On the role of the anions on the anomalous anodic dissolution of aluminium

M. GARREAU, P. L. BONORA*

Université Pierre et Marie Curie, 4, Place Jussieu 75230 Paris Cedex 05, France

The influence of the anions on current efficiency during the anodic dissolution of aluminium, and on the surface state of the electrode, has been studied both from a theoretical and an experimental point of view. The results obtained have some implications both in the field of electropolishing and in the field of electrochemical machining.

1. Introduction

During the anodic dissolution of a metallic electrode, the mass of dissolved metal sometimes exceeds the amount calculated from Faraday's law, assuming as electrovalence the valence of the thermodynamically stable dissolved ion. This kind of dissolution leading to deviations from Faraday's law is generally known as 'anomalous anodic dissolution'. Understanding the mechanism which determines the importance of the anomaly and, therefore, the current efficiency of the dissolution is both of theoretical and practical interest. In the case of electropolishing, for example, the mechanism of this process determines whether polished, etched or pitted surfaces are produced. In the same way the dimensional control in electrochemical machining (ECM) is related to the current efficiency for metal removal [1, 2].

Many papers have appeared on the subject of the anodic anomalous dissolutions of metals, after Wholer and Buff [3] first discovered the phenomenon 100 years ago, but the reaction mechanisms leading to the observed excessive weight-losses however remain controversial.

A comprehensive review of the research work carried out in this field has been recently published by James [4]. We merely recall that all the various interpretations proposed are linked to two quite different concepts concerning the nature of anomalous dissolution.

Some authors consider anomalous dissolution to be nothing more than a mere intervention of secondary parasitic effects: direct chemical attack of the metal during the electrolysis (the 'negative difference effect') [4, 5] or mechanical disintegration of the electrode (the 'chunk effect') [4, 6]; both these secondary effects are due to the dissolution current.

On the other hand, other authors claim that these anomalies are related to the formation of ions of intermediate valency e.g. the formation of transient monovalent ions such as Al^+, Be^+, Mg^+, Zn^+, etc. The life of these ions is long enough to modify, in some cases, the overall reaction [4, 7].

The present study follows the latter point of view. It is based on a deeper analysis of a previously presented reaction model [7, 8] concerning the role of the solvated anions contained in the electrolyte. We will set out this analysis, and the related experimental work.

2. Theory
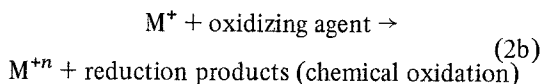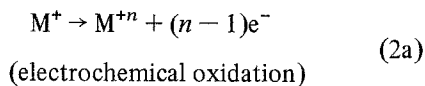
2.1. Reaction model

The formation of transient univalent ions may explain the anomalous dissolution, if we assume that the dissolution of the metal proceeds in two steps, which determine the reaction balance:

Initial anodic formation of univalent ions:

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$$M \rightarrow M^+ + e^-. \qquad (1)$$

Conversion of the transient ions towards their thermodynamically stable form in the solution, with a possible competition between an electrochemical and a chemical oxidation of the ions:

$$M^+ \rightarrow M^{+n} + (n-1)e^-$$

$$\qquad (2a)$$

(electrochemical oxidation)

$$M^+ + \text{oxidizing agent} \rightarrow$$

$$\qquad (2b)$$

$$M^{+n} + \text{reduction products (chemical oxidation)}$$

The value of the apparent dissolution valence, Ne, defined as the average number of electrons leaving the electrode through the external circuit when one atom passes into the solution, is determined by the relative importance of Reaction 2a or b. The anomaly of dissolution (Ne < n) occurs only when Reaction 2b is actually able to compete with Reaction 2a, i.e. when the thermodynamic stability of univalent ions near the electrode is favoured.

Figs. 1 and 2 may help us to find the favourable conditions for the inversion of stability. Fig. 1 shows the free energy changes as a function of distance from the electrode of the various ions which may be formed from the metallic lattice of the anode. This kind of conventional plotting is often used when discussing the activation energies in the electrochemical reactions. Only free energy variations between well-known final and initial states are actually available for the various particles considered. The curves are approximate in the region between the final and initial states.

Curve (a) is related to the formation of an atom in the gaseous state from its equilibrium position in the metallic lattice (sublimation). Curves (a) and (c) show the free energy (G) variations during the formation in vacuum of gaseous Al^+ and Al^{3+} from the metal (ionization). Curves (b') and (c') record the variations of G for the same ions when the solvation energy intervenes. These curves take into account both the adsorption energy and the energy necessary to deplete partially the ion of its solvation shell.
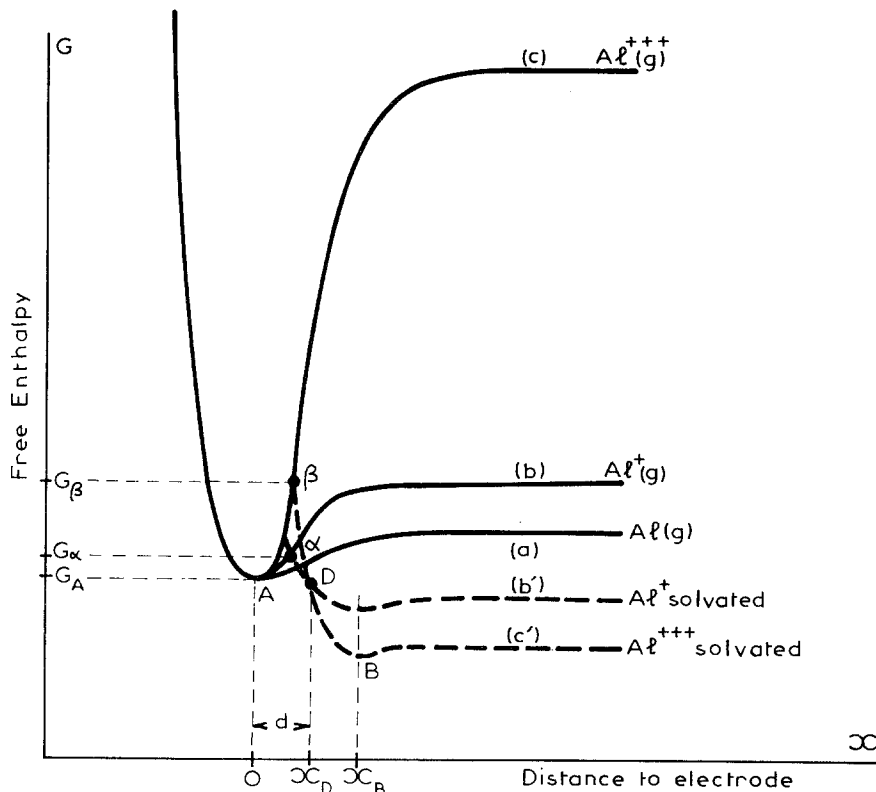

