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Medium effect on electrochemical behaviour of anodized aluminium

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The effect of some anions on the growth of the oxide film on aluminium was studied in acid and neutral media, as well as the effect of pH in presence of the same anion. In all the cases studied an inner barrier layer is formed adjacent to the metal and is covered on top with a porous layer. This latter outer layer differentiates into two regions, the one adjacent to the solution being characterized by a more open structure and a higher degree of anion incorporation as compared to the region embedded between it and the inner barrier layer. The rate of dissolution of the barrier layer is not affected by pH or anion type prevailing in the formation medium, since this layer is formed of pure alumina. The dissolution of the outer porous layer, on the other hand, is affected by both pH and anion type.

1. Introduction

The study of the properties of anodic oxide films on aluminium are of great importance in view of their increasing technological applications. Porous type films form on aluminium in electrolytes in which the oxide film is slightly soluble. These films are generally duplex in nature; a thin inner barrier layer is covered by an outer relatively thick porous layer. The ratio of the thicknesses of these layers were shown to depend on the nature of the forming electrolyte [1]. Porous type films do not form only in acid media; a recent study indicated that the anodization of aluminium in neutral oxalate solution produces also porous type films [2]. The outer layer has been shown to incorporate species from the anodizing electrolyte or their dissociation products [3].

The present study deals with the effect of the formation medium on the subsequent electrochemical behaviour of anodic oxide films on aluminium under open circuit conditions in H_3PO_4. The presence of a number of anions in the formation medium at different pH values, and the variation of pH in presence of the same anion were studied in relation to their effect on the observed behaviour of the film during its spontaneous dissolution in H_3PO_4.

2. Experimental procedure

The electrical circuit, cell and method were the same as used previously [4]. The electrode was cut from a rod of high purity Al (99.999%). It was fixed in a glass tube with an adhesive resin so that a cross section area of 0.196 cm^2 was in contact with the test solution. It was mechanically polished by finer grades of metallurgical papers, the final brightening being made by rubbing with fine tissue paper. All solution were prepared from A.R. reagents and triply distilled water. The electrode was washed with triply distilled water before being immersed in the specified solution for anodization. Oxide film growth and dissolution experiments were carried out at $27 \pm 0.5\,^{\circ}C$ without deaeration or stirring of solutions.

The oxide growth was affected galvanostatically using a stabilized constant current electronic device. All potentials were recorded against a saturated calomel electrode (SCE), using a valve voltameter. The amplitude of the a.c. signal in the bridge was 10 mV. The measured series capacitance, C_m, and resistance, R_m, of the impedance of the aluminium electrode were traced at 1 kHz. The oxide growth was affected in a number of acid and neutral media, the dissolution medium was always 0.1 N H_3PO_4.

3. Results

Anodic oxide films were grown on aluminium by the galvanostatic technique at a constant field of $7\,mA\,cm^{-2}$ in 0.1 N solutions of H_2SO_4, H_3PO_4 or $(COOH)_2$. The experimental results are shown in Fig. 1. In all cases there is an initial induction period during which there is no apparent increase in the cell voltage. The duration of this period depends apparently on the type of anion present in the electrolytic solution. At the end of the induction period the forming voltage was found to rise at a constant rate until it eventually reached the breakdown voltage.

Fig. 1 shows that the breakdown voltage depends on the anion and not upon the acidity of the solution. Readings for malonic acid, not shown in the figure, ran very close and above those for phosphoric acid. At different time intervals, dV/dt decreases and is then followed by appearance of a horizontal line. At this point the current is concentrated in repairing cracks in the oxide film. The results show that breakdown, associated with crystallization of the amorphous anodic oxide film [5] occurs after a short polarization interval and at a much lower voltage in H_2SO_4 as compared to H_3PO_4 and $(COOH)_2$.

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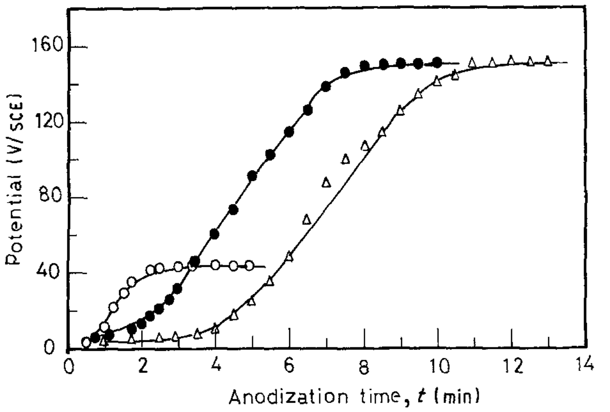

Figure 1 Charging curves for aluminium in different acids: (○) 0.1 N H_2SO_4, (●) 0.1 N H_3PO_4, and (△) 0.1 N $(COOH)_2$.

