SURFACE FILM EFFECT ON THE ELECTROCHEMICAL BEHAVIOUR OF ACTIVE METALS

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Summary

It has been suggested that a film on the surface of an active metal should be a dielectric with low ionic and electronic conductivity. The film–electrolyte boundary can be regarded either as an interface between two electrolytes or as the surface of an insulating electrode. In this zone a potential difference is set up and redox reactions proceed. These processes, controlled by the concentration and by the transfer of charged particles through the film, determine the anode–cathode behavior of metals under consideration.

Corrosion and anodic dissolution of lithium and magnesium have been investigated in dilute solutions of water in propylene carbonate. The potential of the lithium electrode reveals the properties of the equilibrium potential and does not depend on either the content of water in the solution or the lithium corrosion rate. The observed orders of interaction between lithium and water, however, does depend on the water concentration, on the electrolyte concentration, and on the thickness of the initial film.

At the beginning of the process the rate of the interaction between lithium and water is described by the equations of topochemical kinetics, but when the maximum is reached, by the Tamman equation. A stationary potential is realized on magnesium; its value depends on the water content in the solution. The potential shifts towards negative values with increased water concentration.

Introduction

Lithium and magnesium as well as other metals of the main subgroups in Groups I and II of the Periodic Table possess a high reduction potential

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which explains their great reactivity immediately after the bare metal surface is exposed to the environment. The products of the interaction of lithium and magnesium with gaseous and liquid materials are usually of low volatility, are weakly soluble, and form a poreless film of finite thickness on the metal surface. These films reduce the metal reactivity, thus permitting long term contact with such active oxidants as oxygen, sulphur dioxide and thionyl chloride.

For the majority of oxidants the composition and properties of the surface film formed on lithium and magnesium have not been studied sufficiently, if at all, and this complicates the examination of their corrosive and electrochemical behaviour, especially in liquid media.

General principles of the electrochemical behaviour of thin films

It has been proved that when metallic lithium is in contact with the environment, an initial poreless film is formed on its surface as a product of interaction between the metal and the environment [1 - 3]. Under certain conditions a secondary porous film may be formed on the primary, and a change in the environmental composition may lead to chemical changes in both films [4, 5]. All known compounds which form surface films on lithium (oxide, hydroxide, chloride, etc.) possess ionic conductivity and may be considered as solid electrolytes [6, 7].

The behaviour of such thin film solid electrolytes differs from the properties of massive samples of the same chemical composition. The main difference is due to considerable disorder and defects within the thin layers which provide both electron transport and ionic conductivity. The presence of many defects in surface layers is indicated, indirectly, by their dark, almost black colour. The films probably possess high ionic and electronic conductivity. In addition to the transport processes in thin layers (20 - 200 Å) associated with the increased number of charged particles — ions and electrons — the situation is complicated by electric fields produced by surface and space charges. The theory of thin oxide film formation on metals developed by Wagner [8] may be unacceptable when applied to the film formation on lithium and magnesium as it is based on the linear transport equations. An analysis of the electrochemical behaviour of films on lithium reveals an exponential dependence of the current on the potential [9, 10] according to the theory of Vervey *et al.* [11]. In some cases, the process of film growth can be complicated by heterogeneous reactions in the film–solution phase boundary [12]. Attempts to describe these processes phenomenologically have been made in the past for lithium [13, 14] and for magnesium [15].

This paper presents an experimental study and attempts to analyse kinetic characteristics and stationary potentials of lithium and magnesium corrosion in electrolytes based on dipolar solvents.

The nature of stationary potential

The stationary potential of an active metal covered with a poreless film in nonaqueous electrolytes has, in the general case, three components: the potential discontinuity at the metal–film boundary, $\Delta\varphi_{Me}^{film}$, the voltage drop in the film due to the corrosive process, $\Delta\varphi_{film}$, and the discontinuity at the film–electrolyte boundary $\Delta\varphi_{film}^{el}$

$$\Delta\varphi_{Me} = \Delta\varphi_{Me}^{film} + \Delta\varphi_{film} + \Delta\varphi_{film}^{el} \tag{1}$$

Under equilibrium conditions, in absence of the corrosive process, $\Delta\varphi_{film} = 0$, the electrode potential in respect of the solution (the bulk potential of which is considered to be zero) is defined by the sum of potential discontinuities at two phase boundaries

$$\varphi_{Me} = \Delta\varphi_{Me}^{film} + \Delta\varphi_{film}^{el} \tag{2}$$

Describing the potential change corresponding to the reaction

$$Li \rightleftharpoons Li^+ + e^-$$
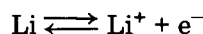
in terms of the ionic equilibrium, which is more convenient for further consideration, we obtain the following expression for $\Delta\varphi_{Me}^{film}$

$$\Delta\varphi_{Me}^{film} = \varphi_{Li}^o + \frac{RT}{nF} \ln C_{Li^+film} \tag{3}$$

where φ_{Li}^o is a standard potential; C_{Li^+film} is the concentration of lithium ions in the film.

