JOURNAL OF APPLIED ELECTROCHEMISTRY 17 (1987) 104–112

Comparative study of the potentiodynamic behaviour of aluminium at low potentials in barrier layer and in pore-forming electrolytes

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Received 7 March 1986

The potentiodynamic behaviour of a 99.9995% aluminium electrode in several barrier layer and pore-forming electrolytes at a temperature of 25° C, with sweep rates in the range 1–200 mV s^{-1} and potentials between -2.00 and 3.00 V (versus SCE), has been studied. In the anodic sweep the potential of zero current, $V_{j=0}$, depends on the pH of the electrolyte and corresponds to a corrosion potential (the cathodic and anodic reactions coexist). In the 0.5 M H_3BO_3–borax solution (pH = 6.3) and after $V_{j=0}$, the current density increases in a convex form, approaching a steady-state value. For this electrolyte and the potential ranges studied, the anodic charges corresponding to the anodic sweep are independent of the sweep rate and are associated with the formation of a barrier layer oxide. In the neutral 0.50 M propanedioic acid solution (pH = 7.0) and the potential ranges studied, the anodic charges are much greater than those corresponding to the H_3BO_3–borax solution, and metal corrosion combined with a solvent effect of the electrolyte is found. The greatest anodic charges are found for the H_2SO_4 solution (pH = 1.0); the anodic current increases rapidly in the potential ranges studied due to pore initiation. The cathodic and anodic behaviour of aluminium depend strongly on the electrolyte employed, basically through the effect of the electrolyte on the oxide film and through the pH of the solution.

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1. Introduction

In the extensive literature on the electrochemical behaviour of aluminium, work based on the potentiodynamic methods is not abundant. However, the method of constant rate of voltage increase (CRVI) is, according to Dignam [1], convenient and useful in the study of ionic currents in oxide films on aluminium. As shown by Dunn in further work [2], the CRVI method is a valuable tool in obtaining information about the nature of porous oxide films and the effect of heat treatment on ionic conduction. This method has also been used to determine the critical pitting potential of aluminium [3, 4], the corrosion resistance of aluminium oxide films [5], the effect of different anions on the electrochemical behaviour of the metal [6] and to investigate the properties of oxide layers [1, 2, 5, 7]. However, few of these works study the initial stages of the oxide formation and its subsequent evolution in the low potential range [4, 6, 7].

In previous papers the study of the initial growth of an anodic oxide film on aluminium in H_2SO_4, propanedioic acid and H_3BO_3–borax solutions was reported [8, 9]. In this work, the effects of different barrier layer and pore-forming electrolytes on the growth of the oxide film on a high-purity aluminium electrode in the low potential range have been studied and compared. Provided that the metal is rapidly oxidized in air, a residual oxide film can be formed after a very short time of exposure of the bare metal to the air, particularly between polishing and transfer to the cell [4, 10, 11]. In order to start with an electrode with a minimum quantity of oxide on its surface, deoxygenated solutions were employed and a cathodic polarization at

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-2.00 V versus SCE in the cell itself was performed. This procedure was found to be useful in obtaining the potentiodynamic active dissolution region of aluminium in certain electrolytes [4, 11].

2. Experimental details

The experiments were carried out with an electrochemical cell (volume, 250 cm^3) previously described [9], in which the SCE, used as reference electrode, was kept in a separate compartment and connected via a Luggin capillary. All the potentials reported in this work are referred to the SCE. The counter electrode was a platinum mesh and the working electrode an aluminium rod, 99.9995% pure, with a cross-section of 0.713 cm^2.