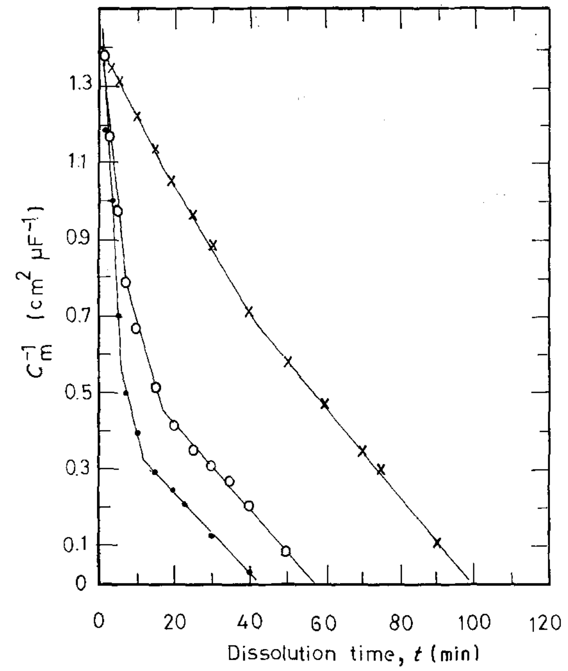

Figure 2 Dependence of the rate of dissolution ($-dC_m^{-1}/dt$) on the pH of the formation medium: (×) 01. M H_3PO_4, (○) 0.1 M NaH_2PO_4 and (●) 0.1 M Na_2HPO_4.

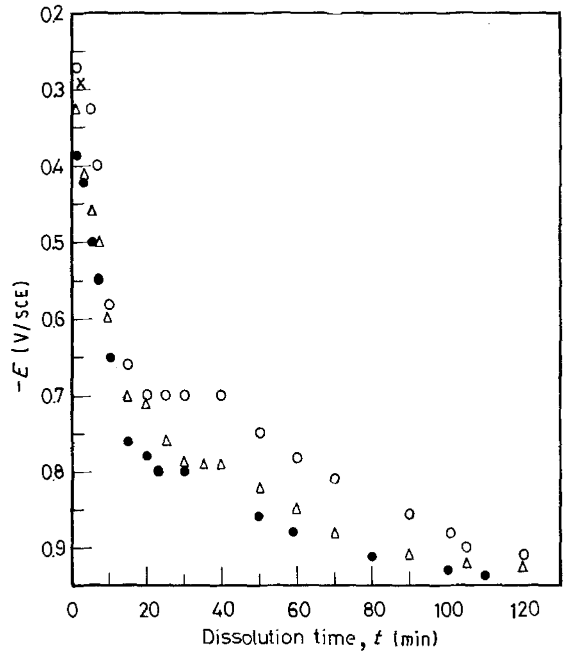

Figure 3 Variation of open circuit potential (E) with time (t) for the aluminium electrode anodized in solution of different pH values: (○) 0.1 M H_3PO_4, (△) 0.1 M NaH_2PO_4 and (○) 0.1 M Na_2HPO_4.

To compare the effect of pH of the formation medium (FM) on the dissolution behaviour of the anodic film on aluminium, the electrode was anodized at a current density (c.d.) of 7 mA cm^{-2} up to 40 V in 0.1 N phosphate solutions of varying pH. The electrode was transferred to the dissolution medium (DM) which was 0.1 N H_3PO_4. The open circuit behaviour of the oxide covered electrode was examined as a function of time.

Fig. 2 shows the variation of C_m^{-1} with time. C_m^{-1} is a relative measure of oxide thickness [6]. Thus, the decrease in C_m^{-1} indicates oxide thinning. The relation in Fig. 2 represents a zero order process, observed in previous cases [7, 8], and may be represented by the equation

$$-\frac{dC_m^{-1}}{dt} = k$$

where C_m is the capacitance in $\mu F\,cm^{-2}$ at time t, $-(dC_m^{-1}/dt)$ is the rate of dissolution and k the dissolution constant, $cm^2\ \mu F^{-1}\ min^{-1}$.

Each linear relation is formed of three segments. There is a marked difference in the slopes of the first two segments in each relation. However, the third segment possesses nearly the same slope, independent of the formation medium.