The potential difference at the "film–electrolyte" boundary can also be described by the electronic and ionic equilibria. In contrast to the "metal–film" boundary, however, these equilibria correspond to different reactions; namely: the ion exchange is determined by the membrane equilibrium
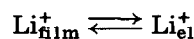
$$Li_{film}^+ \rightleftharpoons Li_{el}^+$$
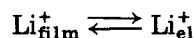
and the electron exchange by the redox equilibrium

$$Ox + ne \rightleftharpoons Red^{n-}$$
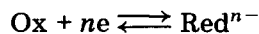
The choice of the equilibrium which determines the potential depends on the relation of concentration of electrons and ions in the film, that is, on the relation of the electron work function for the metal and film material; namely, when $x_{Me} > x_{film}$ the membrane equilibrium will be reached.

The potential change at the film–electrolyte boundary which corresponds to the reaction

$$Li_{film}^+ \rightleftharpoons Li_{el}^+$$

has the form

$$\Delta\varphi_{film}^{el} = \varphi_{Li^+film/Li^+el}^o + \frac{RT}{F} \ln \frac{C_{Li^+el}}{C_{Li^+film}} \tag{4}$$

The sum of relations (3) and (4) provides an equilibrium potential difference between the metal and the electrolyte

$$\varphi_{Me} = \varphi^o_{Li} + \varphi_{Li\,film/Li\,el} + \frac{RT}{F}\ \ln C_{Li^+el} \tag{5}$$

If, at the film—electrolyte boundary, the redox equilibrium is established corresponding to the reaction

$$Ox + ne_{film} \rightleftharpoons Red^n_{el}$$

the potential change is defined by the equation

$$\Delta\varphi^{el}_{film} = \varphi^o_{ox/Red} + \frac{RT}{nF}\ \ln \frac{C_{ox\,el}C^n_{el\,film}}{C^n_{Red\,el}} \tag{6}$$

Thus, the potential difference between the metal and the electrolyte will be as follows

$$\varphi_{Me} = const + \frac{RT}{nF}\ \ln \frac{C_{ox\,el}}{C_{Red\,el}} \tag{7}$$

It should be noted that the equilibrium corresponding to eqn. (7) may take place only with an infinitely large ionic resistance. Under the conditions corresponding to the formation of the potential at the film—electrolyte boundary in accordance with the reaction Ox/Red, the equilibrium does not take place, but the corrosive process will proceed as determined by the work of the galvanic cell Me/Ox on the finite ohmic resistance. Therefore, a new term, $\Delta\varphi_{film}$, appears, which was initially excluded.

Formerly based on the comparison of corrosive and exchange currents, it was determined that the electrode potential of lithium in oxidizing media was in quasi-equilibrium [16]. Special studies showed that in a wide range of water concentration the potential of the lithium electrode did not depend on the content of water [17]. It was also proved that in very-cation-dilute solutions, when the surface film is reformed (that is, the oxide film is changed by the hydroxide film), the electrode potential begins to depend on the water concentration in accordance with eqn. (7). At the same time, independent determinations of the solvation energy changes of lithium halogenides for different solvents were made by open circuit voltage measurements of the circuits (without ion transport) with a lithium electrode [18] and by direct calorimetric measurements: the results were in good agreement. It proves the correctness of applying eqn. (5) to the metallic lithium electrode in electrolytes based on aprotic organic solvents.

Lithium corrosion in the absence of external polarization

It follows from the previous analysis that the corrosive electrochemical processes on the lithium electrode occur at different interfaces: the anodic dissolution of the metal occurs at the "metal—film" boundary, and the
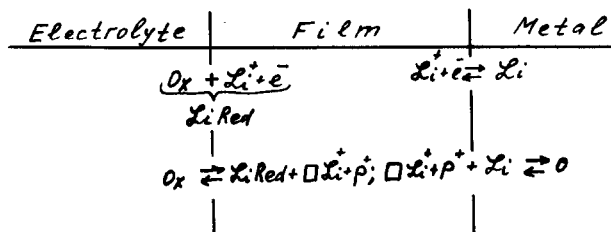
Fig. 1. Illustration of boundary equilibria.

cathodic reduction of the oxidant on the "film—electrolyte" boundary. A charge transfer through the film is necessary for the process to be continuous. One can assume the existence of at least two mechanisms, corresponding to the electron and to the hole conductivity, respectively [3]. The charge transfer processes run in the following ways (Fig. 1):

(i) An atom of lithium enters the film where it dissociates into an electron and an ion (cation — in the interstitial site). The cation and the electron move to the outer side of the film; there the electron is accepted by the oxidant, and the cation together with the reduction product form a low solubility compound which completes the film.

