JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 731–737

# Cathodic polarization characteristics and activation of aluminium in chloride solutions containing indium and zinc ions

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Received 9 January 1996; revised 5 November 1996

This work deals with the study of the cathodic and active behaviour of aluminium in acid chloride solutions containing indium and zinc ions. The cathodic behaviour was studied using potentiostatic and potentiodynamic techniques, complemented by SEM and EDX. During cathodization, preferential adsorption of zinc ions occurs, compared to that of $H^+$ and $In^{3+}$ ions. Once a critical amount of zinc is deposited, preferred indium deposition begins. The synergistic interaction between zinc and indium ions and aluminium leads to its activation in chloride media. This can be explained by displacement reactions that produce an indium accumulation and preferential zinc dissolution. This situation produces a new interface, quasi-free of Zn but rich in In, which favours $Cl^-$ ion adsorption at more negative potentials than aluminium, leading to its activation.

## 1. Introduction

Considerable research has been conducted on the activation of the dissolution of aluminium while reducing aluminium corrosion in aqueous solutions. The electrochemical behaviour of the Al–Zn–In alloy, among others, is of interest because of its application in Al-batteries and as anode material in cathodic protection systems. Aluminium is also activated when placed in chloride solutions containing indium and zinc ions and it is known that the presence of both ions in acid chloride solutions produces a synergistic interaction [1–4]. In deposition on Al electrodes has already been characterized [5]. The objective of this study was to gain a better understanding of the role of In and Zn ions on the corrosion behaviour of Al. Thus, cathodic polarization was carried out to study the interaction between both ions and Al, and to increase the amount of data on the behaviour of Al and Al alloys at relatively high cathodic potentials. The cathodic behaviour of Al was not as intensively studied as for anodic behaviour. In this potential region, once the hydrogen evolution has started by electron tunnelling, diffusion or ionic exchange through the protective Al oxide, the pH under the growing bubble increases and oxide dissolution takes place by local alkalization [6–9]. Under this condition, the deposition of Zn and In ions on bare Al is possible and it should present a similar situation to that given by the active interface of an Al–Zn–In alloy used as anode material. Therefore, to gain insight into this type of interface, the active behaviour of Al in the acid chloride solution containing both ions is described and discussed.

## 2. Experimental details

The experimental setup has been described previously [10, 11]. Pure aluminium (99.999%, Aldrich Chemical Company) and 'Specpure' indium and zinc rod samples (Johnson Matthey Chemicals), each in the form of discs axially mounted in PTFE holders, were used as working electrodes. The Al and Zn electrodes were polished successively with 400, 600 and 1200 emery papers, 1 $\mu$m and 0.3 $\mu$m grit alumina suspensions, and then thoroughly rinsed with triply distilled water. The indium electrodes were pretreated by polishing on roughened glass and green cloth using bidistilled water as lubricant. The auxiliary electrode was a large area Pt sheet. Potentials were measured against an SCE reference electrode properly shielded and connected through a Luggin–Haber capillary tip.

Runs were made in 0.5 M NaCl solutions containing $x$ M $In^{3+}$ + $y$ M $Zn^{2+}$ ($0.001 \leq x,y \leq 0.1$) in a purified nitrogen gas saturated atmosphere at 25 °C. The pH of the solution was adjusted by addition of HCl. The electrolyte solutions were prepared from analytical grade chemicals.

Constant potential steps with potential holding at $E_\tau$, for different times ($\tau$), and conventional triangular potential sweeps at different potential sweep rates ($v$) were applied to the electrode. The electrode surface was observed by SEM and EDX.

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## 3. Results

Curve (a) in Fig. 1 shows the typical *i*/*t* response of cathodically polarized aluminium in 0.5 M NaCl solution containing 0.01 M $In^{3+}$ at pH 3 [5], and curves (b) and (c) are the results from an identical solution except for the addition of 0.001 M and 0.01 M of $Zn^{2+}$, respectively. The electrode with its air formed oxide was immersed in the solution and a potential of −1.50 V, was applied. Addition of $Zn^{2+}$ to the acid solution causes considerably greater cathodic currents. In the solution containing only In, a small number of rounded In grains were obtained by holding the potential constant at −1.50 V for 10 min (Fig. 2).