Fig. 1. Pictorial description of the free enthalpy variations of aluminium ions in relation to distance to electrode. Case of an environment rich in molecules of solvent.
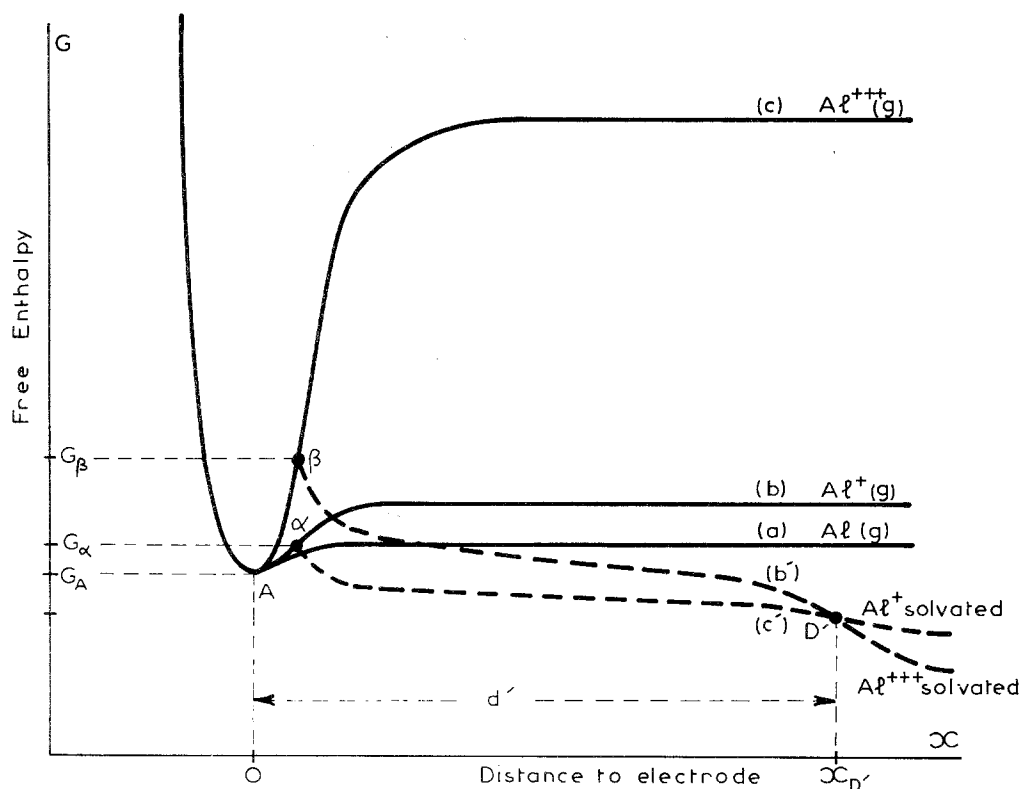
Fig. 2. As Fig. 1, but in the case of an environment deficient in molecules of solvent.

The B position corresponds to the partially solvated ions adsorbed at the metal surface. The D position corresponds to the inversion of stability. The $(x_B - x_D)$ distance is linked with the electrode polarization and to the Stokes' radius of the solvation ion. This radius determines the closest approach distance of the solvated ion.

The study of the curves mentioned previously evidences the peculiar role played by the solvation during the dissolution of the metal and accounts for the different amounts of activation energy $\Delta G^{\neq}$ required for the formation of uni- or trivalen ions (for solvated univalent ions $\Delta G_1^{\neq} = G_\alpha - G_A$ and for trivalent ions, $\Delta G_2^{\neq} = G_\beta - G_A$).

Fig. 1 is related to the case of electrodes immersed in an environment rich in solvent molecules. The formation of univalent ions by Reaction 1, as the first dissolution step, is more likely to occur than the direct formation of ions with higher valences, because of the prohibitively high value of the activation energy $\Delta G_2^{\neq}$ required for the formation of the trivalent ion. The zone where Al^+ ions are more stable than Al^{3+} ions is very small $(x < x_D)$ and close to the electrode;

electrochemical oxidation (2a) occurs at such a rate as to be the only one responsible for the formation of solvated Al^{3+} ions. This latter species becomes stable after the distance x_D. The curves in Fig. 1 correspond to the experimental conditions where Faraday's law is satisfied.

Fig. 2 shows the appropriate curves when solvation is incomplete within the anodic layer. In this case, the 46 eV difference between the ionization energies of Al^+ and Al^{3+} ions is not rapidly counterbalanced by the bonding energies of these ions with the surrounding medium, because of the low concentration of solvating molecules near the anode. An inversion of the stabilities of Al^{3+} and Al^+ ions follows, favouring Al^+ at a distance as far as $d' = x_{D'} - x_A$ from the electrode. The situation in this region is somewhat similar to the one which favours Cu^+ ions in the couple Cu^+/Cu^{2+} when water is replaced by some organic solvents [9].

Reaction 2a in this case involves a long distance electronic transfer. It becomes more difficult, the larger the distance of d'. This reaction is then progressively replaced by Reaction 2b, if experimental conditions cause the d' values to increase.

Following this reaction model, the anomaly of valence is directly related to the length, d', of the layer within which Al^+ is more stable than Al^{3+} and to the oxidizing power of the compounds which form the layer itself. Moreover, it is related to the electric field established near the anode by the potential V applied at the ends of the electrolytic cell (when V increases, the curves (b') and (c') shift downwards, and d' diminishes).