(ii) An atom of lithium leaves the metal and fills a vacancy in the cation sublattice. The electron recombines with the hole. On the outside surface of the film the oxidant injects a hole into the film passing to the reduced state and, simultaneously, removes the cation from the lattice. The cation forms a low solubility compound which completes the film. The hole and the vacancy transport to the metal. Insufficient experimental data do not allow us to choose between the corrosive mechanisms, but the presence of the hole conductivity in the film [19, 20] makes the second mechanism the most likely.

Partially structured lithium oxide, Li_2O, is assumed to be the initial film, with a thickness depending on the oxygen dose received by the freshly-prepared surface of lithium. The same film thickness is formed as a result of either short-term contact with some gas rich in oxygen (say, pure oxygen) or long-term contact with some gas containing little oxygen (say, high purity helium).

The oxide layer has a low conductivity [16, 21]. According to the model the concentration of electrons there is not high. A positive space charge retards the hole injection and ion transport is limited. That is why the corrosion rate on lithium covered by the oxide film is less than 1 mA cm^{-2} and does not depend on the water concentration in the solution. The corrosion rate reduces with the growth in film thickness.

Lithium oxide is not chemically inert in many solvents. After putting lithium into the solution with such compounds, therefore, a reaction starts on its surface which leads to the reformation of the surface film. The higher the reagent concentration in the environment the faster the reaction proceeds. For example, in pure water it is complete in fractions of a second.

If the water content is moderate one can observe different stages in the process.

To determine the mechanism and the law of the film reformation process, data of the gas evolution rate as a function of time, in water solutions of different concentration, were presented in terms of the Kolmogorov–Yerofeyev equation

$$L = 1 - \exp(-k\tau^n)$$

and a linear dependence was revealed (see Fig. 2) [22]. This showed that the process proceeded according to the concepts of topochemical kinetics, and made it possible to estimate, quantitatively, the influence of the thickness of the oxide film on the development of the process [3, 12]. The interaction between lithium and water does not start on the whole surface but on discrete nucleation points. We assume that the number of these nuclei, N, is constant during the reaction, that they are evenly distributed on the surface, and that a nucleus is hemispherical with a radius which increases with time. The rate of the reaction can be seen as the volume of hydrogen, V, evolved from the surface of the sample in the time, τ, $V = V'N$, where V' is the volume of hydrogen evolved from one nucleus. As the nucleus has a hemispheric form one can write the following:
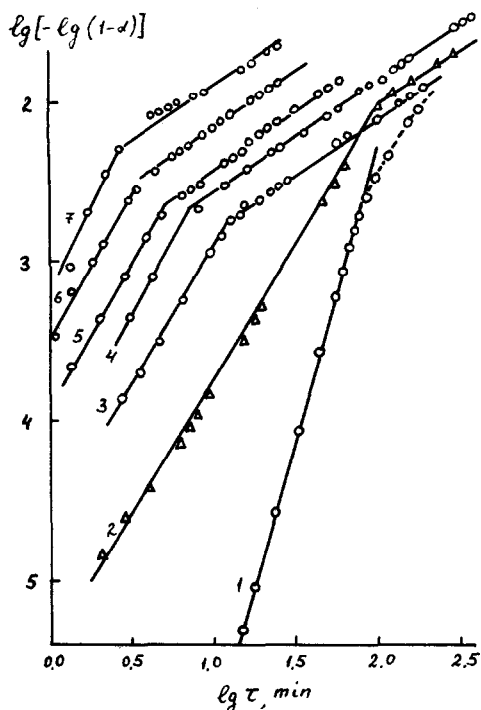

Fig. 2. $\lg|-\lg(1-\alpha)|$ vs. $\lg \tau$ for some concentrations of water: 1, 0.50; 2, 0.96; 3, 1.18; 4, 1.30; 5, 1.42; 6, 1.90; 7, 2.65%.

$$V = \frac{2\pi R^3 \bar{V} N}{3}$$

where: R is the nucleus radius, $\bar{V}$ is the volume of hydrogen evolved as a result of the complete transformation on one volume of lithium, $\bar{V} = 927$ ml (at 25 °C). According to the main statement of topochemical kinetics, R linearly increases with time.