Codeposition of Zn with In significantly alters the characteristics of the deposit (Fig. 3(a)). In this case, the surface of the electrode shows a large number of dendrites. An EDX spectrum demonstrates the presence of In and Zn exclusively (Fig. 3(b)). SEM–EDX analysis of the deposits revealed the presence of 84 and 16 wt% of In and Zn in average, respectively. A line profile analysis (Fig. 3(c)) performed as indicated in Fig. 3(a) corroborates this result.

After cathodic polarization, potentiodynamic runs in anodic direction at 0.001 V $s^{-1}$ were carried out. Curves (b) and (c) of Fig. 4, obtained for different zinc ion concentration added to a solution containing 0.5 M $Cl^-$ + 0.01 M $In^{3+}$, exhibit a steep rise in current

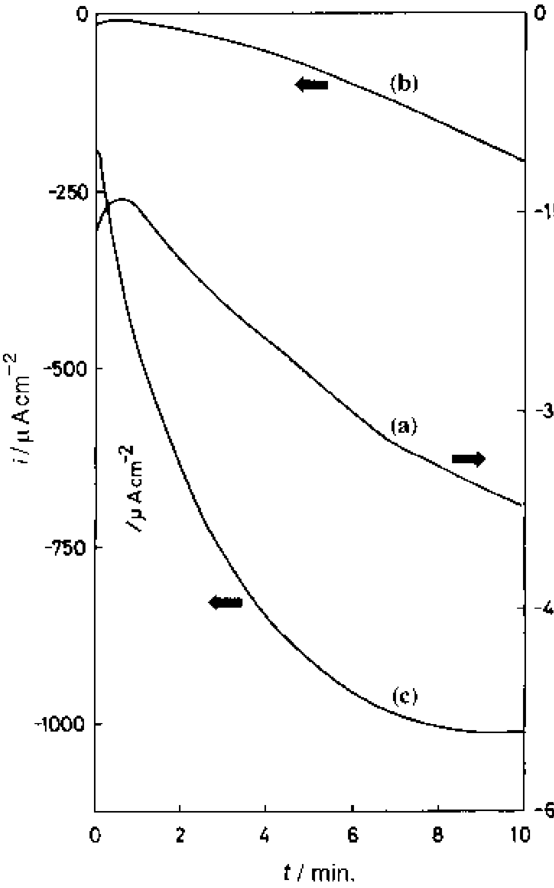

Fig. 1. Current density–time response for Al at $E_\tau = -1.50$ V in 0.5 M $Cl^-$, pH 3 solution with the addition of different concentrations of $In^{3+}$ and $Zn^{2+}$. Curves: (a) 0.01 M $In^{3+}$, (b) 0.01 M $In^{3+}$ + 0.001 M $Zn^{2+}$ and (c) 0.01 M $In^{3+}$ + 0.01 M $Zn^{2+}$.

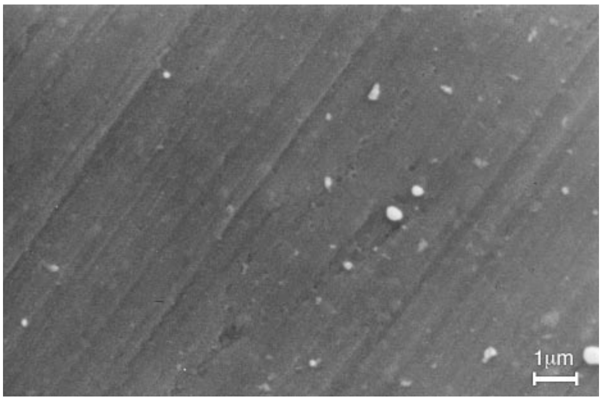

Fig. 2. SEM micrograph of Al surface after potentiostatic polarization at $E_\tau = -1.50$ V for 10 min in a 0.5 M $Cl^-$ + 0.01 M $In^{3+}$, pH 3 solution.

