the electrode, since the solution is relatively highly conducting. The relatively slow variation of the potential near, and preceeding, the critical breakdown potential (Cbp), *i.e.*, the maximum anodic value, points to the existence of

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*A visual examination of the surface of a magnesium electrode during steady-state galvanostatic anodic polarisation suggests that the metal dissolution is highly localised over about 10 - 20% of the surface of the electrode. During steady-state anodic dissolution the metal is therefore still largely film-covered and only partly film-free.

a slow step involving charge transfer across the metal–solution interface. The subsequent shift of potential to low anodic values beyond the 'Cbp', with the observed localised dissolution of magnesium, suggests a gradual disruption of the passive film. In other words, there is a time delay during which the film breakdown occurs over localised regions on the surface and anodic dissolution proceeds in these film-damaged areas.

The galvanostatic potential–time transients of the magnesium anode observed by oscilloscope remain more or less invariant with regard to their shape and to the delay-time characteristics with different rates of stirring of the solution. It therefore follows that the delayed action of magnesium is not controlled by mass-transfer conditions in the solution.

3.3. Quantitative studies with pen-recordings of potential–time transients

The potential–time transients of a Mg anode during the initial stages of galvanostatic polarisation, recorded using an electromechanical X–Y plotter, under different experimental conditions, viz., after different ageing durations of the anode in solution, with different surfactant coatings on the anode, and at varying anodic current densities (typically at two current densities, viz., 0.2 mA/cm^2 and 10 mA/cm^2), are presented in Figs. 4 - 13.
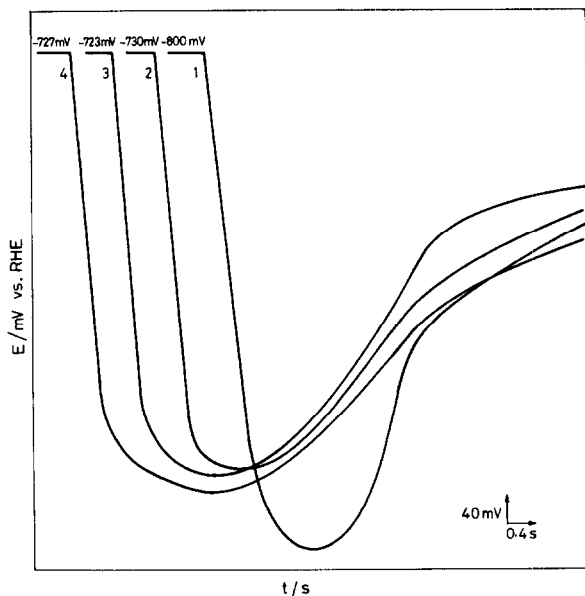

Fig. 4. Galvanostatic potential–time transients of an uncoated magnesium anode in contact with a 1N Mg(ClO$_4$)$_2$ solution saturated with Mg(OH)$_2$ (pH: 8.5) at a current density of 0.2 mA/cm^2 after ageing of the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.
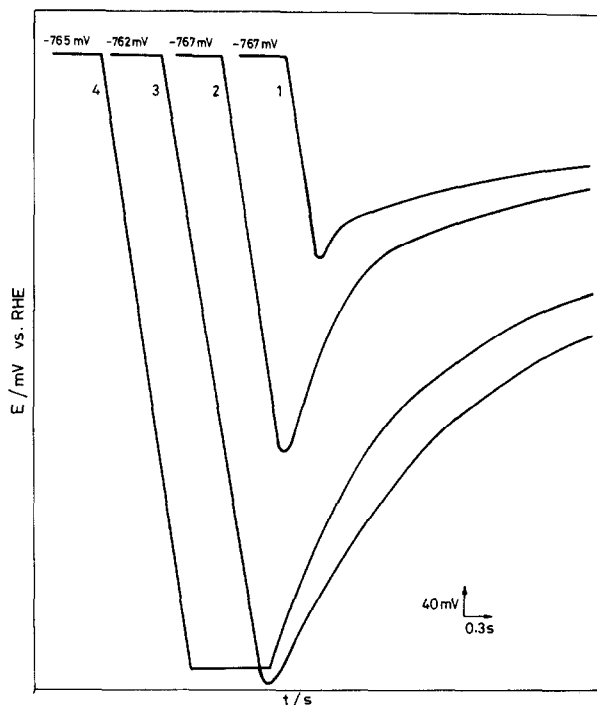
Fig. 5. Galvanostatic potential–time transients of an uncoated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 10 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