The value, K, is found from the conditions under which maximum reaction rate is achieved, and the real surface of the reaction zone is $\Lambda/2$ higher than the geometrical surface of the lithium sample:

$$K = \frac{S_r^{1/2}}{2\tau_{max} N^{1/2}}$$

where S_r is the geometrical surface of the lithium sample, and τ_{max} is the time over which the maximum reaction rate is achieved. From the combination of these two expressions we obtain $V = K\tau^3$,

where $K = \dfrac{\Lambda S_r^{3/2} \bar{V}}{R\tau_{max}^3 N^{1/2}}$

From the slope of the line in V–τ^3 coordinates one can find N. It should be noted that this model does not reflect the overlapping of neighbour nuclei during the reaction and can describe the process only up to τ_{max}. Applying the proposed model to the experimental data shows that the highest number of nuclei is detected on a fresh surface of lithium extruded directly into the solution. On extruding lithium into oxygen the number of nuclei on 1 cm^2 decreases to almost half after two-minutes exposure; after 20 minutes exposure to 0.025. The film, therefore, reforms according to the topochemical kinetics laws. The growth in thickness of the film which forms upon contact with oxygen not only increases the time necessary for reforming but decreases the number of active sites where such a process may begin.

To determine the corrosion rate according to the topochemical kinetics we define the maximum reaction rate as [23]

$$W_{max} = K C_{H_2O}^m$$

where

$$K = k\pi S_{sp} g / d_{max}$$

S_{sp} is the specific initial surface of the initial solid substance; g is the weight of the initial substance, and d_{max} is the average diameter of nuclei at the maximum reaction rate (expressed as the number of atoms or molecules). According to this, the relationship of corrosion rate and water concentration logarithms yields a straight line

$$\lg W_{max} = \lg K + m \lg C_{H_2O}$$

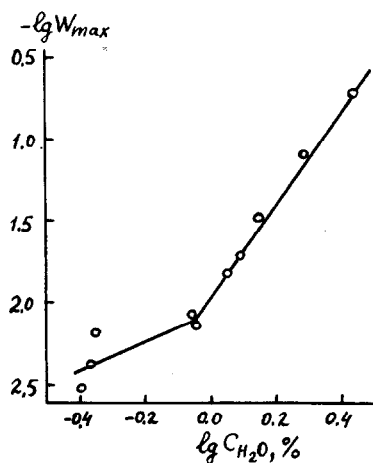Experimental results in Fig. 3 show that the slope of the line changes from 1 to 3.

Fig. 3. The variation of lg W_{max} as a function of lg C_{H_2O}.

Transition from the solution of water in pure solvent to the solution in electrolyte is accompanied by a decrease of water reactivity, as revealed by the corrosion rate decrease and an increase in time necessary for the film reformation with the growth of salt content in the solution (Fig. 4).

It is possible to measure the change of lithium electrode potential in electrolytes without error due to the diffusion potential on the interface "reference electrode–solution". As shown in Fig. 5, the process of film reformation leads to a small potential change at the initial stage only. Neither a significant increase in the corrosion rate in the W_{max} region, nor its subsequent decrease, affects the lithium electrode potential value, indicating that the magnitude of $\Delta\varphi_{film}$ is small and that the potential-determining membrane equilibrium Li^+_{film}/Li^+_{el} does not substantially shift from the equilibrium state. Apparently, during the film reformation, in addition to the growth of the disorder rate, the interchange current of this equilibrium is also increasing; this is to be expected because it depends on the concentration of the cationic defects in the film.