2.2. Role of the anion

The anion can intervene in two ways:

(a) The formation of an environment with a low concentration of solvent molecules, similar to the one in Fig. 2, is associated with the creation of an important electrical field (close to the electrode). The latter may be sufficient to bring about the adsorption of the anions in the solution, rather than the molecules of the solvent on the surface of the electrode. The electrostatic contribution to the adsorption energy of the anions is sufficient to eliminate the molecules of the solvent from the surface of the electrode [9–11]. As suggested by Schmitt and Mark [12], the anions regularly adsorbed on the surface of the anode may form a multilayer. The cohesion of this almost crystalline structure depends on the width of the electrostatic field in the anodic zone. The solvent molecules are eliminated over a distance from the electrode which increases for anions which show a decreasing tendency to be solvated. The importance of anion solvation can be roughly evaluated by examining the ratio r_s/r_c of the Stokes' and crystalline radii.

On examining the Stokes' radii obtained through ionic mobility measurements (the only measurement available for ethanol [13]) we note that the ion ClO_4^- has a particularly low value for the ratio r_s/r_c. The ions SCN^-, NO_3^-, I^-, Br^-, Cl^- follow in this order (for ClO_4^-, $r_s/r_c \simeq 0.9$; for Cl^-: $r_s/r_c \simeq 1.7$). A similar classification applies to methanol.

(b) The anion can also involve itself in anomalous dissolution through its chemical properties. It is in this way that the ion ClO_4^- forms the oxidizing agent in the Reaction 2b in most of the dissolution carried out in organic solutions containing perchlorates. The reduction product formed in this case, the ion Cl^-, was examined both directly

in an anodic layer by means of electronic diffraction [14], and by titrating the number of ions formed in solution during electrolysis [15]. This number of ions accounts for deviations from Faraday's law. ClO_3^- ions have also been identified as intermediates in the reduction $ClO_4^- \rightarrow Cl^-$, by polarographic analysis using a rotating ring-disc electrode [15].

It is difficult to forecast which of these two actions of the anion of the electrolyte will predominate in determining an anomaly of valence. The few incomplete results which can be found in the literature on this subject are not conclusive [4] because they relate to measurements taken in experimental conditions which cannot be compared. In particular, the electrical parameters are not sufficiently well known. The experimental work we are going to present was carried out with the aim of answering a few questions in this field.

3. Experimental details

We first performed certain experiments similar to those described above for ClO_4^- ions, for which we employed solutions of $LiClO_4$ and other salts in ethanol. The behaviour of the $LiClO_4$ solution was adopted as a reference. Methanol solutions were employed for these salts which were barely soluble in ethanol.

The salts and the solvents which were utilized were high purity products and the metal used was aluminium with a very high percentage purity (99·995%). Molecular sieves (3A) were used to dry the solutions. The quantity of water in the solution was determined by the Karl Fischer method. When we speak of 'anhydrous' solutions we mean solutions containing about 0·1 g of water l^{-1}, i.e. roughly 100 ppm or 5×10^{-3} molecules l^{-1}.

The apparent dissolution valence was obtained by the equation:

$$Ne = \frac{Q/F \begin{array}{c}\text{(number of electrons removed} \\ \text{from the anode)}\end{array}}{P/A \text{ (number of dissolved atoms)}}$$

where A = atomic mass of the metal; P = measured weight loss, g; F = Faraday $\simeq 96\ 500$ C g equiv^{-1}; Q = quantity of electricity which passed through the cell, C. All measurements were taken at room temperature. The electrodes were polished mechanically and electrolytically before dissolution, then

they were washed in an ultrasonically stirred solution of ethanol. After dissolution the metal was washed once again.

We can obtain values of Ne which are more precise than 1%, when the surface is not covered by a rough layer. The U_a potentials applied to the anode were measured with respect to a saturated calomel electrode. The surface layer of the anode, after dissolution, was examined with a scanning electron microscope (Cambridge, Stereoscan 600).

4. Results

4.1. Solutions of LiClO$_4$ in ethanol

We adopted an anhydrous 0·5 M LiClO$_4$ solution.

(a) Ne measurements. The curve Ne $= f(U_a)$ shows a well defined 'plateau' as the anodic potential rises above 7 V (Fig. 3). The Ne value for this is about 1·25. The current is high enough here to allow an accurate determination of Ne.

(b) Curve $I = f(U_a)$. With stationary electrodes, which we preferred to rotating ones to determine

the Ne values more accurately, we found that the curves $I = f(U_a)$ were not reproducible. Curve 2 of Fig. 3 shows the general behaviour of this curve. These measurements were determined step by step as the potentials decreased. We noticed a diffusion action which leads to a reduction of the slope of the curve in almost all our range of determination of Ne.

(c) Observation of the surface. The electrodes show a clean surface when the anodic potentials are above 3 V. The surface begins to corrode below this potential, without showing a clear-cut division between the two fields. Careful examination under the scanning electron microscope allowed us to observe the progressive passage from a polished state to a corroded one. With high anodic potentials the electrode shows a very smooth surface. It has, however, a few areas with obvious defects. The metal is covered by a very thin coherent membrane which has the typical granulated surface associated with electropolishing in a bath containing ClO$_4^-$ ions. This membrane can be seen more clearly when it has been torn accidently (Fig. 4;
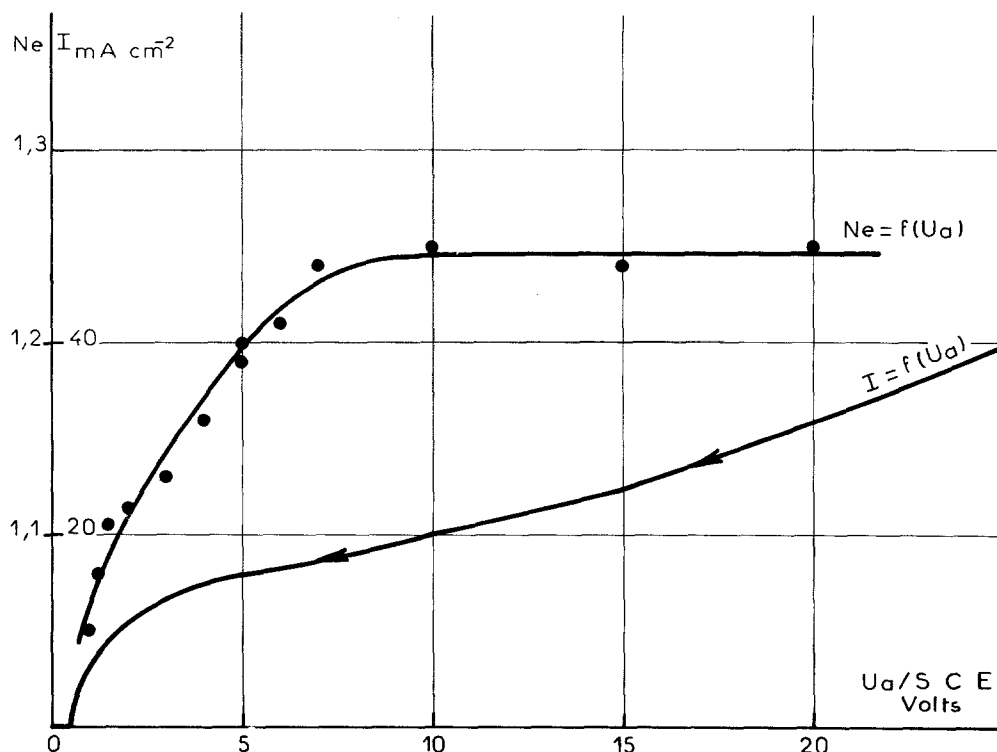