The working solutions were a 0.5 M H_3BO_3–borax solution (pH 6.3), H_2SO_4 (pH 1.0) and a neutral 0.50 M propanedioic acid solution of pH 7.0. These electrolytes were prepared with deionized and doubly distilled water, Merck p.a. H_3BO_3, borax, H_2SO_4, NaOH and Carlo Erba RPE propanedioic acid. The solutions were deoxygenated by N_2 bubbling in and out of the cell itself. The working electrode was mechanically polished, chemically etched in 1.0 M NaOH at 60° C and, finally, mechanically polished up to a mirror finish. For the mechanical polishing, ethanol was employed in order to degrease and remove the smut, the electrode being finally washed in doubly distilled water. The instrumentation used has also been described elsewhere [8], save for the addition to the recorders of a mod. 731 AMEL integrator. In the cell the aluminium electrode was held at -2.00 V versus SCE with stirring until the maximum rate of H_2 evolution was reached: 15 min for the H_3BO_3–borax solution, 15 s in the H_2SO_4 and 5 min in the neutral 0.50 M propanedioic acid solution. Subsequently, the stirring was stopped and the potentiodynamic sweep started at this potential without switching off the cathodic current. The method of carrying out the potentiodynamic curves immediately after the -2.00 V polarization was first proposed by Rozenfel'd *et al.* [4] and was found very useful in obtaining information about the effect of the time of polarization at a high cathodic potential of aluminium oxide-covered electrodes [11]. The sweep rates applied were in the range 1 to 200 $mV\,s^{-1}$. The experiments were carried out at 25.0 ± 0.1° C and the potentiodynamic curves showed good reproducibility.

3. Results and discussion

3.1. *Cathodic region and the potential of zero current*

The experimental curves obtained for the pH = 6.3 H_3BO_3– borax aqueous solution are of the type shown in Fig. 1. The cathodic current approaches the zero value once the anodic sweep starts, the potential of zero current, $V_{j=0}$, being more cathodic when the sweep rate increases. At a sweep rate of 1 $mV\,s^{-1}$, $V_{j=0}$ is -1.210 V, and for 100 $mV\,s^{-1}$ is -1.510 V. From -2.00 V to $V_{j=0}$, the potentiodynamic curve exhibits a convex form. As indicated in Fig. 2, the same trend is found for H_2SO_4 (pH 1.0). However, $V_{j=0}$ is more anodic than that for the former electrolyte: at 5 $mV\,s^{-1}$ this potential is -1.070 V and at 100 $mV\,s^{-1}$ is -1.180 V. This result is not surprising because the potential of H_2 evolution depends on the pH of the solution, being less cathodic when the pH decreases [12]. On the other hand, a large H_2 overvoltage is observed in the potentiodynamic curves of Figs 1 and 2, because the reversible potential for the H_2 evolution is -0.61 V and -0.30 V versus SCE for solutions of pH 6.3 and 1.0, respectively. This indicates a H_2 overvoltage of about 0.55 V for the H_3BO_3–borax solution and of about 0.77 V for the H_2SO_4 (pH 1.0). These values are in agreement with those reported by Hickling and Salt [13], who found H_2 overvoltages on aluminium in the range 0.58–0.78 V by means of the galvanostatic technique. Because of the pH, the absolute value of the cathodic charge between -2.00 V and $V_{j=0}$ is greater for H_2SO_4 (pH 1.0) than in the case of the H_3BO_3–borax solution at pH 6.3 (cf. Table 1).

However, it is for the neutral 0.50 M propanedioic acid solution that the most cathodic values of $V_{j=0}$ were found (cf. Fig. 3). At 1 $mV\,s^{-1}$ this potential is -1.425 V and at 100 $mV\,s^{-1}$ is -1.685 V. This fact may be explained simply by considering the change of the potential