3.3.1. Delayed action effect of ageing of the uncoated Mg anode in solution

The delayed action of uncoated magnesium becomes more pronounced with ageing of the anode in solution, as shown by the families of potential–time transients in Figs. 4 and 5. There is an increase in both the delayed-action parameters, viz., the potential dip as well as the delay time, the increase being more marked at low current densities.

It has been pointed out (cf. Section 3.1.1.) that during ageing of the anode in solution, there is passive film growth by deposition of corrosion products (essentially $Mg(OH)_2$) on the electrode surface. Such a deposition is facilitated by the fact that the electrolyte is at a pH of 8.5 and presaturated with the sparingly soluble $Mg(OH)_2$. Moreover, the flaws in the film are not healed during such a film thickening process, as is evident from the considerably high magnesium corrosion rates even after prolonged ageing.

3.3.1. (a) Mechanism for film breakdown.
A mechanism for film breakdown during anodic polarisation may be proposed at this stage. During galvanostatic anodic polarisation of magnesium, Mg^{2+} ions are generated by anodic dissolution of Mg and are at least partially hydrated at the metal–

film interface, the film being moist and with flaws (such as fissures, cracks, pores, etc.) which permit transport of the electrolyte solution through the flaws towards the metal surface. The hydrated Mg^{2+} ions and their hydrolysis product $Mg(OH)_2$ impart a progressively increasing dilatation stress on the film, eventually leading to film breakdown. In other words, the mechanism for film breakdown on anodic polarisation in this case is, successively, anodic dissolution, film dilatation, and film breakdown.

Accordingly, thick films require a higher dilatation stress for breakdown than do thin films, implying longer times of anodic current flow to initiate a film breakdown process, i.e., a longer delay time. The increased potential dip on ageing may be understood as an increased IR drop across the thicker passive film on the anode.

Direct evidence for film-thickening on lithium [14] and magnesium [15] anodes during cell storage has been obtained by scanning electron microscopy and other spectroscopic techniques. The increase in breakdown voltage with increase in thickness of the passive film is also well known [16]. Further, it has been observed that the breakdown field decreases for thicker films [17, 18], leading to longer relaxation times [19, 20] during electrical breakdown of insulators.

3.3.2. Delayed action effect of ageing of oil-coated Mg electrodes in solution

It may be inferred from the families of potential–time transients* of oil-coated magnesium anodes (Figs. 6 - 11) that, at any given current density and anode ageing duration in solution, the delayed action of oil-coated Mg anodes is significantly reduced compared with uncoated Mg anodes. In other words, the increase in the delayed action parameters, viz., potential dip and delay time on ageing, is largely suppressed with an oil-coated anode. Moreover, this beneficial effect of oil coating on the delayed action is not influenced by the degree of unsaturation in the ester hydrocarbon chain, just as in the case of corrosion inhibition achieved by these coatings described above (cf. Section 3.1.3.).

Consistent with the proposed dissolution–dilatation model of film breakdown (cf. Section 3.3.1.(a)), it follows from the above observations that the increase in the delayed-action parameters of a magnesium anode on ageing is proportional to the open-circuit corrosion rate of the anode in the given solution. The higher the corrosion-inhibition, the less will be the increase in the delay time for a given set of conditions on ageing.