The corrosion of lithium at the anode polarization

Important information concerning the processes which take place during the corrosion of lithium can be obtained from investigations of the corrosion rate under anode polarization. Figure 6 shows the relationship of the hydrogen evolution rate plotted as a function of time with different polarization currents. It can be seen that the magnitude of the maximum hydrogen evolution rate and the time to reach it depends on the current strength. In Fig. 7 one can see the relationship between the maximum hydrogen evolution rate and the current density during anode polarization; the maximum hydrogen evolution rate on extruding lithium directly into the same solution (without polarization) is plotted as a dashed line.
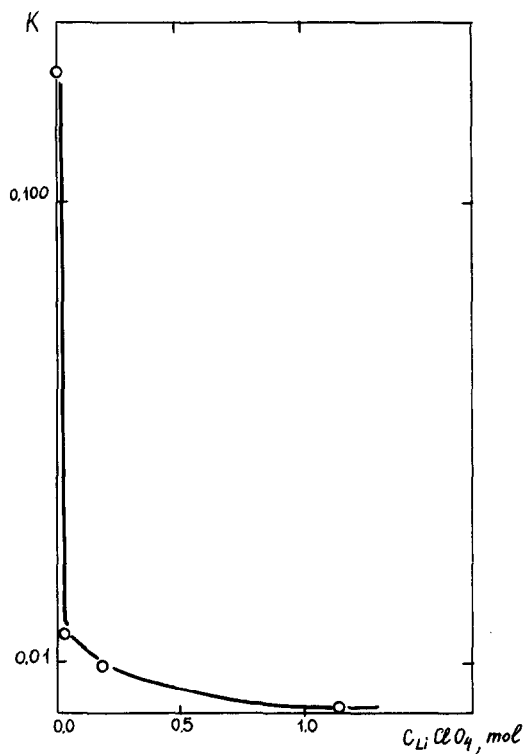
Fig. 4. The corrosion rate of lithium as a function of salt concentration in solution.
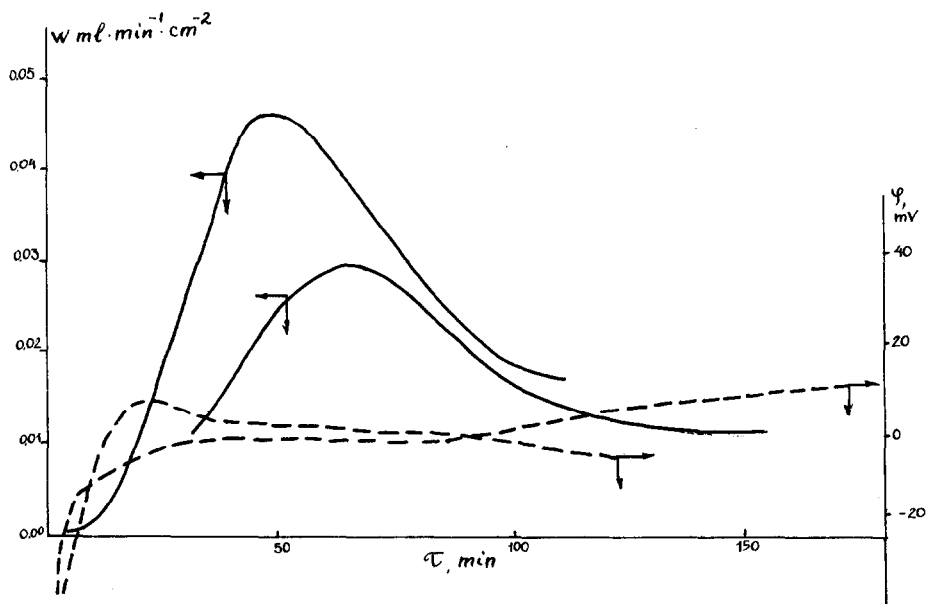

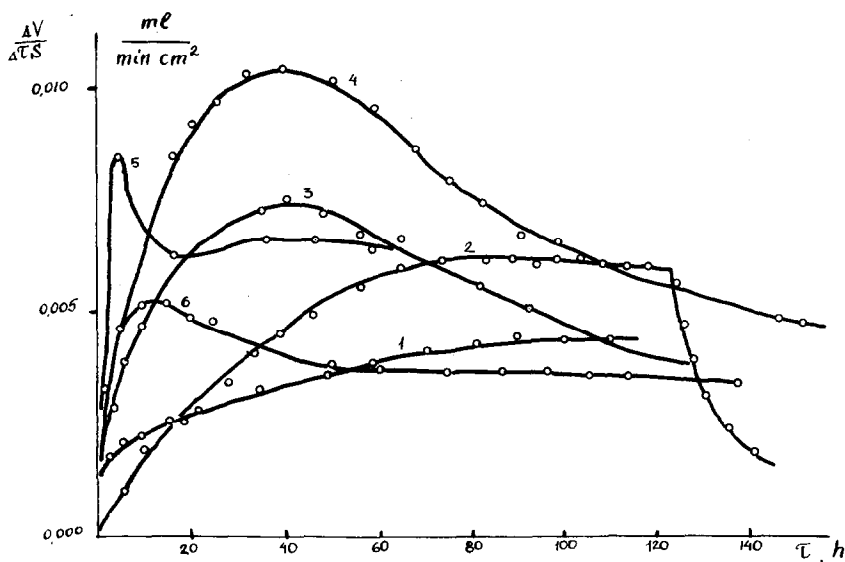Fig. 5. Lithium stationary potential as a function of time.