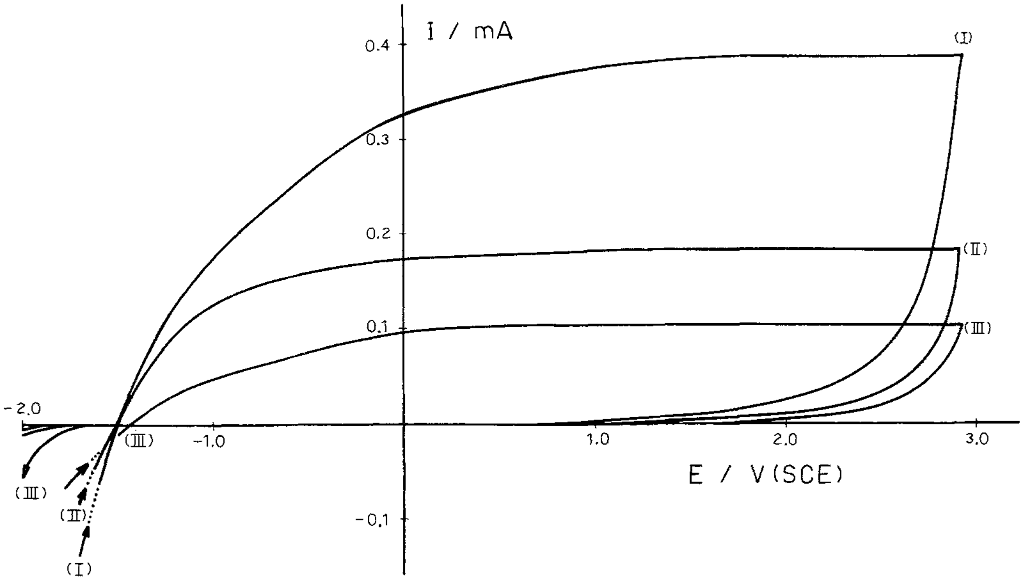

Fig. 1. Potentiodynamic curves corresponding to the 0.5 M H_3BO_3–borax solution (pH 6.3) at different sweep rates. The cycles start at −2.00 V (versus SCE), but the first part of the curves is not shown. (I) 200 mV s^{-1}; (II) 100 mV s^{-1}; (III) 50 mV s^{-1}.

corresponding to the H_2 evolution on aluminium as a function of the pH with a H_2 overvoltage of about 0.77 V (the reversible potential is −0.66 V versus SCE). However, the absolute values of the cathodic charges between −2.00 V and $V_{j=0}$ are much greater for this electrolyte than those for the H_3BO_3–borax solution at pH 6.3 (cf. Table 1). According to the values of these charges, the electrolyte must destroy the residual oxide film present on the electrode (formed by air exposure when transferring to the cell or in the working solution). On the other hand, comparing the cathodic charges given in Table 1 for the different electrolytes used, a local alkalization of the electrode seems to be implied.

The film-destroying effect of the neutral 0.50 M propanedioic acid is also supported by the experimental results obtained in a previous work [11], where the effect of a −2.00 V polarization in the same electrolyte was studied. The conclusion reached was that the aluminium could be substantially activated in this electrolyte (because of the oxide removal) and as a result the potentiodynamic curves obtained showed an active dissolution region at sweep rates equal or greater than 10 mV s^{-1} [11]. This is

Table 1. Cathodic charges (given in mC) between −2.00 V versus SCE and $V_{j=0}$ for the different electrolytes used, as a function of sweep rate, v

v ($mV s^{-1}$)	0.5 M H_3BO_3–borax (pH 6.3)	H_2SO_4 (pH 1.0)	$HOOC–CH_2–COOH$ + NaOH (pH 7.0)
2	−22.5		−410
5	−8.72	−225	−360
10	−4.25		−133
20		−110	−90
50	−1.17	−54	−35
100	−0.97	−26	−12.1
200	−0.53		