3.3.3. Delayed action effect of ageing of chromate-passivated Mg anodes in solution

The potential–time transients of chromate-passivated Mg anodes (Figs. 12 and 13) suggest that the delayed-action parameters are remarkably

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*The potential–time transients of oil coated Mg anodes are, in general, characterized by a faster potential recovery, especially in the initial stages of recovery, compared with those obtained from uncoated Mg anodes. This may be due to the fact that the relaxation time for film breakdown is reduced by oil-coating, with the molecules of oil acting as impurities and therefore as breakdown centres in the film.
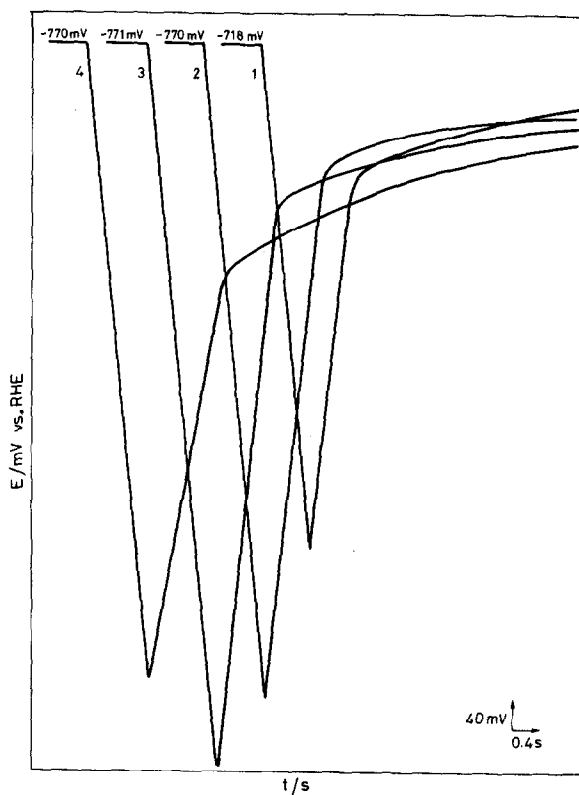
Fig. 6. Galvanostatic potential–time transients of a coconut oil-coated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 0.2 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

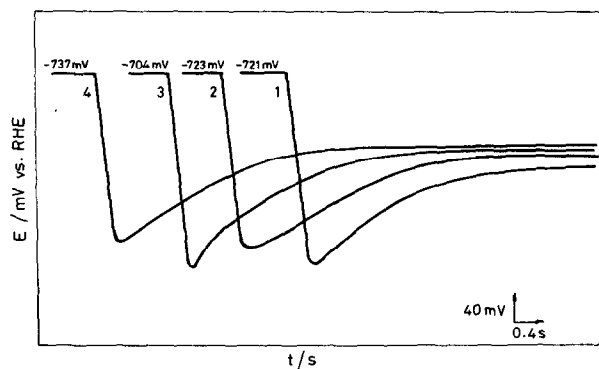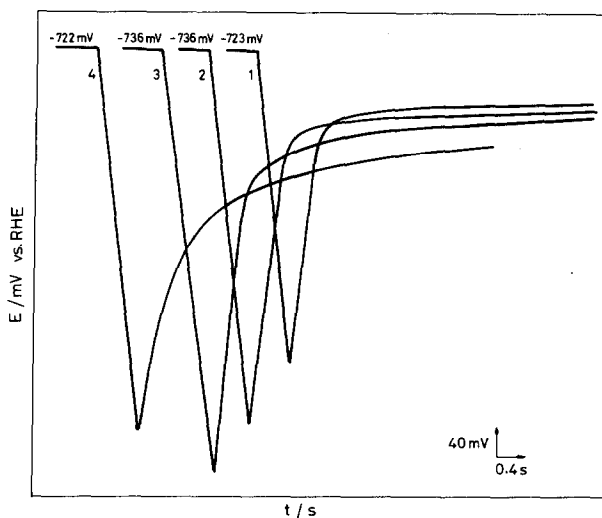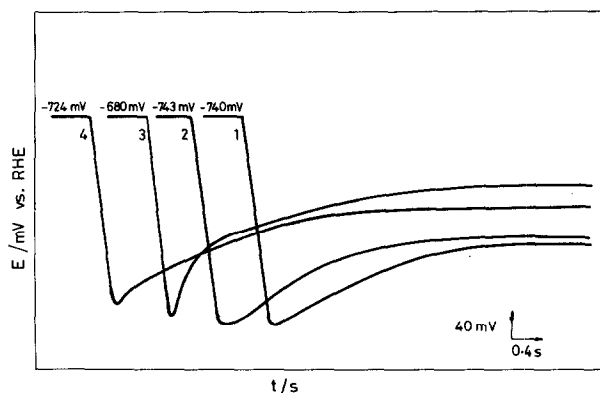Fig. 7. Galvanostatic potential–time transients of a coconut oil-coated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 10 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