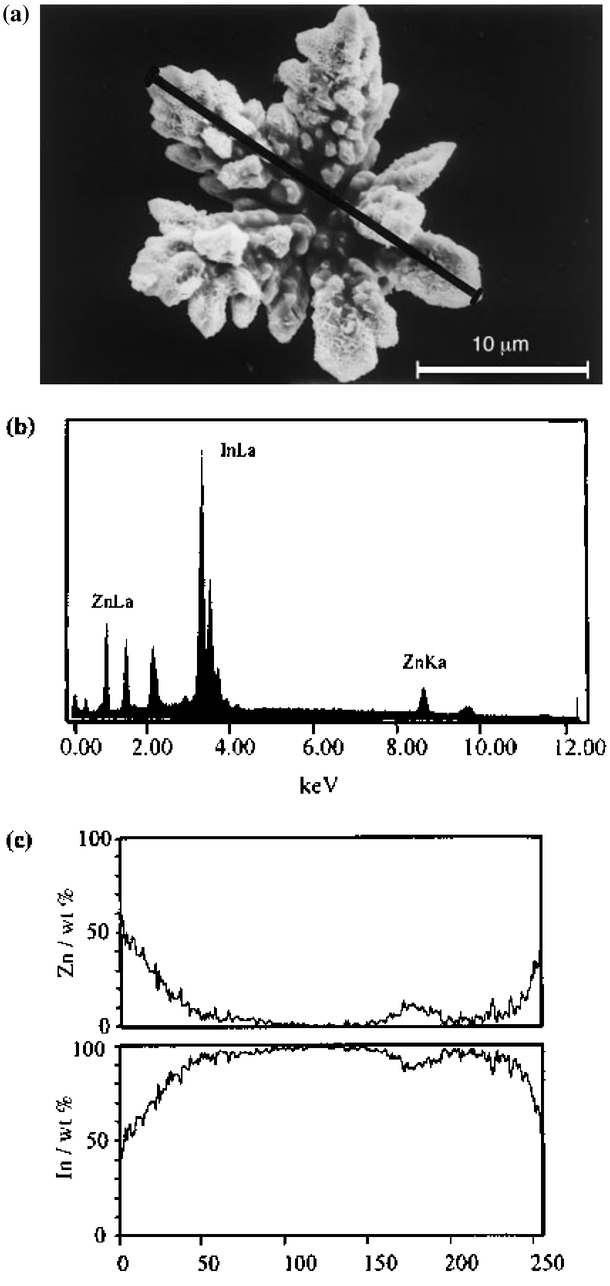

Fig. 3. (a) SEM micrograph of Al surface after potentiostatic polarization at $E_\tau = -1.50$ V for 10 min in a 0.5 M $Cl^-$, pH 3 solution containing 0.01 M $In^{3+}$ + 0.01 M $Zn^{2+}$. (b) EDX spectrum on dendrite shown in Fig. 3(a). (c) Zn and In EDX line profile analysis performed on line shown in Fig. 3(a).

that denotes the onset of pitting corrosion (activation of the Al electrode), detected by microscopic observation. On the other hand, in the absence of $Zn^{2+}$ (Fig. 4, curve (a)), a flat polarization curve is observed until the pitting potential of Al is reached. (This potential, −0.74 V, is not shown in the Figure).