Fig. 3. Anodic dissolution of aluminium in a ternary mixture of ethanol, lithium perchlorate (0·5 M), and water [H$_2$O] $=$ 0·1 g l^{-1}). Curves 'current–anodic potential' $I = f(U_a)$, and 'apparent dissolution valence–anodic potential'. Ne $= f(U_a)$; T $= 25°$ C.
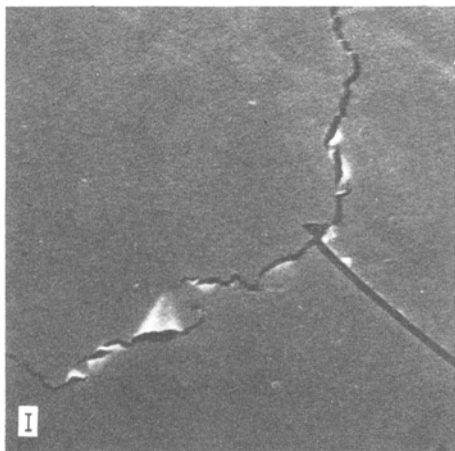
Fig. 4.I. Scanning electron micrograph (I–IX). Anodic dissolution of aluminium. Solution of $LiClO_4$ (0·5 M) in ethanol; $U_a = 5$ V. $\times$ 750
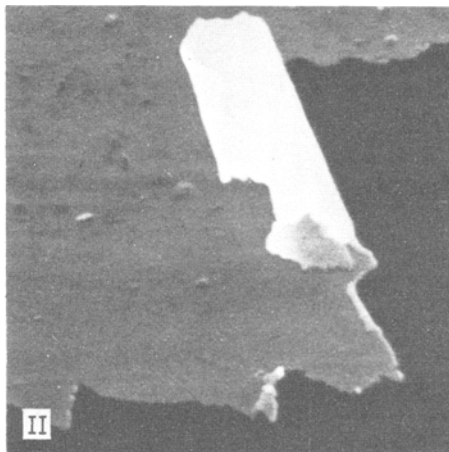

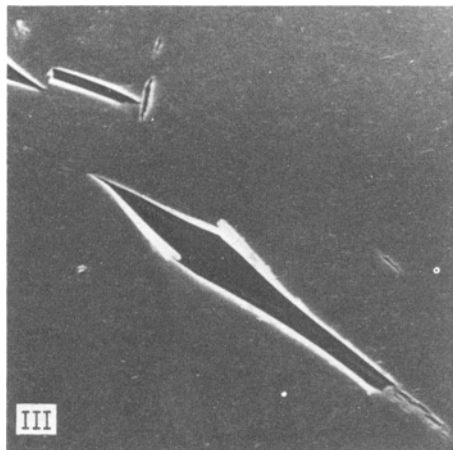Fig. 4.II. Aluminium . $LiClO_4$ (0·5 M) in ethanol; $U_a = 5$ V. $\times$ 3000

Fig. 4.III. Aluminium . $LiClO_4$ (0·5 M) in ethanol; $U_a = 15$ V. $\times$ 375
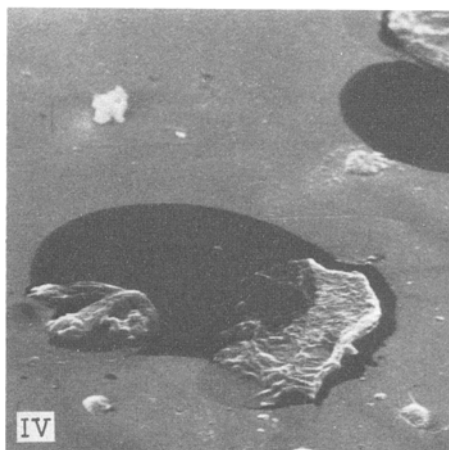

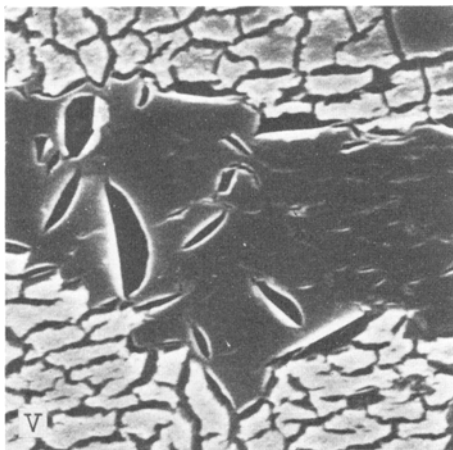Fig. 4. IV. $LiClO_4$ (0·5 M) in ethanol; $U_a = 10$ V. $\times$ 1100

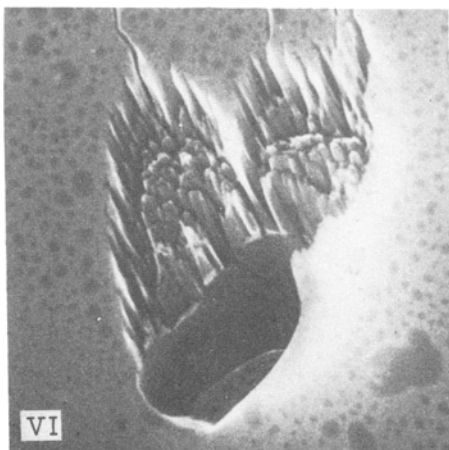Fig. 4.V. Aluminium . $LiClO_4$ (0·5 M) in ethanol; $U_a = 2$ V. $\times$ 750