Fig. 8. Galvanostatic potential–time transients of an olive oil-coated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 0.2 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

Fig. 9. Galvanostatic potential–time transients of an olive oil-coated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 10 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

reduced with chromate-passivation, even to a greater extent than with oil coating. Moreover, there is almost no noticeable increase in the delayed-action parameters of a chromate-passivated electrode during its ageing in solution.

Chromate-passivated electrodes thus apparently behave contrary to the above 'dissolution–dilatation' model according to which the delayed action increases during ageing at a rate proportional to the open-circuit corrosion rate of the magnesium anode. However, if the facts that the open-circuit corrosion rate of the chromate-passivated Mg anode is nearly
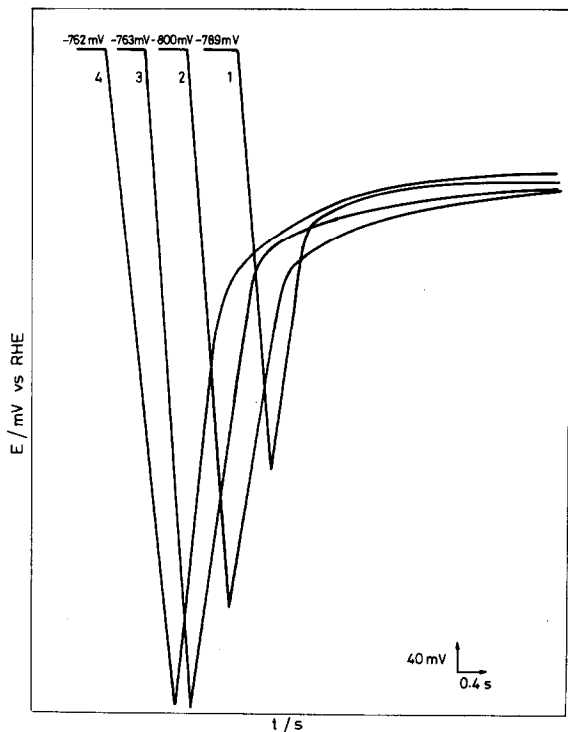
Fig. 10. Galvanostatic potential–time transients of a cottonseed oil-coated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 0.2 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

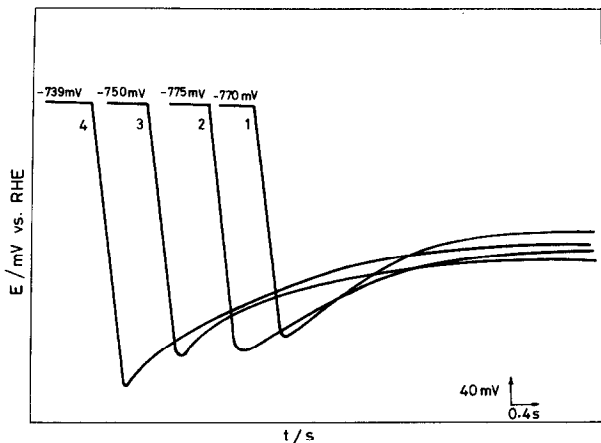Fig. 11. Galvanostatic potential–time transients of a cottonseed oil-coated magnesium anode in contact with a 1N $Mg(ClO_4)_2$ solution saturated with $Mg(OH)_2$ (pH: 8.5) at a current density of 10 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.
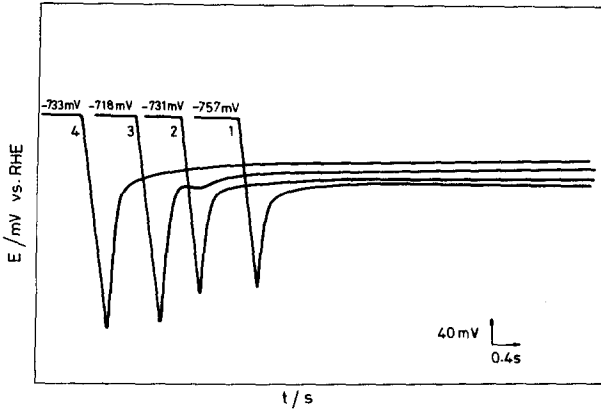
Fig. 12. Galvanostatic potential–time transients of a chromate-passivated magnesium anode in contact with a 1N Mg(ClO$_4$)$_2$ solution saturated with Mg(OH)$_2$ (pH: 8.5) at a current density of 0.2 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.