Fig. 3 represents the tendency of the anodized electrode, under open circuit conditions, towards more negative potentials which is associated with oxide dissolution. The figure shows some inflections which do not occur exactly at the same time intervals as in Fig. 2. After the first inflection, a plateau zone appears during which there is no appreciable change in potential, followed by a second inflection. The rate of decrease in potential with time is observed to be lower after the second inflection. The results in Figs 2 and 3 indicate that the pH of the formation medium affects the dissolution behaviour of the oxide.

To study the effect of the presence of different anions during the anodization of aluminium on its dissolution behaviour, the electrode covered by an oxide formed under conditions described in Fig. 1 up to 20 V was transferred to the dissolution cell containing 0.1 N H_3PO_4. The impedance of the electrode was followed with time. Fig. 4 shows the C_m^{-1} – time linear relations, formed of three segments and representing the dissolution of the oxide formed in different acids. It is clear that the anion present in the formation medium is important in determining the subsequent dissolution behaviour of the anodic oxide formed. For example, a clear difference in the rate of dissolution of the oxide formed in H_2SO_4 and H_3PO_4 is observed. The oxide formed in malonic acid possesses a dissolution behaviour which is very close to that of the oxide formed in H_3PO_4, in spite of the expected pH difference. This indicates, in addition to results shown in Fig. 2, that both pH and type of the anion prevailing

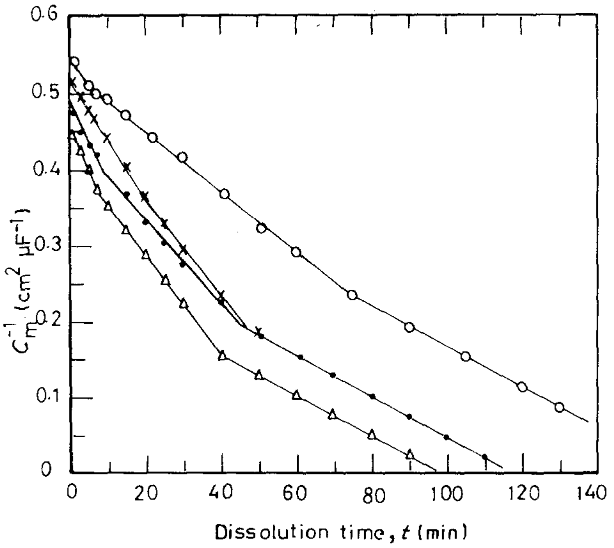

Figure 4 Dependence of the rate of dissolution ($-dC_m^{-1}/dt$) on the acid formation medium: (○) 0.1 N H_2SO_4, (×) 0.1 N H_3PO_4, (●) 0.1 N $CH_2(COOH)_2$ and (△) 0.1 N $(CH_2)_2(COOH)_2$.

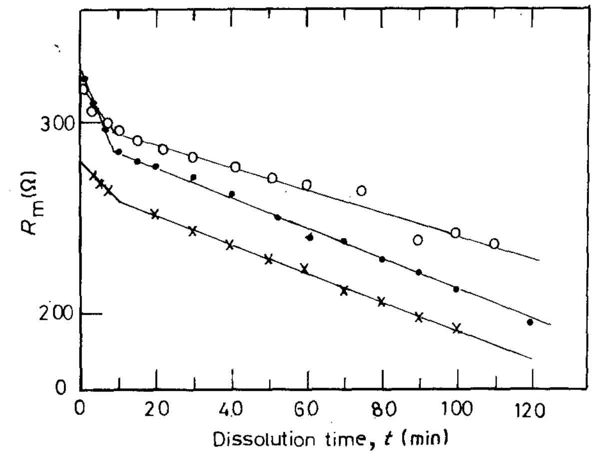

Figure 5 Variation of the resistance of the anodized aluminium electrode (R_m) with time (t) for the different acid formation media: (○) 0.1 N H_2SO_4, (●) 0.1 N $CH_2(COOH)_2$ and (×) 0.1 N H_3PO_4.

in the formation medium affect the dissolution behaviour of the formed oxide.

A simultaneous decrease in resistance with time was observed, Fig. 5. However, since R_m is a less sensitive index of oxide dissolution than C_m^{-1}, the variation of R_m with time was not as well defined as C_m^{-1}.