A representative attack morphology is observed (Fig. 5(a)) when the Al electrode is subjected to a potential holding at −1.05 V for 2 min in 0.5 M $Cl^-$ solution where 0.1 M $In^{3+}$ + 0.1 M $Zn^{2+}$ was added. The pits are of hemispherical shape with a relatively smooth surface similar to that obtained from the indium-containing electrolyte [11]. SEM–EDX analysis of the surface showed In particles inside the pits while Zn was practically not detected (Fig. 5(b)). This fact was corroborated by EDX line profile analysis of an Al specimen at a pit-cavity cross section, shown in Fig. 5(a). Zinc combined with In only appears at the border of the cavity. Some dendrites were also found on the electrode surface (Fig. 6) with an average of 81 wt% for In and 19 wt% for Zn.

The minimum $In^{3+}$ concentration required to produce activation after previous cathodic polarization at −1.50 V ($\tau = 10$ min) was 0.1 M at pH 3.8 [5]. The simultaneous addition of $Zn^{2+}$ and $In^{3+}$ diminishes the $In^{3+}$ minimum concentration necessary to produce the activation, compared to that obtained when a $Zn^{2+}$-free electrolyte is used (Fig. 4).

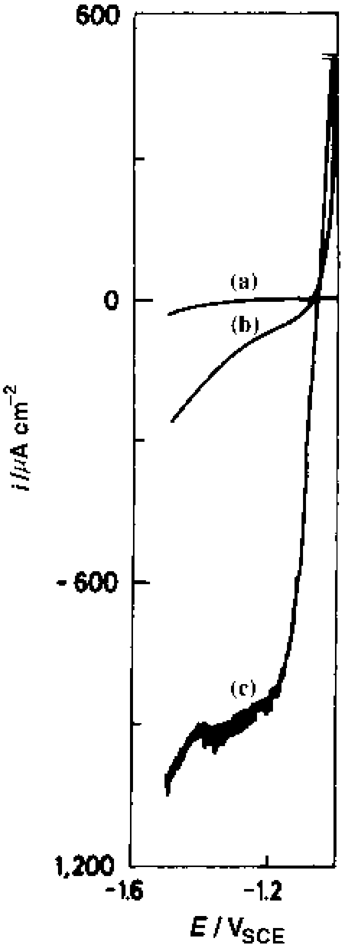

Fig. 4. Potentiodynamic polarization curves of Al in 0.5 M $Cl^-$ + 0.01 M $In^{3+}$, pH 3 solution in presence of different concentrations of $Zn^{2+}$, at $v = 0.001\ V s^{-1}$. The electrode was previously cathodized at −1.50 V during 10 min. Curves: (a) without $Zn^{2+}$, (b) 0.001 M $Zn^{2+}$ and (c) 0.01 M $Zn^{2+}$.