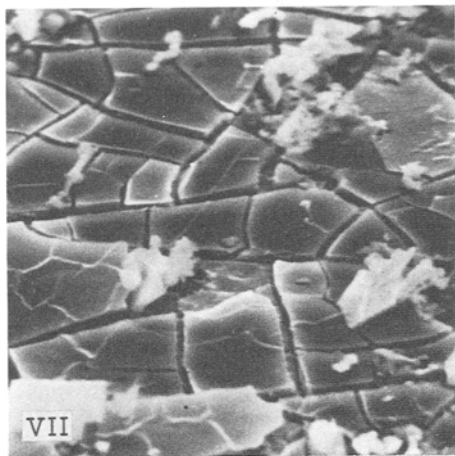Fig. 4.VI. Beryllium . $LiClO_4$ (0·5 M) in ethanol; $U_a = 20$ V. $\times$ 4500

Fig. 4.VII. Aluminium . Na_2CO_3 (0·5 M) in ethanol; U_a = 50 V. × 450
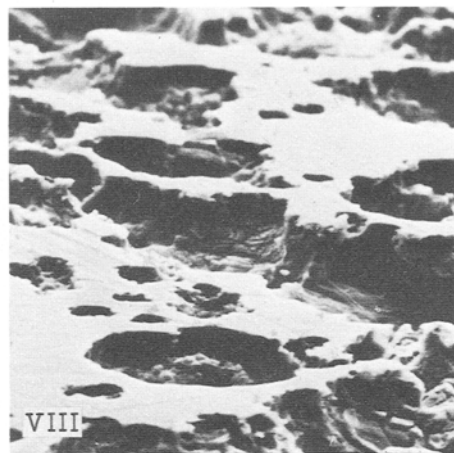

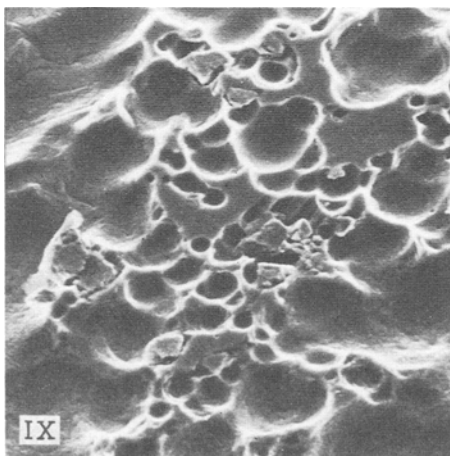Fig. 4.VIII. Aluminium . LiCl (0·5 M) in ethanol; U_a = 10 V. × 375

Fig. 4.IX. Aluminium . KSCN (0·5 M) in ethanol; U_a = 6 V. × 375

I–IV). It can be seen clearly from the photograph that the granulation is part of the thin membrane which covers the electrode during dissolution. The metal underneath this layer (on the right in the second micrograph) does not show the same irregularity. When the anodic potential decreases, areas with very close cracks distributed at random appear on the sides of the polished areas (Fig. 4; V). At this point the dissolution becomes very irregular, and finally leads to the metal breaking up (chunk effect). Part of the metal dissolves without either chemical or electrochemical reactions taking place. A detailed description of the diminution of Ne due to this mechanism was given in a previous publication [7]. The division of the surface into areas, subject to different conditions of anodic dissol-

ution, confirms the fact, often observed, that the anodic potential actually available for the electrolytic dissolution of the metal is not uniform over the entire surface.

The consequences of the chunk effect begin to show themselves when the anodic potential decreases, in sparse regions, probably initiated by defects in the original surface. Along the current lines that penetrate as far as the bottom of the cracks that bear these defects, an ohmic drop appears which is more important, the narrower the crack. The anodic potential actually available at the bottom of the defects is therefore much lower than the average potential (U_a) imposed on the electrode. In these conditions the mode of dissolution is that produced by low potentials. This ex-

plains our difficulty in indicating a U_a value of potential below which the chunk effect intervenes in a general way on the surface. On the other hand we would like to point out that when the width of the cavity becomes larger because of dissolution, the ohmic drop decreases and at the bottom of the defects one can progressively obtain the conditions of electrolytic polishing. This leads to cavities with wells and bottoms that are smooth and flat like those in Fig. 4; VI which correspond to the dissolution of a beryllium anode.

The relative importance of these areas where the potential drops below a polishing threshold becomes more and more evident when the potential decreases. A regular diminution of Ne follows and the progressive development, observed on the surface, from a polished state to a corroded one. We also noted that the granulation, which can be clearly seen when the anodic potential is high, tends to disappear when the anodic potential decreases.

4.2. Solutions containing different anions dissolved in ethanol

We utilized the following anions, in anhydrous solutions.

Cl^- (solution 0·5 M of LiCl; 0·5 M of $AlCl_3$ and 0·5 M of KCl);

NO_3^- (solution 0·5 M of $LiNO_3$);

SCN^- (solution 0·5 M of KCSN);

I^- (solution 0·5 M of KI);

CO_3^{2-} (solution saturated in Na_2CO_3).

(a) Ne measurements. In Fig. 5 are shown the values obtained with the above solutions and the Ne curve $= f(U)$ which corresponds to the ClO_4^- ion. Firstly, it can be seen that all the solutions lead to a dissolution anomaly. Deviations from Faraday's law are however, obviously less important than that obtained with solutions containing ClO_4^- ions.

The substituting of Li^+ ions for K^+ or Al^{3+} ions, in chloride-containing solutions, leads to no perceptible changes in the apparent valency. The Ne value tends to increase slightly with anodic potential, with the exception of solutions containing NO_3^- ions.

(b) Curve $I = f(U_a)$. The $I = f(U_a)$ curves follow a noticeably linear course in the potential range utilized (Fig. 6, trend of curve 'a' with a

slope that varies according the the nature of salt dissolved) with the exception of the solution containing NO_3^- ions which shows a modification in the slope due to diffusion as in the case of the ClO_4^- ions (Fig. 5, curve 'b'). With regard to the chloride solutions, the line of curve $I = f(U_a)$ is similar to that obtained with aqueous solutions of NaCl at pH 2 [18].