The effect of anions present in more or less neutral formation media was also studied. Fig. 6 shows the decrease in C_m^{-1} with time, hence the dissolution of the oxide formed in presence of CrO_4^{2-}, $Cr_2O_7^{2-}$, $Fe(FeCN)_6^{3-}$ and CO_3^{2-} up to 40 V at 7 mA cm^{-2}. The dissolution medium was 0.1 N H_3PO_4. The clearest difference in slope was that observed for the first segments in the relations. Similar slopes of the second segment were observed for CrO_4^{2-} and $Cr_2O_7^{2-}$ anions. However, the third segment apparently possesses the same slope, indicating a nearly constant rate of dissolution.

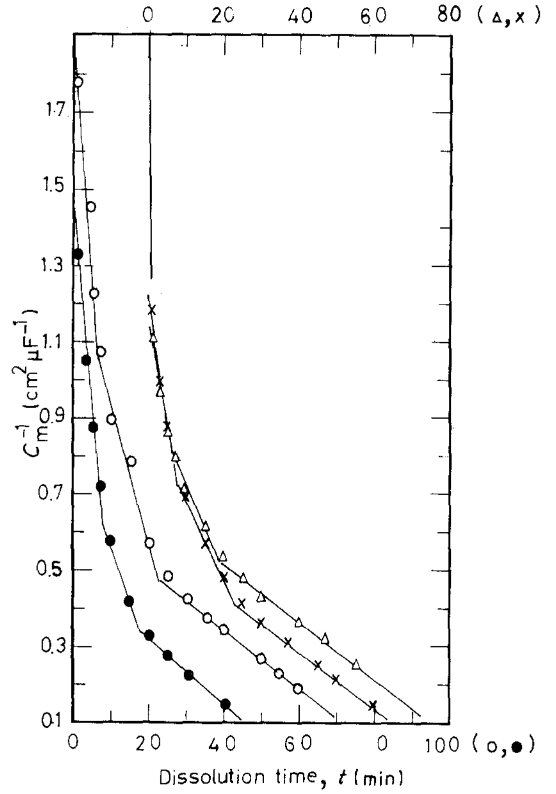

Figure 6 Dependence of the rate of dissolution ($-dC_m^{-1}/dt$) on the anion present in the anodization medium: (△) 0.1 N K_2CrO_4, (×) 0.1 N $K_2Cr_2O_7$, (○) 0.1 N $K_3Fe(FeCN)_6$ and (●) 0.1 N K_2CO_3.

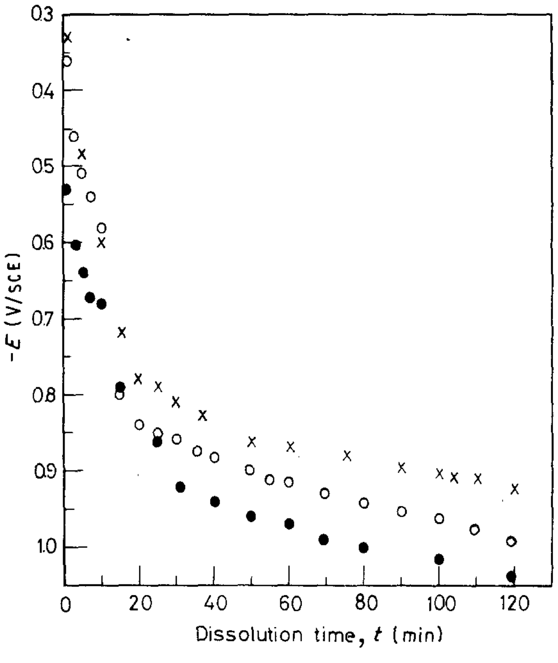

Figure 7 Variation of the open circuit potential (E) with time (t) for the aluminium electrode anodized in presence of different anions: (×) 0.1 N $K_2Cr_2O_7$, (○) 0.1 N $K_3Fe(FeCN)_6$ and (●) 0.1 N K_2CO_3.

A decrease in resistance was observed during the dissolution of the oxide as in Fig. 5. The open circuit potential also tended towards more negative values with time, Fig. 7. The figure shows a sharp decrease in E with time, followed by a slower decrease which is consistent with the results in Fig. 6.

4. Discussion

The formation of porous anodic films on aluminium in H_2SO_4, H_3PO_4 and $(COOH)_2$ has been established; the film being formed of a thin compact inner barrier layer and a thicker porous outer layer [1]. The barrier layer is formed of pure alumina while the porous layer incorporates acid anions. The inner barrier layer of the film was shown to crystallize more rapidly than the outer layer [9], thus the polarization behaviour shown in Fig. 1 is mainly controlled by the growth of the inner barrier layer. This was also observed in case of oxide growth in neutral boric-borate solutions [10].