Fig. 13. Galvanostatic potential–time transients of a chromate-passivated magnesium anode in contact with a 1N Mg(ClO$_4$)$_2$ solution saturated with Mg(OH)$_2$ (pH: 8.5) at a current density of 10 mA/cm^2 after ageing the electrode for (1) 12 h, (2) 24 h, (3) 36 h, and (4) 48 h in the solution.
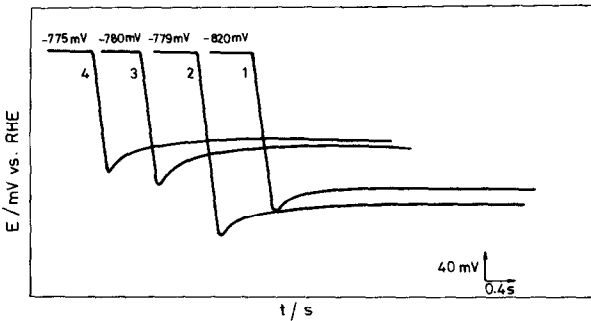
the same as that of the uncoated anode and that this rate is not decreased much on ageing are taken into account, it may be inferred that the accumulation of corrosion products over a chromate-passivated Mg electrode occurs not as a coherent passive film but as a porous film, which therefore does not contribute to an increase in the delayed action of the anode on ageing.

3.3.4. Effect of anodic current density on the delayed action of a Mg anode

According to the 'dissolution–dilatation' model for the breakdown of a passive film on Mg during anodic polarisation, the injection of higher current densities generates the required dilatation stress in a shorter time, implying a reduced delay time. The potential–time transients of Mg anodes

with, or without, a surfactant coating confirm the above hypothesis, *viz.*, that the delay time of a Mg anode (measured as the time required for the electrode potential to reach the asymptotic region of the transient) decreases with increasing anodic current density*. However, at high anodic current densities, especially with oil coated anodes, the final approach rate of the potential to the steady-state value is rather sluggish, probably due to a significant contribution from charge-transfer, mass-transfer, and ohmic polarisation phenomena.

At very low anodic current densities (*i.e.*, $\leqslant 0.2$ mA/cm^2) the delay time is significantly increased (Fig. 4), probably due to the slow, film breakdown process occurring almost at a rate comparable with that of the film-reformation process at these low current densities.

3.4. Discharge transients of Mg–MnO$_2$ dry cells

It may be expected from the earlier discussion (*cf.* Section 3.1.3.) that if a film on a chromate-passivated electrode is porous and partly corrosion-inhibiting, while the film on an oil-coated electrode tends to be coherent and strongly corrosion-inhibiting, a combination of the two, *viz.*, oil-coating of a chromate-passivated Mg electrode, may have a synergistic influence on the corrosion-inhibition as well as on the related delayed-action parameters. The synergistic effect is expected because of the porous chromate film which, besides providing some corrosion-inhibiting effect, will also sustain a higher concentration of the corrosion-inhibiting oil within the pores of the film than in the absence of such a microporous film.

The cell voltage–time discharge transients at different current densities of Mg–MnO$_2$ dry cells fabricated in different ways, *i.e.*, with different surfactant coatings on the chromate-passivated Mg anode are presented in Figs. 14 - 16.

A significant result emerging from these Figures is that the increase in the delayed-action parameters on storage of Mg–MnO$_2$ dry cells at ambient temperatures is largely suppressed by oil-coating the chromate-passivated Mg anode, in agreement with the synergistic corrosion-inhibition model suggested above.