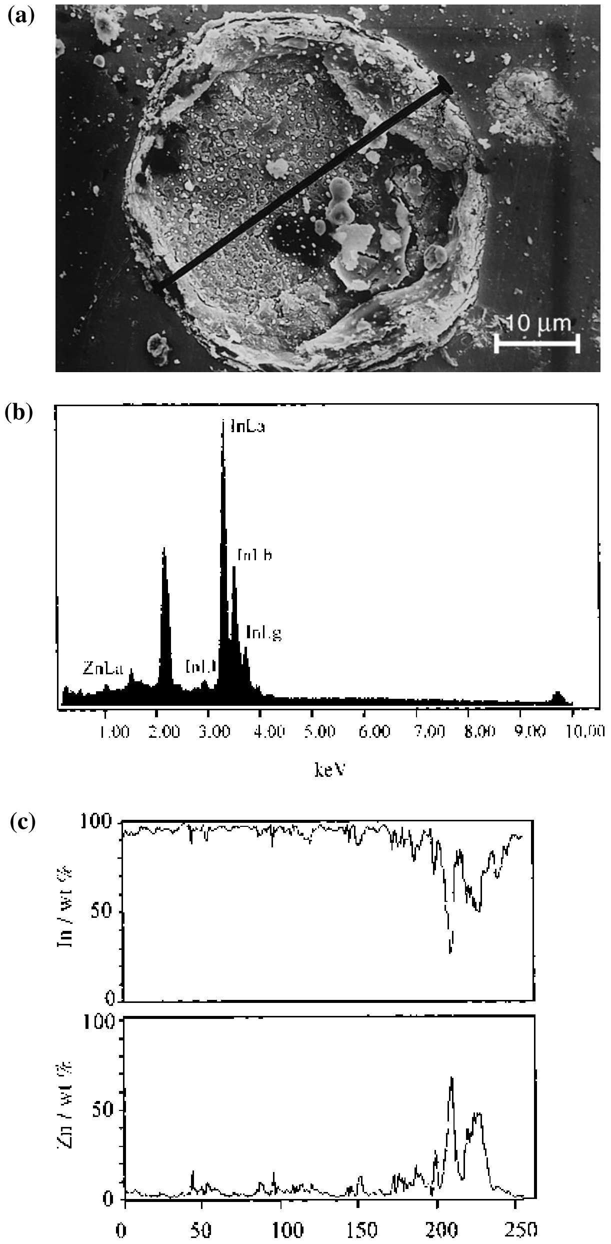

Fig. 5. (a) SEM micrograph of pitted Al surface after potentiodynamic polarization at $v = 0.001\ V s^{-1}$ in a 0.5 M $Cl^-$, pH 3 solution containing 0.1 M $In^{3+}$ + 0.1 M $Zn^{2+}$, between −1.50 V and −1.05 V and potential holding at $E_\tau = -1.05$ V for 2 min. (b) EDX spectrum inside the cavity shown in Fig. 5(a). (c) Zn and In EDX line profile analysis performed on line shown in Fig. 5(a).

To compare the effect produced only by $Zn^{2+}$ on Al with the synergistic effect produced by the presence of both ions ($Zn^{2+}$ + $In^{3+}$), experiments were performed in $Cl^-$ solution containing only different concentrations of $Zn^{2+}$. A current density–time profile was recorded for an Al specimen polarized at $E_\tau = -1.50$ V in a 0.5 M $Cl^-$, pH 3 solution containing 0.01 M $Zn^{2+}$ (Fig. 7(a)) and 0.1 M $Zn^{2+}$ (Fig. 7(b)). After double layer charging, the current initially decreases (not shown in the Figure), later increases to reach a maximum and, finally, decreases to approach the corresponding steady value (Fig. 7, curves (a)

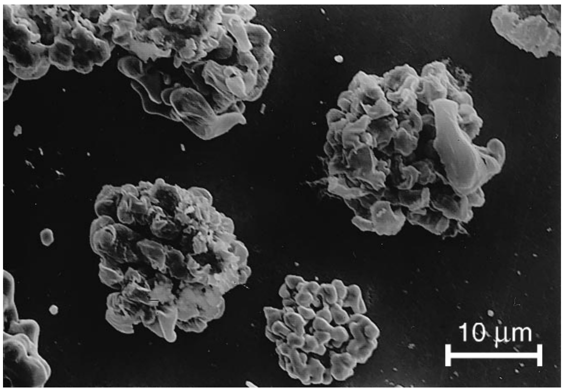

Fig. 6. SEM micrograph of dendrites at cathodic sites of Al surface which coexist with pits shown in Fig. 5(a). After potentiodynamic polarization at $v = 0.001\,\mathrm{V\,s^{-1}}$ in a 0.5 M $Cl^-$, pH 3 solution containing 0.1 M $In^{3+}$ + 0.1 M $Zn^{2+}$ between −1.50 V and −1.05 V and potential holding at $E_\tau = -1.05$ V for 2 min.

and (b)). Figure 8(a) shows equally sized hexagonal Zn platelets, corroborated by an EDX spectra (Fig. 8(b)). The diameters of the zinc platelets show little scatter which probably indicates instantaneous nucleation. The diameters were of order 2–3 µm.

