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Potentiodynamic behaviour of aluminium in propanedioic acid solutions

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The electrochemical behaviour of aluminium in propanedioic acid solutions has been studied potentiodynamically, the sweep rates ranging from 1 to 100 mV s^{-1} and the concentrations of the diacid being 0.05, 0.10, 0.50 and 1.00 M. The experimental work has been carried out with and without stirring of the electrolyte. The potentiodynamic curves are simple but reflect a complex behaviour. The potential of zero current in the anodic sweep is made considerably more anodic when the concentration of propanedioic acid increases, when the sweep rate decreases and when stirring is introduced. For a certain sweep rate the cathodic charge increases with both stirring and concentration of propanedioic acid. However, the anodic charge, although increasing with concentration, does not depend on stirring within experimental error (potential ranges between −2.00 and 0.400 and −2.00 and 2.90 V vs SCE). The experimental curves are explained by the increase of the quantity of reducible species near the electrode with diacid concentration, by the fact that the cathodic process is pore diffusion-controlled (H_2 evolution) and that near the potential of zero current the cathodic and anodic processes coexist (oxide formation and possible direct migration of the cation towards the solution).

1. Introduction

The anodic behaviour of aluminium is still an area of active interest because of the great technical importance of this metal and the peculiar evolution of the morphology of the growing oxide film. The morphology, composition and properties of the anodic oxide films on aluminium greatly depend on the electrolyte employed [1–9]. Electron-optical methods are the most powerful tool for determination of the morphology and composition of the oxide and also to study metal corrosion [3, 5–8]. On the other hand, analysis of the experimental curves obtained by electrochemical methods has been clearly correlated with the morphological findings and electrode surface changes demonstrated by means of many SEM, TEM and STEM studies [1, 3, 7, 8].

Although the galvanostatic and potentiostatic techniques have been widely employed [1, 10–12], the constant rate of voltage increase method has not been applied so much [2, 3, 13–16]. However, it has been shown to be a useful technique in characterizing the properties of the anodic oxide films [3, 14, 15], in evaluating the corrosion resistance of the aluminium and in determining the effect of different electrolytes on the oxide [2, 3, 13, 16–19]. The most common method is reanodizing an already oxidized sample. However, little work on the initial growth of the oxide film in the very thin film region is found in the literature.

The initial stages of the anodic oxidation of aluminium in propanedioic acid aqueous solutions has been studied previously by means of galvanostatic [20, 21] and potentiostatic [22] techniques and the behaviour has been compared with that for other electrolytes. In the present work the initial stages of the anodic oxidation of aluminium in propanedioic acid solutions have been studied potentiodynamically and the results compared with those obtained from the latter techniques.

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2. Experimental details

The experiments were carried out in a Pyrex glass cell previously described [21]. The instrumentation used has also been described elsewhere [21]. A platinum mesh and a SCE were used as counter and reference electrodes, the latter being connected via a Luggin capillary and kept in a separate compartment. All the potential data reported in this work are referred to the SCE. The working electrode was a cylindrical rod of 99.9995% purity aluminium with a diameter of 9.53 mm (Pierce Eurochemie, B.V.). Prior to the experiments, the aluminium was mechanically polished and chemically etched in 1 M NaOH at 60° C for 1 min. The electrode was then transferred immediately to the cell.

The working electrolytes were propanedioic acid solutions at concentrations 0.05, 0.1, 0.5 and 1 M (the pH values ranging between 2.1 and 1.4). These electrolytes were prepared with water which had been deionized, doubly distilled and subsequently purified by means of a Millipore Milli-Q system. The working solutions were deoxygenated by N_2 bubbling. N_2 was also bubbled through the working solution in the cell itself until the constant set temperature of 25.0 ± 0.1° C was reached (10 min).

Before applying the potential sweep, the working electrode was held at -2 V vs SCE with stirring, performed by means of the electrolyte circulation, up to a maximum rate of H_2 evolution [18]. The stirring was then stopped and the potentiodynamic sweep started immediately from this potential without switching off the cathodic current. This potentiodynamic polarization technique has been found to be very useful in the study of the active dissolution region of aluminium [13, 18], the experimental curves obtained showing good reproducibility. The effect of stirring in these curves was also studied in separate experiments. The sweep rates applied covered the range 1–100 mV s^{-1}.