Second, the delay time of Mg–MnO$_2$ dry cells with, or without, oil coating on the chromate-passivated Mg anode, decreases with increasing discharge current density, as expected from the dissolution–dilatation model of the breakdown of a passive film on a Mg anode.

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*As expected, the potential dip increases with increasing anodic current density, but only up to 1 mA/cm^2, and decreases beyond that value. The decrease in potential dip with increasing c.d. beyond a threshold value may be partly caused by a faster initiation of the film-breakdown process and partly caused by the slow response of the recorder.
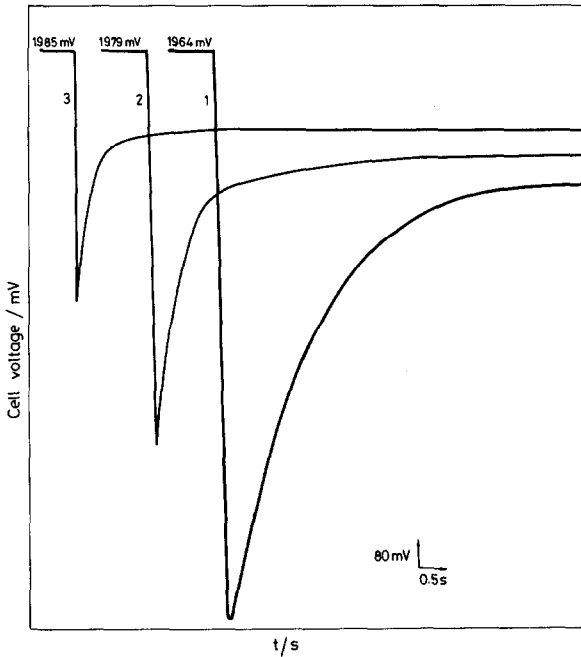
Fig. 14. Delay-time curves of (1) chromate-passivated, (2) chromate-passivated and olive oil-coated, and (3) chromate-passivated and cottonseed oil-coated magnesium anode-based Mg–MnO$_2$ dry cells at a discharge current density of 3 mA/cm^2 (on the magnesium anode) and after a cell storage period of three months at room temperature.
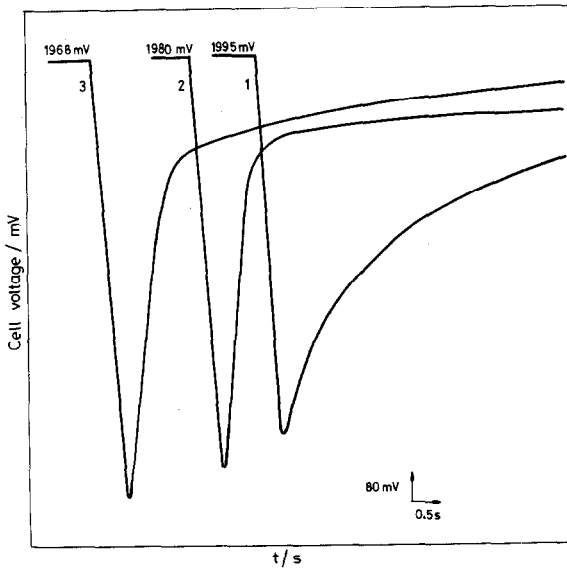