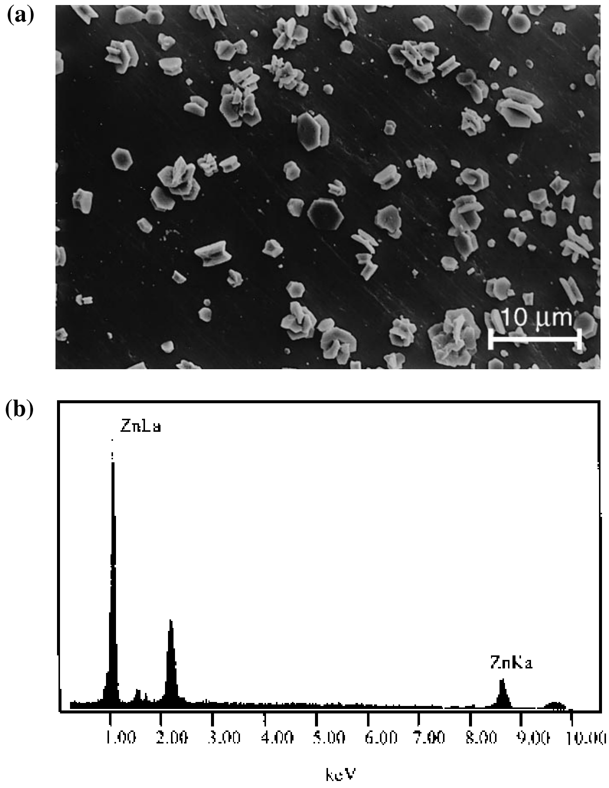

Fig. 8. (a) SEM micrograph of Al surface after potentiostatic polarization at $E_\tau = -1.50$ V for 10 min in a 0.5 M $Cl^-$ + 0.01 M $Zn^{2+}$, pH 3 solution. (b) EDX spectrum on platelets shown in Fig. 8(a).

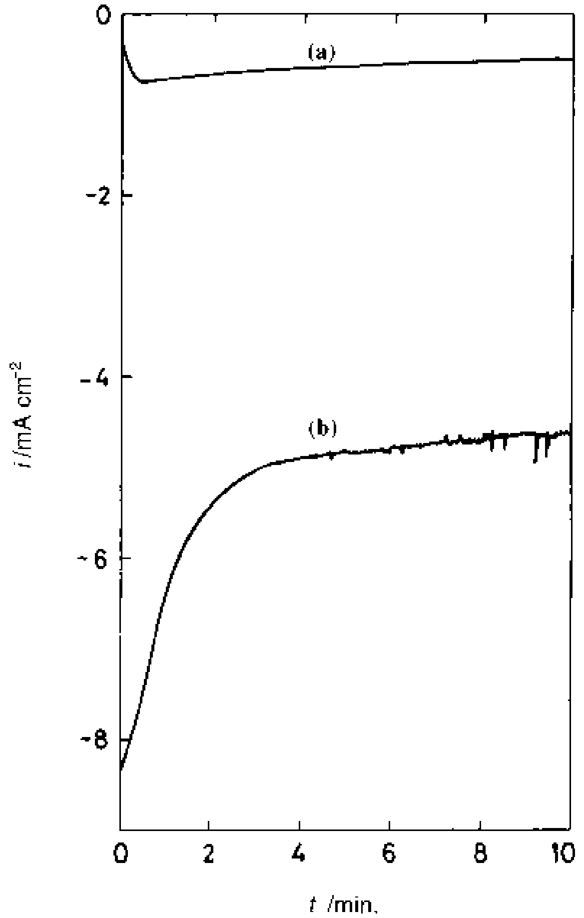

Fig. 7. Current density–time profile recorded for Al at $E_\tau = -1.50$ V in a 0.5 M $Cl^-$, pH 3 solution containing (a) 0.01 M $Zn^{2+}$ and (b) 0.1 M $Zn^{2+}$.