3. Results and discussion

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

The experimental curves obtained for the different propanedioic acid solutions, with and without stirring, are of the type shown in Figs 1–3. As expected, the cathodic currents corresponding to the beginning of the potentiodynamic curves are more negative when the concentration of propanedioic acid increases.

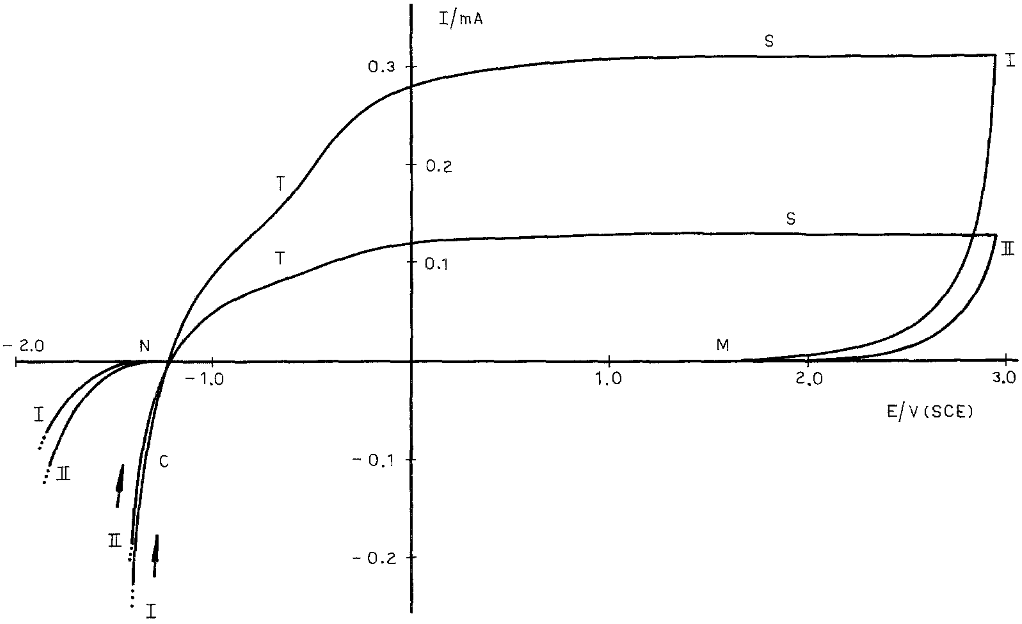

Fig. 1. Experimental potentiodynamic curves for 0.1 M propanedioic acid. These curves commence at -2 V vs SCE. However, the initial part has not been represented due to the high values of the cathodic current at this potential. (I) 100 mV s^{-1} without stirring; (II) 50 mV s^{-1} with stirring.

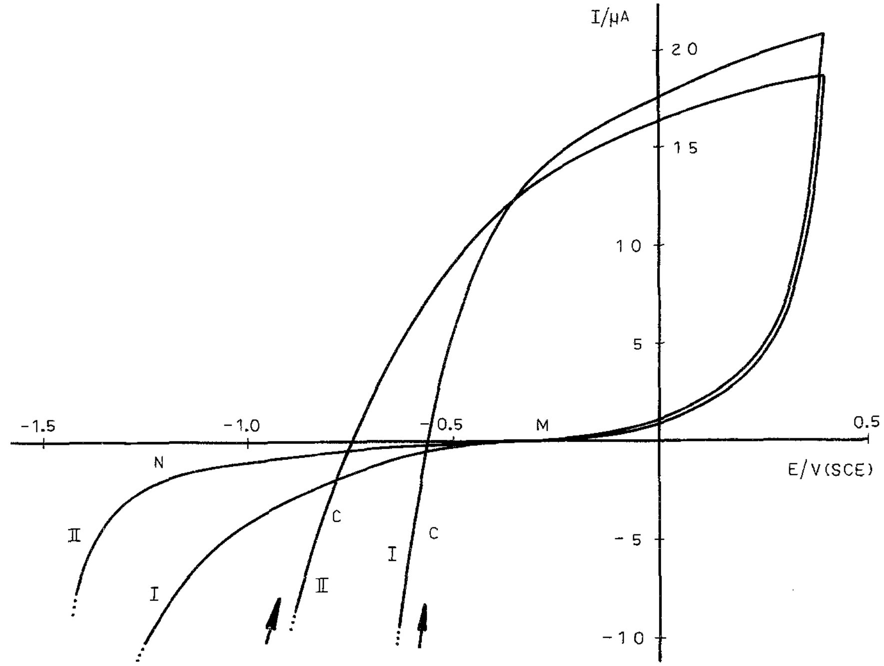

Fig. 2. Potentiodynamic curves obtained for 0.5 M propanedioic acid at a sweep rate of 1 mV s^{-1}. (I) With vigorous stirring; (II) without stirring. These curves start at -2 V vs SCE, but the initial part has not been shown because of the high value of the cathodic current at this potential.