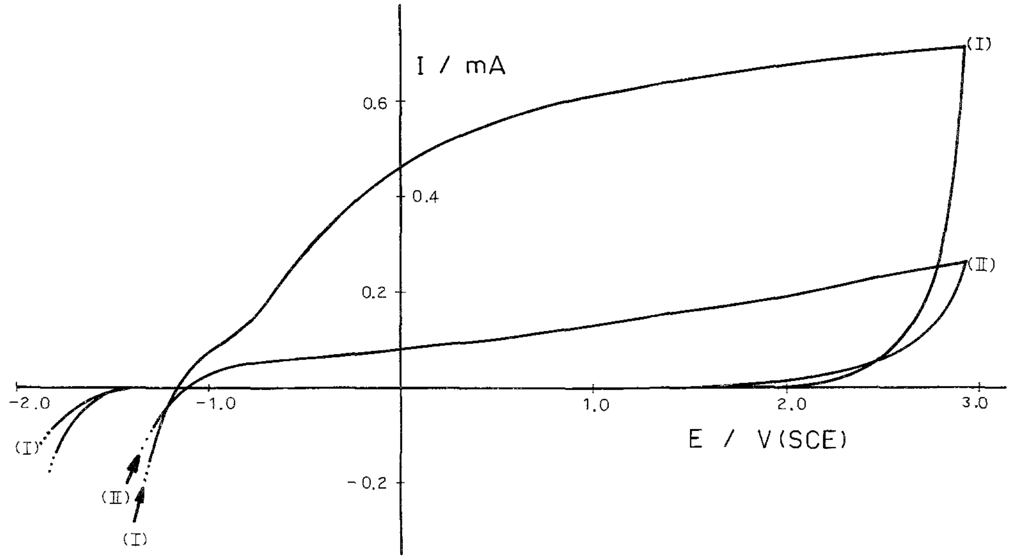

Fig. 2. Potentiodynamic curves corresponding to the H_2SO_4 solution (pH 1.0). Although these curves start at −2.00 V (versus SCE) the initial part has not been shown because of the high value of the cathodic current at this potential. (I) $100\,mV\,s^{-1}$; (II) $20\,mV\,s^{-1}$

not the case in the H_3BO_3–borax solution at pH 6.3 nor in H_2SO_4 (pH 1.0). If the metal is substantially activated with the cathodic polarization at −2.00 V, a shift of $V_{j=0}$ towards more cathodic values is expected compared with the $V_{j=0}$ values for an oxide-covered electrode [14]. This explanation is consistent with the experimental results obtained in the present work.

As shown in Table 1, the absolute values of the cathodic charges between −2.00 V and $V_{j=0}$ decrease with the sweep rate, indicating that the cathodic reaction which takes place is diffusion-controlled. This explains the shift of $V_{j=0}$ towards more cathodic values when the sweep rate increases. On the other hand, and because of the form of the potentiodynamic curves near $V_{j=0}$ (cf. Figs 1, 2, 3), the anodic current is significant immediately after this potential. The experimental curves do not exhibit the typical sigmoidal shape which clearly separates the anodic from the cathodic part. Macagno and Schultze [15], Bartels *et al.* [16] and Metikoš-Huković [17] have reported this sigmoidal shape near $V_{j=0}$ in the potentiodynamic curves obtained for tantalum, hafnium and bismuth, respectively, which, like aluminium, are also valve metals. In the case of tantalum and hafnium an initial film formed in water or in air was also shown to exist, the thickness being calculated to be about 2.0 nm [15] and about 4.1 nm [16], respectively. The oxide film on bismuth is an exception in the group of valve metals because while the other oxides are formed irreversibly [11, 12, 15–17], Bi_2O_3 can be reduced electrochemically to the metal [17] and, consequently, bismuth can be made free of oxide. The reversible potential for Bi_2O_3 formation at a pH of 8.2 is −0.35 V versus SCE which coincides with the experimental value, and as a high H_2 overvoltage is found on this metal, the anodic and cathodic currents are separated [17]. The sigmoidal shape found in the cases of tantalum [15] and hafnium [16] may be due to the existence of a residual oxide film formed in air or in water or to a high H_2 overvoltage or both. However, the anodic and cathodic reactions on aluminium appear to coexist in the conditions of the present work in a certain potential region near $V_{j=0}$. This is not unreasonable because the reversible potential for the aluminium oxide formation according to the reaction