Fig. 6. The hydrogen evolution rate from lithium perchlorate solution (1.17 mol) in propylene carbonate ($C_{H_2O} = 2.01\%$) $vs.$ time. Numbers correspondent to currents: 1, 0.674; 2, 1.12; 3, 1.65; 4, 2.52; 5, 3.62; 6, 5.57 mA cm^{-2}.
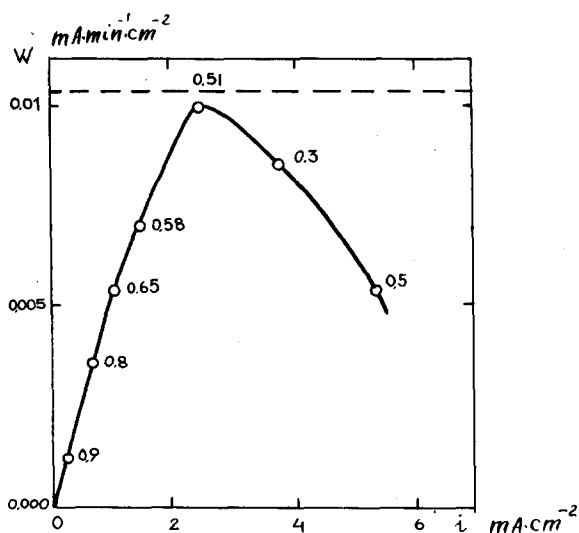

Fig. 7. The relationship between W_{max} and current density in lithium perchlorate ($C_{H_2O} = 2.01\%$). Numbers are ratios of corrosion to polarization currents.

The growth of the hydrogen evolution rate during anode polarization (negative difference effect) is related to the increase of electronic flow in the direction from the metal to the solution which, from the viewpoint of the combined diffusion of ions and electrons [24], is related to the

increased flow of lithium atoms through the film. It can be assumed that the anode polarization creates conditions for the growth in concentration of lithium atoms near the "metal–film" interface, and this results in the growth of atom flow in the direction of the solution. At the same time, the film thickness grows due to the ionic flow. As the growth of lithium atom concentration is limited at certain magnitudes of current, the maximum hydrogen evolution rate diminishes. It is obvious that as anode polarization increases it is possible to achieve a current density at which the negative difference effect can become positive due to the growth of electronic flow to the anode. It is known from the literature that at high water contents in the solution during the anode lithium dissolution a positive difference effect is observed [18].

Investigation of magnesium corrosion in non-aqueous media

The initial magnesium potential measured immediately on immersion of the electrode in the solution of propylene carbonate (PC) is equal to -1.60 ± 0.1 V measured against a silver reference electrode and this affirms that, in our conditions, water is an oxidant. The influence of water cannot be reliably described by eqn. (6) because the measured potential is not an equilibrium one and the magnitude of $\Delta\varphi_k + \Delta\varphi_{film}$ is also dependent on the water concentration. Nevertheless, the water content of the electrolyte strongly influences the magnesium corrosion rate, showing that it is water which is the active agent [25]. At the same time, the almost-linear, measured potential depends on the magnesium ion concentration in the solution, and the conditions of sample surface preparation also affect the potential magnitude [26].

The corrosion process on magnesium is developed in all solvents according to the parabolic equation $\Delta g^n = K\tau$ (with all the studied water contents being between 0.008 and 1.5 mol kg^{-1}), Fig. 8. The activation energy of the process is 17 ± 1.0 kJ mol^{-1}. This testifies to the diffusional control of the process corrosion rate. At the same time, the magnitude of the initial potential does not depend on the rotational speed of the disc. Hence, at the initisl stage, corrosion proceeds without outside diffusional limitations. All the above indicates that the combined diffusion of the charged particles through the film is a slower stage of the process.

Considering the development of the corrosion process with time (Figs. 8 and 9), one can see two regions corresponding to low (0.008 - 0.5 mol kg^{-1}) and high (1.0 - 5.0 mol kg^{-1}) water contents. Significantly, different slopes of the lg i_{cor}–lg C_{H_2O} line correspond to these regions.

The first of the above regions is characterized by the low corrosion rate $\Delta g \sim 10^{-5}$ g cm^{-2}. The growth rate with increase in water content is insignificant ($\Delta i/\Delta\tau \leqslant 0.5$).