The formation of the oxide film is more or less accompanied by its dissolution [10]. The dissolution would be dependent on the local interfacial pH. In the present case, and at low pH, the breakdown occurs when the film attains a limiting thickness, and hence, the internal compressive stresses lead to film cracking. The internal compressive stresses arise when a new oxide is formed [11]. Breakdown is associated with type and degree of contamination with the anion [12]. After reaching the breakdown voltage, the oxide continues to thicken. Since breakdown is associated with crystallization of the amorphous anodic oxide [5], the increase in oxide thickness after breakdown is essentially in the porous layer. This occurs by a deposition process of Al^{3+} ions ejected at the film solution interface by ionic migration [13].

The decrease in dV/dt, i.e. breakdown, occurs under the same anodizing conditions in the sequence H_2SO_4, $(COOH)_2$ then H_3PO_4. This is the same order of the relative thicknesses: barrier to porous layers, which increase $H_2SO_4 > (COOH)_2 > H_3PO_4$ [1]. The results indicate that the films formed in H_3PO_4 would possess a relatively thicker inner barrier layer.

The results in Fig. 2 show that the pH of the formation medium affects the dissolution behaviour of anodized aluminium in H_3PO_4. The inner barrier layer of the oxide was shown to be formed of pure alumina while phosphate ions are incorporated within the porous layer [13]. The relative thicknesses of porous to barrier layers was reported to be 2:1 in phosphate medium [1, 13]. Using secondary ion mass spectrometry, it has been shown that the oxide grown on aluminium in phosphate solutions contained a maximum yield of phosphate secondary ions in the outermost layer, followed by a lower relatively constant yield over the second layer and a zero yield at the layer adjacent to the metal [14].

The three segments appearing in each of the relations in Fig. 2 point to a triple layer model for the oxide. The outermost layer possesses the highest rate of dissolution (k_1) due to a higher degree of acid anion incorporation, followed by a second layer of lower contamination and hence, a lower rate of dissolution (k'_1) (Table I). Both layers form jointly the outer porous layer and $\bar{k}_1$ represents their average rate of dissolution. The third layer, which is the inner barrier layer, possesses the lowest rate of dissolution (k_2) because of the compactness of its structure and due to absence of anion incorporation [9, 14, 15]. There is evidence in the literature to support the triple model in aluminium anodizing in malonic acid [16], as well as in oxalic acid [15] and oxalate solutions [9]. The outer two thirds of the oxide formed in oxalate contained the ions or their dissociation products, and was differentiated into two zones depending on the degree of incorporation [9, 15].

TABLE I Dissolution rate constants ($cm^2\ \mu F^{-1}\ min^{-1}$) of the anodic oxide film formed on aluminium in solutions of different pH values. (c.d. 7 $mA\ cm^{-2}$, FV 40 V)

pH	$k_1 \times 10^2$	$k'_1 \times 10^2$	$\bar{k}_1 \times 10^2$	$k_2 \times 10^2$
0.1 M H_3PO_4	1.86	1.67	1.75	1.20
0.1 M NaH_2PO_4	8.90	3.20	6.84	1.10
0.1 M Na_2HPO_4	15.0	3.33	12.6	1.06

The plateau zones, which appear in the potential relations in Fig. 3, were observed before in open circuit potential studies of the anodic oxide films on tungsten in acidic chloride solutions [19]. The duration of the plateau was a function of the applied voltage and acid dilution. Most of the dissolution is considered to occur during this plateau zone. It is apparent that the pH also affects the duration of this zone; it lasts longer at lower pH.

The results show that the formation medium has an effect on the structure of the oxide film. The lower rates of dissolution of each layer with decreasing pH may be due to a lower degree of anion incorporation, as a result of proton entry during oxide formation [18]. Possibly the incorporation modifies the compressive stresses and the degree of crystallinity [11], so that the higher degree of dissolution is observed for films formed at higher pH values. The rate of dissolution of the inner barrier layer, k_2, is apparently the same irrespective of the formation medium. This indicates that the structure of this layer is not affected by pH of the formation medium.