$$2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e$$

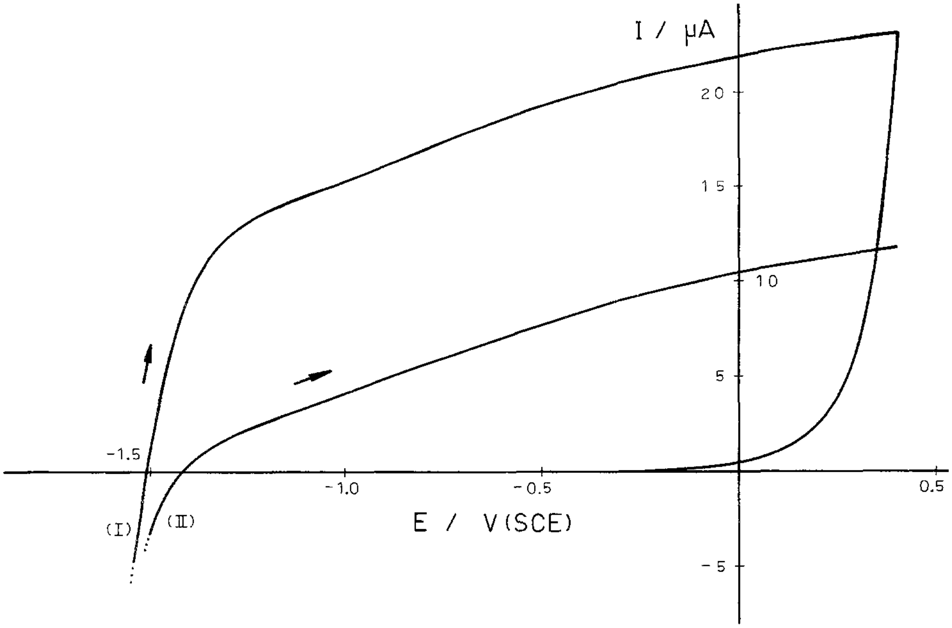

Fig. 3. Potentiodynamic curves obtained for the neutral 0.50 M propanedioic acid solution (pH 7.0). These curves commence at −2.00 V (versus SCE), but the initial part has not been represented because of the high value of the cathodic current at this potential. (I) 5 mV s^{-1}; (II) 1 mV s^{-1}.

is negative (as given by $E = -1.7915–0.0591$ pH V (SCE), the potentials being −2.1638, −2.2052 and −1.8506 V(SCE) at pHs 6.3, 7.0 and 1.0, respectively. The coexistence of cathodic and anodic reactions has also been suggested by Nisancioglu and Holtan [18] for the potentiostatic polarization of aluminium in acetate-buffered 0.53 M NaCl (pH 4.5) solutions at potentials of approximately −1.1 V (versus SCE). Then, although the potential for the oxide formation is made more anodic because of the residual film formed in air and in water, it appears to be more cathodic than the reported values of $V_{j=0}$; that is, $V_{j=0}$ corresponds to a corrosion potential.

3.2. *Potentiodynamic oxidation in the H_3BO_3–borax solution at pH 6.3*

In the case of the 0.5 M H_3BO_3–borax solution (pH 6.3) and after the potential $V_{j=0}$, the anodic current increases in a convex form and approaches a stationary value which depends on the sweep rate applied. These stationary values, I_s, are shown in Table 2. As Dignam [14] has indicated, the attainment of such a stationary value of the anodic current is to be expected for the growth of a barrier, non-porous oxide film. On the other hand, the formation of a passive oxide on the anodic side of the potentiodynamic curve is shown by the cathodic sweep from 2.90 to −2.00 V, where a significant cathodic current is found only near the latter potential (cf. Fig. 1). Moreover, if after this first potentiodynamic cycle a second consecutive cycle is performed, the anodic current is significant only near 2.90 V. In