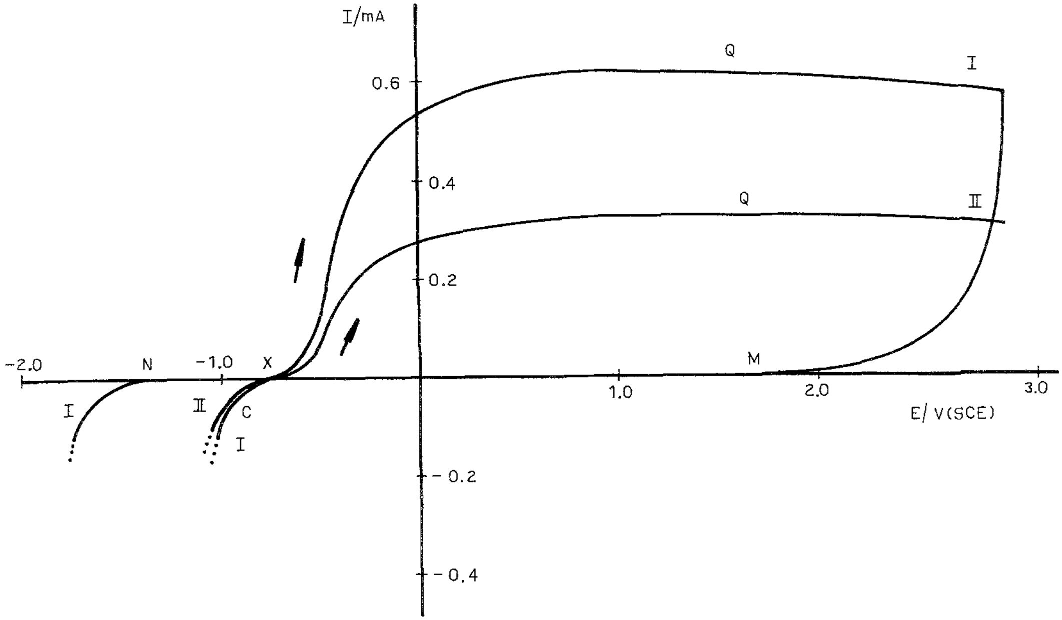

Fig. 3. Experimental curves corresponding to 1 M propanedioic acid without stirring. (I) 100 mV s^{-1}; (II) 50 mV s^{-1}. The potentiodynamic curves start at -2 V vs SCE, but they have not been represented for potentials lower than -1 V vs SCE due to the high values of the cathodic current at these potentials.

Between -2 V and the potential of zero current ($E_{j=0}$), the cathodic current decreases, exhibiting a convex form (region C in Figs 1–3). The potentiodynamic curves do not show a point of inflexion at $E_{j=0}$, except in the case of the 0.5 and 1 M propanedioic acid solutions and sweep rates equal to or greater than $5\,\mathrm{mV\,s^{-1}}$ (point X in Fig. 3).

For the experiments without stirring, it is found that $E_{j=0}$ is more negative when the sweep rate increases (for example, being -1.07 V at $1\,\mathrm{mV\,s^{-1}}$ and -1.23 V at $100\,\mathrm{mV\,s^{-1}}$ for the concentration of 0.1 M). For a certain sweep rate, when the concentration of propanedioic acid increases, $E_{j=0}$ shifts in the anodic direction; thus at the concentration 1 M, $E_{j=0}$ is -0.695 V for a sweep rate of $1\,\mathrm{mV\,s^{-1}}$ and -0.76 V at $100\,\mathrm{mV\,s^{-1}}$. The same trend is observed when the potentiodynamic curves were performed with vigorous stirring of the electrolyte. However, for a certain sweep rate and propanedioic acid concentration, stirring makes the cathodic current more negative and moves $E_{j=0}$ in the anodic direction (cf. Fig. 2); for example, in 0.1 M propanedioic acid solution and with a sweep rate of $10\,\mathrm{mV\,s^{-1}}$, the values of $E_{j=0}$ are -1.11 and -1.16 V when the electrolyte is stirred and unstirred, respectively. The effect of stirring on the change in $E_{j=0}$ is greater at low sweep rates.