A measurement of ohmic drop, by the current interruptor technique, allowed us to check that the electrode in anhydrous solutions of chloride behaved like an electrode which is not polarized (a vertical curve when U_a is corrected for ohmic drop).

(c) Observation of the surface. All our specimens showed a corroded appearance except those dissolved in solutions containing NO_3^- ions which presented relatively smooth and shining surfaces. Observation under a scanning microscope showed that the corroded surfaces had undergone strongly localized dissolution (pits and cracks; Fig. 4; VII–IX).

The surfaces with a polished appearance have a slightly granulated surface which is however different from that which we observed with aluminium polished in a perchlorate solution.

4.3. Solutions of different anions dissolved in methanol

4.3.1. The effects of the solvent on the anodic dissolution of aluminium in the presence of ClO_4^- ions.

The number of ions that can be introduced in great quantity into a solution of ethanol is quite small. To extend the field of the studies we have used another solvent, methanol, with which the same behaviour was observed if the dissolved salt were lithium perchlorate. Therefore, it can be reasonably assumed that a change of solvent does not upset the previous reaction path, in spite of the well known variations in the chemical reactivity of the ions in different solvents. The following organic solvents give very important anomalies, similar to those obtained with ethanol (Ne $\simeq$ 1·3): acetonitrile; propylene carbonate; dimethyl formamide (DMF); tetrahydrofuran (THF); methanol. With DMF and methanol the trend of the curve $I = f(U_a)$ is the same as that obtained with ethanol. However, the same does not apply to acetonitrile, propylene carbonate and THF. In Fig. 7 as an
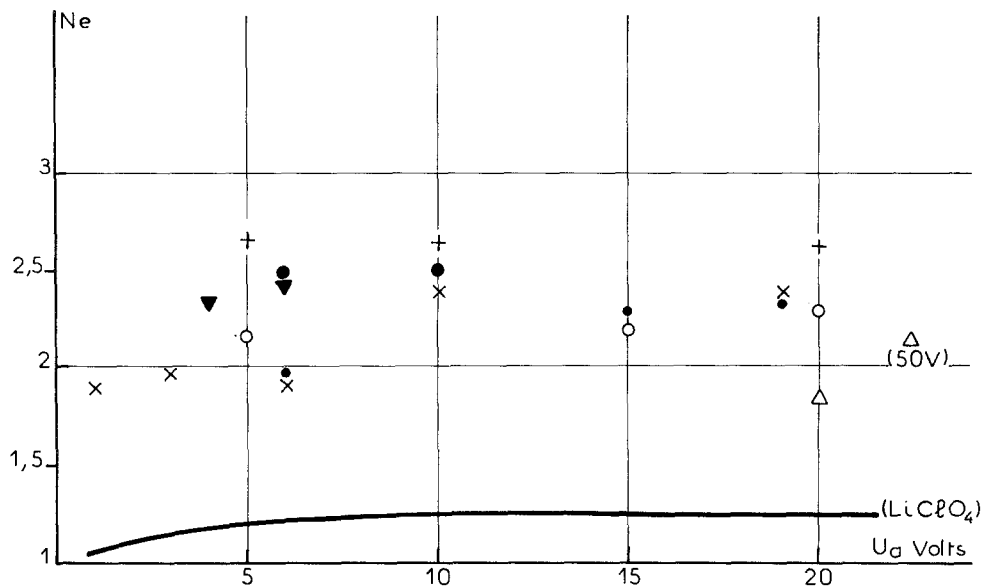
Fig. 5. Anodic dissolution of aluminium in solutions containing various anions [0·5 M] dissolved in ethanol. [H$_2$O] = 0·1 g l^{-1}; T = 25° C. × LiCl; • KCl; ○ AlCl$_3$; △ Na$_2$CO$_3$; ▼ KSCN; ● LiNO$_3$; + IK.
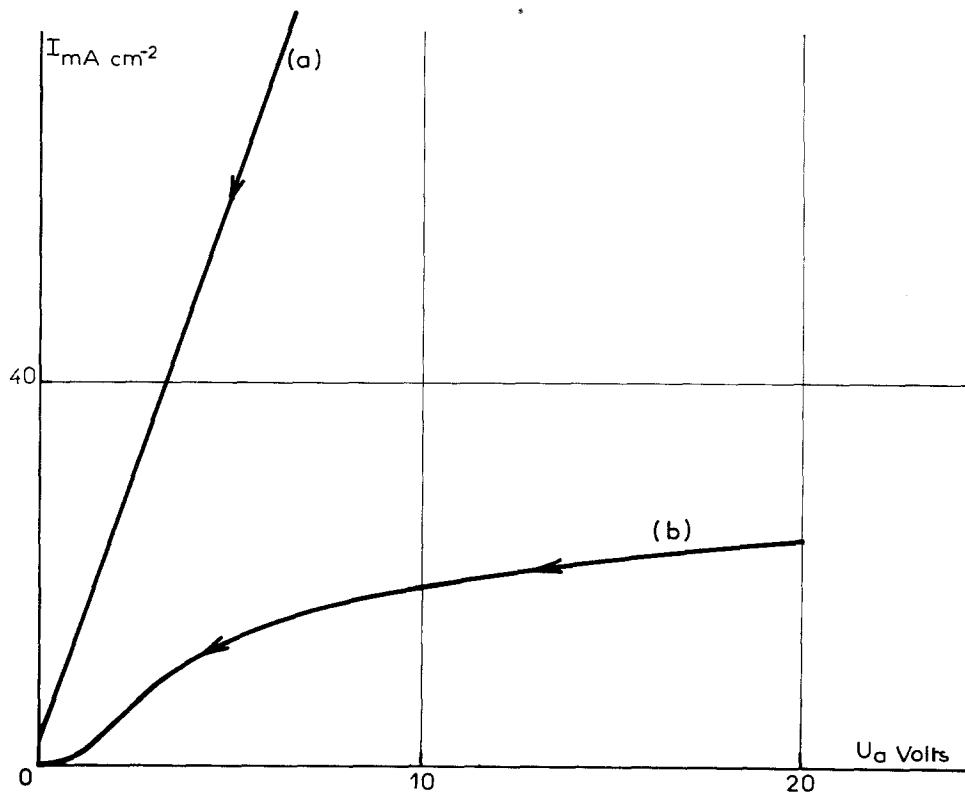

Fig. 6. Two types of current—anodic potential curves for the anodic dissolution of aluminium.

example, we have indicated the results obtained with THF (0·5 M LiClO₄ in solution).