The replacement in the electrolyte of the magnesium salt by a lithium salt shows (Fig. 10) that the electrolyte salt takes part in the formation
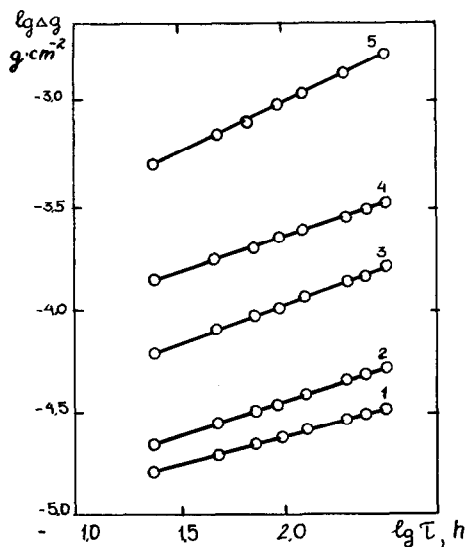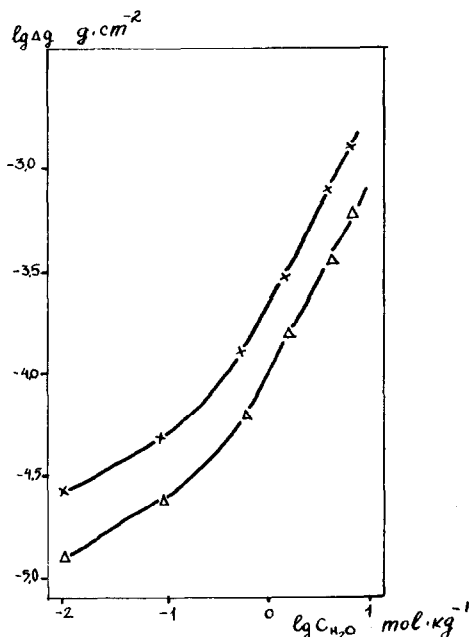
Fig. 8. The relationship between weight of magnesium electrode in propylene carbonate with 0.4 mol kg^{-1} Mg(ClO$_4$)$_2$ and water concentration. 1, τ = 24 h; 2, τ = 150 h.

Fig. 9. The weight of magnesium electrode in propylene carbonate solution with 0.4 mol kg^{-1} Mg(ClO$_4$)$_2$ as a function of time. The numbers correspond to the water content: 1, 0.008; 2, 0.056; 3, 0.561; 4, 1.462; 5, 6.137 mol kg^{-1}.
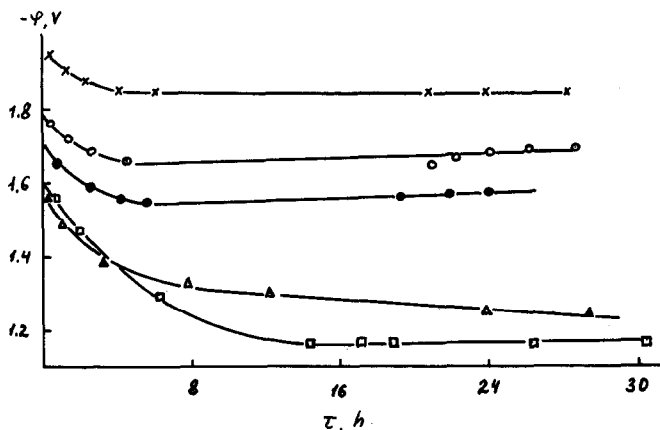

Fig. 10. Electrode potential of Mg-95 $vs.$ time for 1.0 mol kg^{-1} Mg(ClO$_4$)$_2$ in propylene carbonate. The concentrations of water are the same as in Fig. 9.

of insoluble products and this part is about 30%. The initial value of the electrode potential (1.7 ± 0.15 V measured against a silver reference electrode) depends only slightly on the water content. During the first 20 h

of corrosion it exhibits a significant shift — up to 600 mV in the positive region. The potential stabilizes long before the end of the film resistance growth, indicating that the main part of the shift is attributed to a decrease of the kinetic member. In other words, with decreasing process rate the potential shifts to the equilibrium value.

The second region is characterized by the high corrosion rate, $\Delta g \sim 10^{-3}$ g cm^{-2}. The rate growth with the increase in water content is considerable ($\Delta i/\Delta g \geqslant 1$). With the growth in water content the initial potential value shifts to the negative region by up to -2.0 V, indicating the increase of $\Delta\varphi_k$. The electrode potential does not change during the first 50 h, remaining near to the initial value.

All the above information leads to the assumption that, depending on the water content, both mechanisms shown in the scheme in Fig. 1 take place: the first at low water content, and the second at high water content, because only in the case of the first mechanism do cations of both film and electrolyte take part in the film formation, and only with the second mechanism is there a source of charge carriers dependent on water concentration.

Anode magnesium polarization exhibits a negative difference effect. The ultimate current, the magnitude of which is dependent on the water content in the electrolyte, is registered on the cathode branches of the polarization curves in the potential regions up to ~ 3.2 V (Fig. 11).

The cleaning of the electrode in the solution results in a potential shift to the negative region and growth in the corrosion rate.