The present results also indicate that the inner barrier layer is completely free of phosphate anions or its dissociation products, as observed in a previous case [19]. The outer porous layer, which is of a cellular structure, shows anion incorporation within the intercellular regions, as evidenced by the high rate of dissolution of this layer. It has been reported that the thin barrier layer is covered by a thicker layer with a controllable regular pore structure [20]. This layer mechanically protects the barrier layer. When the outer porous layer dissolves completely, the dissolution of the barrier layer starts, as shown in Fig. 2 (second inflection). According to Hoar and Mott [21], the formation of the porous layer occurs by ion migration of Al^{3+} outward and OH^- inwards through the oxide. The pores in the outer layer taper inwards [20] so that the incorporation of anions decreases also in going inwards, due to the decrease in the rate of anion diffusion. Since the OH^- ions are responsible for porous layer growth, the increase of its concentration is reflected in the formation of a relatively thicker porous layer, as evidenced from Fig. 2. Taking C_m^{-1} at zero time as relative total oxide thickness, and that at the second inflection the relative barrier layer thickness, it is evident that the difference between both increases with pH.

Fig. 4 shows that the dissolution behaviour of anodized aluminium is also affected by anion type as well as pH of the formation medium. The effect is mainly in the outer porous layer which also differentiates into a high anion incorporation region adjacent to the solution and a low anion incorporation region lying between it and the inner barrier layer. This is clear from the dependence of the rates of dissolution of the first region k_1, and the second region k'_1, as well as their average $\bar{k}_1$, on the formation medium. On the other hand, the rate of dissolution of the barrier layer k_2, is nearly constant (Table II). The clear variation in k'_1 reflects the degree of openness of this layer. The values of k_1 are higher since this outermost region in contact with the electrolyte is expected also to be more hydrated [22]. It was observed that k_1 increases with increase of pH of the formation media (Tables I and II).

During anodic polarization a very thin oxyhydroxide film AlOOH is formed that changes to the oxide Al_2O_3 during polarization [23]. This would dissolve in acid medium according to

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + H_2O$$

The anodization of aluminium actually produces Al_2O_3 [10, 24], with a probability of trapping some bound water [24].

In near neutral solutions, as shown in Fig. 6, there is a pronounced effect of the anion of the formation medium. This may be also inferred from Table III. The formation of anodic films on aluminium in chromic acid produces a relatively pure alumina layer [1]. In the presence of chromate salts the formation of a porous layer is enhanced probably by facilitating the inward migration of OH^-. It is known that chromate and phosphate inhibitors tend to penetrate the alumina film material, probably at intercrystalline sites, and slowly dissolve it [13, 14]. This may explain the results in Fig. 6, which show that the outer porous layer grows to higher thicknesses in $KFe(FeCN)_6$ and K_2CO_3. k_1, k'_1 and $\bar{k}_1$ are higher than in case of K_2CrO_4 and $K_2Cr_2O_7$, which reflects a lower degree of anion incorporation in chromate salts. The rates of dissolution are similar in both chromium containing salts. However, there is a small increase in the thickness of the outer porous layer for films formed in $K_2Cr_2O_7$ which may be attributed to the large size of incorporated $Cr_2O_7^{2-}$ anions as compared to the less bulky CrO_4^{2-} anions.

In all cases the rate of dissolution of the barrier layer is not affected by the anions of the formation medium. The structure of both layers is expected to be Al_2O_3, since no $Al(OH)_3$ precipitation occurs, due to formation of the soluble complexes of aluminium [10].

TABLE II Dissolution rate constants ($cm^2 \mu F^{-1} min^{-1}$) of the anodic oxide film formed on aluminium in different acids. (c.d. 7 mA cm^{-2}, FV 20 V)

0.1 N acid	$k_1 \times 10^3$	$k'_1 \times 10^3$	$\bar{k}_1 \times 10^3$	$k_2 \times 10^3$
H_2SO_4	5.63	3.89	4.10	2.69
H_3PO_4	8.14	6.52	7.26	2.75
$CH_2(COOH)_2$	10.1	5.56	6.79	2.75
$(CH_2)_2(COOH)_2$	12.0	6.50	7.85	2.64

TABLE III Dissolution rate constants ($cm^2 \mu F^{-1} min^{-1}$) of the anodic oxide film formed on aluminium in presence of different anions. (c.d. 7 mA cm^{-2}, FV 40V)

0.1 N salt	$k_1 \times 10^2$	$k'_1 \times 10^2$	$k_1 \times 10^2$	$k_2 \times 10^3$
K_2CrO_4	5.50	2.26	4.09	7.57
$K_2Cr_2O_7$	6.19	2.13	4.56	7.33
$K_3Fe(FeCN)_6$	13.8	3.85	9.26	8.00
K_2CO_3	10.6	2.82	8.60	8.50

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