Table 2. Experimental values of the stationary current, I_s, as a function of the sweep rate, v, for the H_3BO_3–borax solution at pH 6.3. The calculated values of the electric field, E_v, the stationary current densities, j_s, and the roughness factor, σ, are also reported. The electric field has been calculated from Equation 4; j_s from Equation 2; σ from Equation 5

v(mV s^{-1})	I_s(mA)	E_v(MV cm^{-1})	j_s(mA cm^{-2})	σ
2	0.0044	7.55	0.0048	1.29
5	0.0100	7.75	0.0116	1.21
10	0.0190	7.91	0.0228	1.17
50	0.104	8.28	0.109	1.34
100	0.184	8.43	0.213	1.21
200	0.384	8.56	0.419	1.29

this case the shape of the potentiodynamic curve is sigmoidal, as Dignam has obtained for higher potentials [14], with the current density approaching the same steady-state value as that found in the previous potentiodynamic cycle. Dunn [2] has deduced the relation between the electric field and the sweep rate under steady-state conditions for a non-porous oxide film growing at a 100% coulombic efficiency, which can be written as

$$v = \frac{M}{nF\varrho} E_v j_s \qquad (1)$$

where v is the sweep rate, E_v the electric field at sweep rate v, M the weight of oxide obtained with n moles of electrons, F the Faraday constant, ϱ the density of the oxide film and j_s the steady-state current density, which in turn is related to E_v according to the high-field ionic conduction equation:

$$j_s = \alpha \exp(\beta E_v) \qquad (2)$$

Equation 2 can also be written as

$$j_s = \alpha \exp(\beta \Delta\varphi_{ox}/d) \qquad (3)$$

where $\Delta\varphi_{ox}$ is the potential drop in the oxide film and d its thickness. By combining Equations 1 and 2 the relation between E_v and v can be finally expressed as

$$v = \frac{M}{nF\varrho} E_v \, \alpha \exp(\beta E_v) \qquad (4)$$

As seen from Equation 4, it is possible to calculate E_v for every sweep rate if the parameters α and β for the particular electrolyte are known. For non-porous films obtained in ammonium pentaborate dissolved in ethylene glycol (30% by weight of salt), the oxide film is formed with a 100% coulombic efficiency, and $\alpha = \exp(-37.79)\text{mA cm}^{-2}$ and $\beta = 4.30 \times 10^{-6}\text{cm V}^{-1}$ [2, 19, 20]. As these values of α and β have been obtained for relatively thick films (about 150-V film), it is expected that they correspond to a roughness factor, σ, of approximately one [21]. Thus, if the same values of α and β are presumed for non-porous oxide films obtained in the H_3BO_3–borax aqueous solution used in this work, and an efficiency of 100% for the oxide formation is considered as a second approximation, it is possible to calculate the roughness factor for the aluminium electrode when the oxide film is very thin (cf. Fig. 1). These two latter hypotheses are not unreasonable because Bernard and Cook [19] have shown, by means of the capacitance method, that the oxide films found in these two electrolytes have identical properties, and according to further studies [22, 23], the efficiency of the oxide formation in 0.5 M H_3BO_3–borax solution of pH 7.4 is near 100% at 20° C when the porous layer has not already begun to form. Taking $\varrho = 3.17\text{ g cm}^{-3}$ [2, 19], $M = 50.9806\text{ g}$ ($\frac{1}{2}$ Al_2O_3) when $n = 3$, and the values of α and β reported above, the electric field, E_v, corresponding to a certain value of v can be determined by iteration from Equation 4. Then, j_s can be calculated from Equation 2 and the value of σ obtained, since

$$j_s = I_s/S\sigma \qquad (5)$$

where S is the cross-section of the aluminium electrode. The calculated values are summarized in Table 2, from which a mean value of 1.25 is found. This is in good agreement with previous data obtained for the same electrolyte from the galvanostatic technique [24] where a mean value of 1.27 was found using the same parameters employed here, and also with roughness-factor data of Lewis and Plumb [21]. By using radiotracer techniques these authors determined a value of $\sigma = 1.28$ for an electrode polished with a paste of MgO and 1.17 for an electrode polished with a paste of MgO and electropolished (10 min in 3% fluoboric acid electrolyte). These values are not unreasonable because of the smoothing effect of anodizing, as discussed by Lewis and Plumb [21] (the roughness factor of those metals leading to soluble species on anodizing are usually much greater).