Fig. 15. Delay-time curves of (1) chromate-passivated, (2) chromate-passivated and coconut oil-coated, and (3) chromate-passivated and olive oil-coated magnesium anode-based Mg–MnO$_2$ dry cells at a discharge current density of 0.33 mA/cm^2 (on the magnesium anode), and after a cell storage period of sixteen months at room temperature.
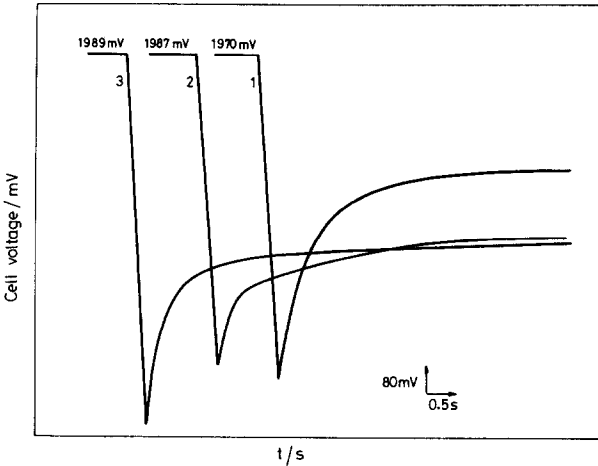
Fig. 16. Delay-time curves of (1) chromate-passivated, (2) chromate-passivated and coconut oil-coated, and (3) chromate-passivated and olive oil-coated magnesium anode-based Mg–MnO$_2$ dry cells at a discharge current density of 3.33 mA/cm^2 (on the magnesium anode) and after a cell storage period of sixteen months at room temperature.

3.5. Open-circuit potential–time transient of a Mg electrode on cessation of galvanostatic anodic polarisation

On interruption of galvanostatic anodic polarisation, the magnesium electrode exhibits a negative overshoot in potential of the order of 100 mV beyond the steady-state, open-circuit potential, followed by, at first a rapid, and then a slow decay to the steady-state value (Fig. 1). Further, the open-circuit transient is more or less invariant with the nature of the surfactant coating on the Mg and with the ageing of the electrode in solution. On the other hand, it is influenced by the anodic current density prevailing before its interruption becoming more pronounced at higher current densities. Based on these observations, a physical model for the decay transient may be proposed as follows.

During steady-state galvanostatic anodic polarisation, magnesium undergoes pitting-type localised dissolution and, hence, would be still largely film-covered and only partly film-free. Moreover, at the film-free areas, the magnesium electrode exhibits a more negative corrosion potential than at the film-covered areas, owing to an increased reactive site area for the anodic metal dissolution reaction in the local cells. In other words, the corrosion potential of the magnesium anode during steady-state galvanostatic polarisation is more negative than the steady-state open-circuit value, due to, at least, the partial exposure of bare Mg sites. Consequently, there is a negative potential overshoot beyond the steady-state open-circuit value. The subsequent decay of potential to more anodic values is a result of re-passivation of the electrode, which progressively decreases the film-free area

on the electrode. Accordingly, the transient excursion of the electrode potential in the cathodic direction is influenced by the film-free area during anodic polarisation and therefore should increase with increasing anodic current density, as found experimentally.

4. Conclusions

The delayed action of the Mg anode is ascribed to a field-induced breakdown of the passive film on its surface. The breakdown of the passive film is visualized as a consequence of the progressively increasing dilatation stress imparted by the hydrated Mg^{2+} ions generated at the metal–film interface during anodic polarisation. The increase in the delayed-action parameters on ageing of the anode in solution is associated with the continued open-circuit corrosion of the anode and the resultant growth of the passive film on the anode. Corrosion inhibitors, such as esters of long-chain fatty acids or chromate ion, have a beneficial effect in suppressing the increase of delayed action during ageing. Chromate-passivation of the anode leads to the formation of a porous film of corrosion products which, while not decreasing the corrosion rate of the Mg anode to any significant extent, does not contribute to an increase in the delayed action. Esters of long-chain fatty acids acting as cathodic inhibitors suppress the corrosion rate of Mg by apparently forming a compact hydrophobic layer and physically screening the electrode from the ions and molecules of the solution. A combination of the two, viz., oil-coating of a chromate-passivated Mg anode exerts a synergistic action and provides a decrease in the open-circuit corrosion rate and decreased delay time on ageing. These conclusions are verified with $Mg–MnO_2$ dry cells. The delayed action of the Mg anode (and, hence, of $Mg–MnO_2$ dry cells) becomes increasingly severe at low anodic (discharge) current densities.

The unusual open-circuit transient of Mg on interrupting anodic polarisation is related to the significant difference in the corrosion potentials of the film-free and the film-covered regions, and the subsequent succession of passive states from an imperfect film-covered surface of the electrode to a nearly completely film-covered surface during the course of this transient.

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