The reversible potentials for H_2 evolution at the pH values corresponding to the working solutions are in the range -0.33 to -0.37 V vs SCE. Consequently, large H_2 overpotentials are found, being approximately 0.75 V for 0.05 M propanedioic acid and 0.4 V for the 1 M concentration when the solution is unstirred. These values are comparable with those reported by Hickling and Salt [23], who determined H_2 overvoltages in the range 0.58–0.78 V by means of the galvanostatic technique (current densities between 1 and $10^3\,\mathrm{mA\,cm^{-2}}$).

The effect of the different variables studied on the cathodic side of the anodic sweep is clearly observed from the data shown in Table 1. In the cathodic region, an increasing rate of H_2 evolution with propanedioic acid concentration is always observed because of the pH decreasing in the same sense. On the other hand, and for a certain concentration, the cathodic charge decreases when the sweep rate increases. Also, for certain sweep rates and electrolyte concentrations, the cathodic charge increases with stirring. These facts can be interpreted by assuming that H_2 evolution is controlled by pore diffusion of the protons towards the electrode. This, of course, can promote significant local pH changes. Local alkalization during H_2 evolution has been suggested in previous works in order to explain metal corrosion [18, 24].

Table 1. Cathodic charges, mC, corresponding to the anodic sweep between -2.00 V and $E_{j=0}$, for different sweep rates and propanedioic acid concentrations, with and without stirring of the electrolyte

v (*$\mathrm{mV\,s^{-1}}$*)	*Propanedioic acid concentration (M)*			
	0.05	*0.10*	*0.50*	*1.00*
1		−416	−2070	−3570
1 (S)			−2735	
2	−190	−232	−990	−1790
5	−80	−104	−480	−720
10	−41	−55	−270	−395
10 (S)		−62		
20	−22	−28	−130	−180
20 (S)		−31		
50	−9.1	−11.8	−52	−94
50 (S)		−12.0		
100		−6.0	−28	−44
100 (S)		−6.0	−27	

(S) Indicates stirring.

3.2. *Anodic region of the potentiodynamic curves*

On the anodic side of the potentiodynamic curves, the current density increases up to stationary or quasi-stationary values (regions S and Q in Figs 1 and 3, respectively). Current transitions are found near -0.70 V for 0.05 and 0.1 M propanedioic acid and sweep rates equal to or greater than $10\,\mathrm{mV\,s^{-1}}$ (T in Fig. 1), this potential being approximately equal to the $E_{j=0}$ values corresponding to the 0.5 and 1 M solutions (X in Fig. 3) and also to the open-circuit potentials in these solutions before the potentiodynamic polarization [21].

As long as the anodic current density approaches stationary or quasi-stationary (slightly increasing) values, the analysis of the

Table 2. Anodic charges, mC, corresponding to the potential range between $E_{j=0}$ *and the potentials indicated, as a function of the propanedioic acid concentration, stirring and sweep rate*

v (mVs^{-1})	0.05 M	0.10 M		0.50 M	1.00 M	
	0.400 V	0.400 V	2.90 V	0.400 V	0.400 V	2.90 V
1		3.17		14.60	13.91	
1 (S)				14.67		
2	2.91	2.97			11.68	
5	2.99	2.92		9.39	8.90	
10	3.04	3.14		7.83	6.83	
10 (S)		3.25	11.60	7.79		
20	3.50	3.08		6.19	5.88	
20 (S)		3.06	10.22			
50	3.10	3.15		4.72	4.63	20.22
50 (S)		2.84	9.11			
100		2.96		4.41	4.58	19.46
100 (S)		2.96	9.90	4.14		

(S) Indicates stirring.

anodic charges between $E_{j=0}$ and 0.4 V and between $E_{j=0}$ and 2.9 V are significant in providing information on the anodic behaviour of aluminium in these solutions (cf. Table 2). As shown in Figs 1–3, the anodic current approaches zero after reversing the cycle at the anodic limit (region MN), and the cathodic current is significant only at potentials much more negative than the value of $E_{j=0}$ for the anodic sweep; the cathodic charges corresponding to the cathodic half-cycle are much lower than those reported in Table 1, which belong to the anodic sweep. On the other hand, when the anodic limit increases, the cathodic charge corresponding to the cathodic half-cycle decreases. If a second potentiodynamic cycle is performed immediately after the first, a significant anodic current is found only at potentials near the anodic limit of the first cycle. Moreover, the anodic charges corresponding to the anodic sweep in the first cycle are independent of stirring within experimental error. All the latter findings provide strong evidence for the growth of a passive oxide film on the electrode during the anodic half-cycle.