By comparing curve $I = f(U_a)$ of Fig. 7 with corresponding curves obtained with ethanol (Fig. 3) it can be seen that low Ne values are not necessarily linked with a limitation of the anodic current by diffusion.

Following these results, the study of the anions was pursued substituting ethanol by methanol.

(a) Ne measurements (methanol solutions). The action of three new anions was studied:

$B_4O_7^{2-}$ (anhydrous solution saturated with $Li_2B_4O_7$);

With the SO_4^{2-} ions a straight line like that obtained with a solution of chloride in ethanol was observed.

(c) Observation of the surface. In all three cases the surface was corroded and dissolution developed beginning from the pits. In solutions containing BrO_3^- ions, dissolution progresses but a large part of the original surface is left intact. Some thin parts of the membrane, stripped off in the course of dissolution and washing, remain in the cavities. The whole appearance suggests that disintegration is taking place. With $B_4O_7^{2-}$ and SO_4^{2-} ions the surfaces present the same appearance although
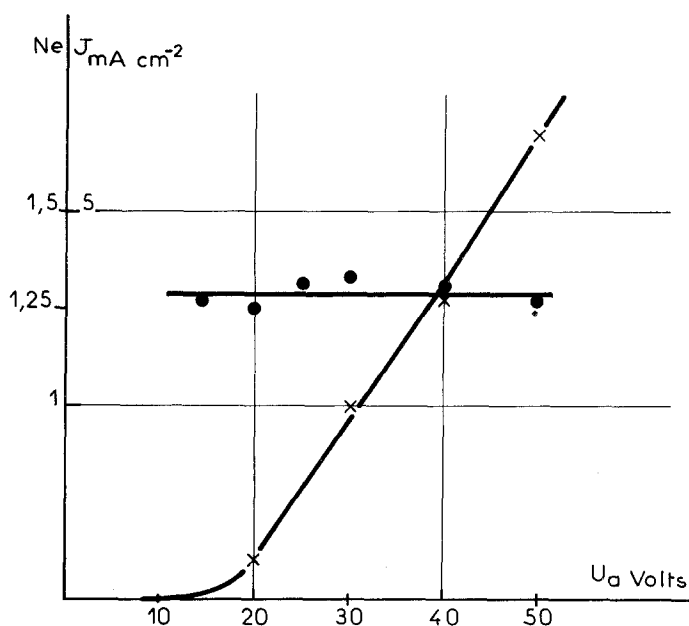

Fig. 7. Anodic dissolution of aluminium in a solution of LiClO₄ (0·5 M) in tetrahydrofuran (THF). Curves $I = f(U_a)$ and $Ne = f(U_a)$.

BrO_3^- (anhydrous solution saturated with LiBrO₃);

SO_4^{2-} (solution saturated with CuSO₄ [H₂O] ≃ 25 g l⁻¹).

In all three cases the results obtained for Ne are between the values 1·95 and 2·10. These results generalize our previous observations on ethanol.

(b) Curve $I = f(U_a)$. With the $B_4O_7^{2-}$ ions a thick uniform adherent layer forms which provokes a uniform lowering of current in the course of dissolution. In these conditions it is impossible to plot significant $I = f(U_a)$ curves. With the BrO_3^- ions a layer also forms but this is less noticeable. On carrying out a quick analysis we obtained an $I = f(U_a)$ curve which is more or less a straight line.

they seem to be covered in a spongy thicker layer.

The persistence of thin layers, resistant to washing, can result in slightly erroneous Ne values which would be higher than normal due to an excess weight of the anode after dissolution.

4.4. *Solutions containing a mixture of ClO_4^- and other ions*

The preceding results confirm the special role played by the ClO_4^- anions with regard to the dissolution anomaly. Following the interpretation described in the first part, this must be attributed to a specific disposition of the ClO_4^- to be absorbed close to the electrode and to form a particularly consistent layer. With this hypothesis, the large

dissolving anomaly, characterized by a Ne value around 1·3 must persist when other anions compete with the ClO_4^- ions to be absorbed on the anode.

In order to check this point we added some ClO_4^- anions to a solution previously studied.

4.5. Solutions of LiClO₄ (0·5 M) and LiCl (0·5 M) in ethanol

(a) Ne measurements. At high anodic potentials, we obtained the same values as those previously obtained with solutions containing only ClO_4^- (Fig. 8). The presence of Cl^- ions, despite their well-known aggressive action in dissolving metals, does not in any way disturb the total balance of the reaction.

In contrast with average anodic potentials where there is a decrease of Ne in the presence of ClO_4^- ions [minimum of the curve Ne = $f(U_a)$] we obtained an increase of this parameter. For low current densities the Ne value has exactly the same level as that obtained with solutions containing only Cl^- ions. At still lower current densities, the chunk effect becomes immediately important and leads to very low Ne values, particularly in the case of Cl^- ions.

(b) Curve $I = f(U_a)$. The line of the curve that we observed with only Cl^- ions (Fig. 6, curve a) was not altered in any noticeable way by the addition of ClO_4^- ions. However, it was difficult to determine the ohmic drop by the current interruptor technique, because with anhydrous solutions containing ClO_4^- ions a break in the current no longer leads to such a rapid drop in potential as that obtained with solutions containing Cl^- ions.