Figure 12 shows the "magnesium–electrolyte" interface capacity as a function of the contact time with a solution. Such extreme capacity behaviour can be explained by a simultaneous rapid dissolution of the oxide film on the surface of the magnesium and growth of a new coating. Considering the general capacity as
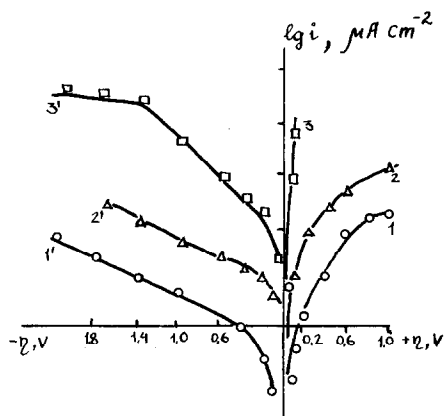

Fig. 11. The polarization curves of magnesium in propylene carbonate with 0.4 mol kg^{-1} Mg(ClO$_4$)$_2$ for water concentrations: 1, 0.009; 2, 0.56; 3, 6.13 mol kg^{-1}.

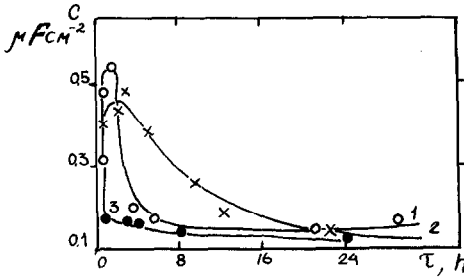Fig. 12. Capacitance *vs.* time for: 1, acetonitrile–1.0 mol kg^{-1} Mg(ClO$_4$)$_2$, U_{imp} = 0.48 × 10^{-2} V; 2, U_{imp} = 0.24 × 10^{-2} V; 3, propylene carbonate–0.4 mol kg^{-1} Mg(ClO$_4$)$_2$, U_{imp} = 0.12 × 10^{-2} V.

$$C = \frac{C_1 C_2}{C_1 + C_2}$$

where C_1 and C_2 are the capacities of the initial and secondary layers, respectively, we can assume that up to a certain time the change of layer thickness proceeds according to the degree relationship

$$L_1 \sim K_1 t^{1/2} \quad \text{and} \quad L_2 \sim K_2 t$$

Such behaviour can be attributed to a slowing-down of the diffusional dissolution of the initial oxide layer and the linear growth of a new layer due to an heterogeneous reaction of the initial film products with a component of the solution. The dependence of general capacity on time can be written as follows:

$$C = \frac{\epsilon_1 \epsilon_2}{\epsilon_1 K_2 t + \epsilon_2 [L_0 - K_1 t^{1/2}]} \tag{8}$$

where ϵ_1, ϵ_2 are the dielectric constants of the initial and secondary layers, respectively, and L_0 is the initial thickness of the oxide layer. The maximum capacity value written as

$$C_{max} = \frac{\epsilon_1 / L_0}{1 - \dfrac{\epsilon_2 K_1^2}{4\epsilon_1 K_2 L_0}} \tag{9}$$

is achieved when

$$t_{max} = \left(\frac{\epsilon_2 K_1}{2\epsilon_1 K_2} \right)^2 \tag{10}$$

Conclusions

Our investigation of lithium and magnesium corrosion behaviour in electrolytes based on aprotic solvents reveals two types of active metal

behaviour: the establishment of a quasi-stationary potential by the metal under consideration corresponds to membrane equilibrium; in the case of a prevailing redox process the equilibrium is not achieved and a stationary potential is established. The corrosion rate is determined by the processes of conjugated ion and electron chemical diffusion in the film.

Acknowledgements

List of symbols

C	Capacity
c_i	Concentration of species i
e^-	Symbol of electron
g	Mass of electrode
i	Electrical current density
i_{corr}	Corrosion current
k, k_i, K	Proportionality constants
L_0	Initial thickness of oxide film
L_1, L_2	Thickness of film 1 and film 2
m	Exponent (power)
N	Numbers of nuclei on surface films
p^+	Symbol of hole
R	Nuclear radius
S	Sample area
t	Time
t_{min}	Time to reach minimum capacity
U_{imp}	Impulse amplitude
V	Volume of hydrogen at time t
$\bar{V}$	Hydrogen volume discharged from one volume of lithium
W	Rate of hydrogen discharge
W_{max}	Maximum rate of hydrogen discharge
α	Degree of transformation
ϵ_i	Dielectric constant
η	Overpotential
x_{Me}, x_f	Partial conductivity of metal and oxide films
τ	Time
τ_{max}	Time of maximum rate of hydrogen discharge
φ_{Me}	Potential of metal
$\Delta\varphi_{Me}^f$	Potential difference between film and metal
$\Delta\varphi_f^{el}$	Potential difference between electrolyte and film

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