All the anodic charges appearing in Table 2 are greater than those reported for pH 6.3 H_3BO_3 (0.5 M)–borax solution in previous work [19] (2.6 and 7.2 mC, independent of sweep rate, for the potential ranges $E_{j=0}$ to 0.4 V and $E_{j=0}$ to 2.9 V, respectively). These differences between the corresponding anodic charges (and with more reasons considering that $E_{j=0}$ is more negative for the boric–borax solution), suggest different values of the parameters α and β in the ionic conduction equation, $j = \alpha \exp(\beta E)$, for both electrolytes and the existence of a low efficiency for the oxide formation in the diacid used in this work.

From these results, the experimental potentiodynamic curves have been interpreted as shown in Fig. 4. Near $E_{j=0}$, the anodic and cathodic processes coexist. Curve II would correspond to H_2 evolution, which is supposed to be controlled by pore diffusion of the H^+ towards the electrode. When the concentration of propanedioic acid increases or stirring is introduced, the cathodic current shifts to more negative values, moving down the total curve in the region near $E_{j=0}$ (A and B in Fig. 4). For the anodic region at least two processes must be taken into account: curve I corresponds to oxide formation and curve III to a secondary process, possibly a migration of aluminium ions directly towards the solution. Curve III accounts for the low efficiency of oxide formation at low current densities when anodizing in pore-forming electrolytes (it is well known that propanedioic acid leads to porous anodic oxide films on aluminium [20–22, 25]. There is evidence of such a direct cation migration to the solution. This has been suggested by Nisancioglu and Holtan [24] to interpret the potentiostatic polarization of

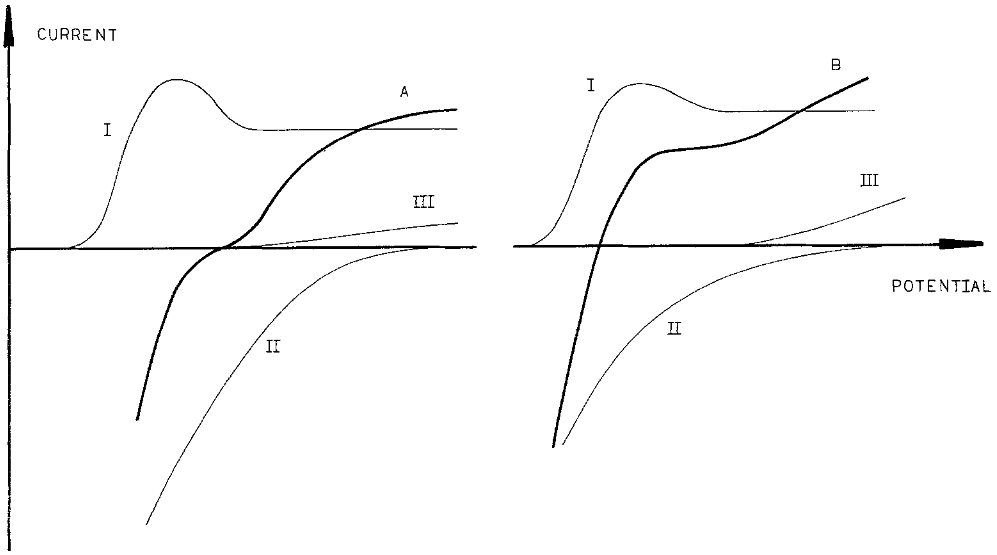

Fig. 4. Schematic representation of potentiodynamic curves near the potential of zero current. The curve A corresponds to 0.5 and 1 M propanedioic acid and the curve B to 0.05 and 0.1 M. (I) Oxide formation; (II) H_2 evolution; (III) secondary processes, presumably oxide dissolution or cation migration towards the solution.

aluminium at − 1.1 V vs SCE in acetate-buffered solutions at pH 4.5. Also, in previous potentiostatic work with propanedioic acid [22], a good quantitative agreement was found with the model of Chao *et al.* [26], which supposes oxide formation controlled by anion migration through the film coexisting with direct migration of the aluminium cation towards the solution. Therefore, the assumptions concerning curve III appear to be justified.

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