From these data it is also possible to calculate the thickness versus voltage ratio for this electrolyte. According to Equation 3, the thickness varies linearly with the potential and, if the interfacial overvoltages are constant (possibly zero as indicated in [14]), then

$$\Delta d = k(E_2 - E_1) \qquad (6)$$

where $E_2 - E_1$ is the increment of voltage applied. For every sweep rate the anodic charge corresponding to an increment of voltage of 1.00 V in the steady-state region has been

Table 3. Thickness versus voltage ratio, k, *calculated from Equations 6 and 7. The values of* Q *have been determined for an increment in voltage of 1.00 V in the steady-state region of the potentiodynamic curve*

$v(mV s^{-1})$	$Q(mC)$	$k(Å V^{-1})$
2	2.20	13.3
5	2.00	12.9
10	1.90	12.7
50	2.08	12.1
100	1.84	11.9
200	1.92	11.6

measured. The variation in thickness associated with this change in potential will be, according to Faraday's law and assuming a 100% efficiency for the oxide formation,

$$\Delta d = \frac{M}{nF\varrho}\left(\frac{Q}{S\sigma}\right) \qquad (7)$$

From this equation and data for σ and Q reported in Tables 2 and 3, the values of k obtained are in the range 11.6 to 13.3 Å V^{-1} (cf. Table 3), with a mean value of 12.4 Å V^{-1}. These values, which are somewhat less than those determined by Hass (14 Å V^{-1}) [25], are in agreement with the data reported by Bernard and Cook [19], who found thickness–voltage ratios changing from 14.4 to 11.3 Å V^{-1} (for a solution of ammonium pentaborate in ethylene glycol) when the current density applied varied from 10^{-4} to 1 mA cm^{-2}. It must be noted, however, that this agreement is due to the fact that the values of σ have been calculated using the same values of the parameters α, β and ϱ that Bernard and Cook determined for a different electrolyte.

More recently, Takahashi and Nagayama [23] determined a thickness versus voltage ratio of 17 Å V^{-1} by electron microscopy for an oxide layer (measured density of 2.95 g cm^{-3}) formed galvanostatically on a 99.99% aluminium electrode anodically oxidized in 0.5 M H_3BO_3–0.05 M $Na_2B_4O_7$ (pH 7.4) up to a potential of 50 V (versus SCE) and at a temperature of 20° C. In the same conditions the thickness versus voltage ratio decreased with temperature. As this film grew at 1 mA cm^{-2} it is expected that this ratio increases when the current density decreases. Taking $k = 17$ Å V^{-1} and $\varrho =$ 2.95 g cm^{-3}, the roughness factor of the electrode used in the present work can be recalculated employing Equation 7 and the values of Q given in Table 3, on the assumption of a 100% efficiency for the oxide formation. The mean value obtained in this way is $\sigma = 0.98$. Therefore, the oxide film obtained in a 0.5 M H_3BO_3–borax solution (pH 6.3) at potentials lower than 3.0 V (versus SCE) appears to be similar to that formed in ammonium pentaborate in ethylene glycol. However, this may be due to the existence of a residual oxide film which is formed in air or water prior to the anodization [10, 12]. According to the results of Jung and Metzger [26], the thickness of the oxide film at 3 V (versus SCE) is about (3.0 + 1.0) × 14 Å = 56 Å and the residual oxide formed in air and water can be a significant percentage of the latter value.