(c) Observation of the surface. At high anodic potentials we found the same appearance as that obtained with solutions containing only ClO_4^- ions. With low potentials dissolution takes place locally beginning and growing from pits, as for solutions containing only Cl^- ions. Some parts of the original surface were found to be left intact in both cases. The chunk effect exists but it is seldom found. The surface is not affected in a uniform way by dissolution as it was with the solution containing only ClO_4^- ions. For this zone of potentials we agree with the conclusions of Kinoshita et al. [17] who state that: 'With the electrolyte containing a high concentration of Cl^- ions, nothing can modify the aggressive nature of such an electrolyte [17]'. But this statement is no longer valid when the anodic potential is made sufficiently high; we can say that, when the anodic potential increases, there is a change from a typical surface condition corresponding to dissolution which has
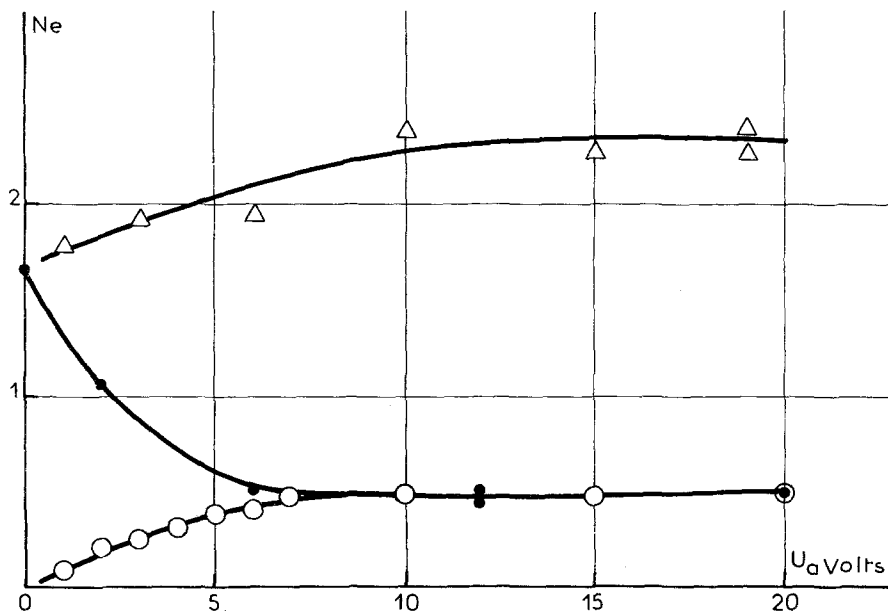

Fig. 8. Anodic dissolution of aluminium in 0·5 M solutions in ethanol: △ LiCl; ○ LiClO₄; ● mixture LiCl/LiClO₄. Curves Ne = $f(U_a)$.

taken place in the presence of only Cl^- ions, to a surface condition that is typical of a dissolution brought about by ClO_4^- ions alone.

4.6. Solution of $LiNO_3$–$LiClO_4$ in ethanol

After adding ClO_4^- ions to an anhydrous solution, 0·5 M of $LiNO_3$, we found with high anodic potentials a Ne value $\simeq 1·25$ which is characteristic of anhydrous solutions of perchlorate. But as with the chlorides, for potentials below 5 V, the Ne value increases rapidly when the anodic potential is lowered.

4.7. Solution of $Li_2B_4O_7$–$LiClO_4$ in methanol

We have pointed out earlier that aluminium, polarized anodically in a solution of $Li_2B_4O_7$ in methanol, acquires an adherent layer which increases regularly in thickness in the course of dissolution.

In order to establish in a more precise way the role that ClO_4^- ions play in the dissolving mechanism, we added ClO_4^- ions to a solution which originally contained only $B_4O_7^{2-}$ ions and in which we dissolved an electrode covered in a thick layer formed by passing a high quantity of electricity $(50\ C\ cm^{-2})$ over it. We noticed that by adding a quantity of ClO_4^- ions, equal to a concentration of $8\ g\ l^{-1}$, we could make the layer covering the anode disappear in a few seconds and the current increase; at the same time a polished surface was obtained and the Ne measurements in the new solution resulted in values similar to those observed with a solution containing only perchlorate.

5. Discussion

This study has shown first that the anodic dissolution of aluminium in an anhydrous medium always leads to important anomalies of valence. The strong dissolution anomaly exhibited by ClO_4^- ions in an anhydrous medium indicates the contrast between ClO_4^- and other anions in this respect. However, this ion loses its privileged position when a sufficient quantity of water is added to the solution (Ne $\simeq 2$ for H_2O concentration $100\ g\ l^{-1}$). It is difficult to establish whether this result is due to the small size of the water molecules or to their greater capacity for polarization; in comparison organic molecules encourage surface adsorption

[19] and are more difficult to eliminate later. The SCN^-, NO_3^-, I^- ions may be classified in relation to the importance of the anomaly they cause and in the order provided in the table describing the theoretical development in Section 2. The oxidizing character of the NO_3^- ion does not alter this classification. The Cl^- ions whatever the nature of the associated cations (Li^+, Na^+, Al^{3+}) produce on the other hand a more pronounced anomaly than expected. The important particular adsorption (not electrostatic) of the Cl^- ions could explain these Ne values which are slightly lower than those observed with the SCN^-, NO_3^- and I^- ions.

This study also allows us to define the role played by the anodic potential in forming the layer which is responsible for the dissolution anomaly and the smoothing action. Above all we were able to check that a relatively high threshold potential must be exceeded so that the Ne value reaches a stable value corresponding to a limited structuralization of the anodic layer. This threshold is the same for the chloride, percholate solution and for a Cl^-/ClO_4^- ($U_a = 10\ V$) mixture. In the case of solutions containing a Cl^-/ClO_4^- mixture Cl^- ions do not appear in great quantities in the anodic layer except at anodic potentials below 10 V. This agrees with the fact that the particular order effect imposed by the electrostatic field in the anodic layer, acts above all on the non-solvated anions like ClO_4^- which do not need to eliminate a part of their solvent molecules in order to approach the electrode surface. On the other hand, the experiments carried out supplied information on the role played in the dissolution mechanism by the layer covering the metal before its introduction into the electrolyte. In fact, we were able to see that the ClO_4^- ions can impose their particular way of dissolving (Ne $\simeq 1·3$, a strong current density, electropolishing) independently of whether or not other anions are present or whether the electrode is covered by layers of different types.

The characteristic layer which forms in the presence of ClO_4^- ions does so regardless of the existence of other layers. This is true for the layers formed by electrolytes in the absence of ClO_4^- ions and also for the oxide layer produced by atmospheric oxidation. We always found that dissolution took place in the same way after a short transition period. We may therefore consider that at high anodic potentials, the layer disappears very

quickly and in no way interferes with the mechanism which brings about the dissolution anomaly.

Finally, we wish to point out that by adding ClO_4^- ions to solutions causing damage to the aluminium following pitting corrosion, we can prevent this damage from becoming worse. It is also noticed that solutions containing ClO_4^- anions may be of interest in electrochemical machining because of their great Faradaic efficiency (230%) and their smoothing action.

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