3.3. *Potentiodynamic behaviour in H_2SO_4 (pH 1.0) and neutral 0.50 M propanedioic acid*

As shown in Fig. 2, the potentiodynamic curves corresponding to the H_2SO_4 solution (pH 1.0) are different from those obtained for the H_3BO_3–borax solution (pH 6.3) in that no stationary current is achieved in the anodic sweep in the potential range studied. After $V_{j=0}$, the current density increases rapidly, being much greater than those values found for the H_3BO_3–borax solution (cf. Figs 1, 2). This behaviour is reflected in the values of the anodic charges corresponding to certain potential ranges, which are shown in Table 4 as a function of the sweep rate and the electrolyte employed. Two main differences are found for these two electrolytes. First, the anodic charges corresponding to the H_2SO_4 solution are much greater at a certain sweep rate than those obtained for the H_3BO_3–borax solution. The second difference is that the anodic charges corresponding to the latter electrolyte are independent of the sweep rate within experimental error, while for the former these charges decrease when the sweep rate increases. There is evidence of oxide formation in the anodic region of the potentiodynamic curves obtained for this sulphuric acid solution because the cathodic sweep shows only a significant

Table 4. Anodic charges (given in mC) corresponding to the anodic sweep of the potentiodynamic curves, between $V_{j=0}$ *and the potentials indicated, as a function of the sweep rate and the electrolyte*

v ($mV s^{-1}$)	H_3BO_3–borax (pH 6.3)		H_2SO_4 (pH 1.0)		Neutral NaOH + HOOC–CH_2–COOH
	0.4 V	2.9 V	0.4 V	2.9 V	0.4 V
1					13.1
2	2.78				9.43
5	2.96	7.37	6.08	59.78	6.69
10	2.31	6.92			5.44
20			4.71	25.91	5.33
50	2.63	7.66	5.09	24.29	7.40
100	2.63	7.17	4.91	20.91	6.49
200	2.27	6.96			

cathodic current at potentials near −2.00 V; also, a second consecutive potentiodynamic cycle shows a significant anodic current only at potentials near the uppermost anodic potential of the previous cycle. The rapid increase in current density after $V_{j=0}$ is very probably due to a transformation of the oxide film. In previous work, the potentiostatic behaviour of aluminium in H_2SO_4 solution (pH 1.0) was studied [8]. The experimental curves obtained at low potentials showed the typical shape corresponding to the formation of a porous oxide film [12]; that is, an initial exponential decrease of j, a minimum, a maximum and subsequently the current density approaching a steady-state value. The time associated with the minimum current density in the potentiostatic curves obtained at potentials between 1.00 and 3.50 V (versus SCE) was in the range 30 to 40 s. As these values of time correspond approximately to the morphological transformation of the oxide film to a porous structure, it is apparent that the rapid increase of current density in the potentiodynamic curves shown in Fig. 2 is associated with the porous evolution of the oxide formed.

As shown in Table 4, the anodic charges corresponding to the solutions of sulphuric acid and neutral propanedioic acid decrease with the sweep rate, while for the H_3BO_3–borax solution these charges are constant within experimental error. This latter result indicates that in this electrolyte the oxide film grows with a very high efficiency (in agreement with the arguments discussed in the previous section). For the sulphuric acid solution the anodic charges decrease with the sweep rate, possibly because of the time of anodizing; the long time taken to facilitate the processes associated with the pore formation which is reflected by the increasing current.

A third different case is found with the neutral 0.50 M propanedioic acid solution because, although the anodic charges decrease with the sweep rate until 20 $mV s^{-1}$, they are significantly greater for 50 and 100 $mV s^{-1}$. The reason is that anodic maxima appear for sweep rates equal or greater than 10 $mV s^{-1}$. These anodic maxima are associated with the active dissolution of aluminium and reflect the removal of the oxide film (formed in air and water) at −2.00 V (versus SCE) in this electrolyte [11]. After these anodic maxima, an oxide film grows by ionic conduction [11]. As shown in Table 4, the anodic charges are much greater than those reported for the H_3BO_3–borax solution, indicating a considerable solvent effect of the neutral propanedioic acid solution. However, a porous film is not expected in these conditions. Consequently, the behaviour of the electrode in this solution at a pH of 7.0 should be interpreted on the basis of metal corrosion combined with a solvent effect of the electrolyte on the oxide formed. The latter hypothesis is not unreasonable because complexes of Al^{3+} with propanedioic acid have been reported [27].

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