After holding the potential of each specimen constant at −1.50 V for 10 min, voltammograms in the anodic direction were performed (Fig. 9). The *i/E* curve shows a constant cathodic current which increases as the $Zn^{2+}$ concentration increases. At more positive potentials, an anodic current initiates at about −1.15 V, which is coincident with the corrosion potential of pure Zn in 1 M NaCl at pH 3.8 [12]. Further increase of the potential shows a passive region followed by a breakdown potential, which is slightly more noble than that measured in $Zn^{2+}$-free solution. The specimen follows a crystallographic attack (Fig. 10), similar to that of pure Al.

To obtain more information about the interaction between the $In/In^{3+}$ and $Zn/Zn^{2+}$ couples in $Cl^-$ solution, the polarization behaviour of metallic In in presence of $Zn^{2+}$, and vice versa, were also studied. The anodic potentiodynamic run of In at $0.001\,\mathrm{V\,s^{-1}}$ in 0.5 M $Cl^-$, pH 3 solution with the addition of $Zn^{2+}$, shows a comparatively greater charge of Zn dissolution, which initiates at about −1.10 V, with respect to that related to the possible formation of the indium oxide layer, in the same potential range. Both processes can be better distinguished at pH 5.3. For 0.5 M $Cl^-$ + 0.1 M $Zn^{2+}$, pH 5.3, the voltammogram run between −1.00 V and −0.66 V at $v = 0.001\,\mathrm{V\,s^{-1}}$, exhibits a pair of conjugated peaks (I and I′) associated with the electroxidation and electroreduction of a very thin indium oxide layer (Fig. 11). The oxidation peak potential is shifted towards more positive values compared to that obtained from the $Zn^{2+}$-free electrolyte. When the voltammetric run is applied between −1.15 V and −0.66 V, Zn deposition initiates at −1.12 V. Figure 11 also reveals a high reversibility of the initial stages of the electrodeposition of Zn and its

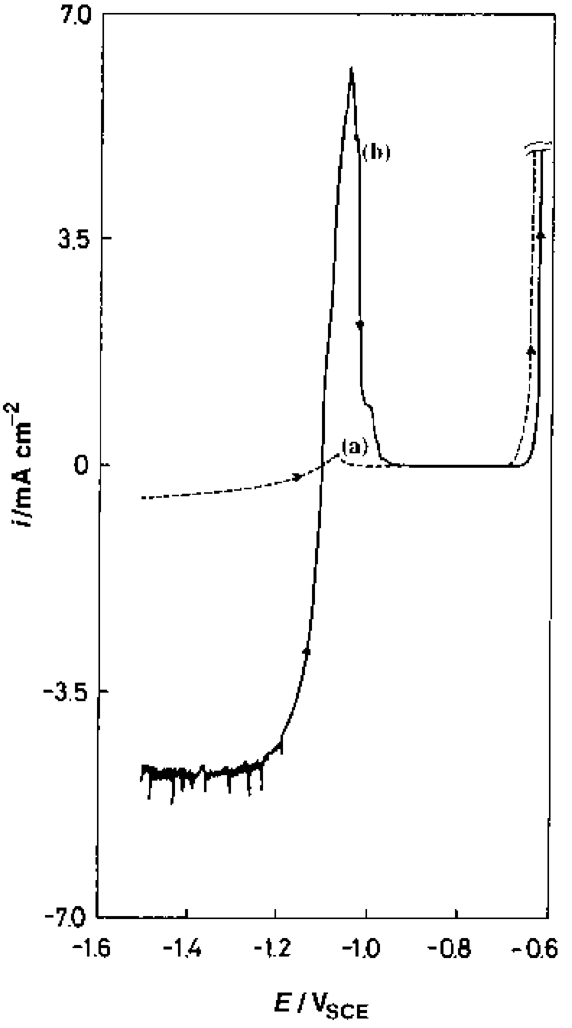

Fig. 9. Potentiodynamic polarization curves of Al in 0.5 M $Cl^-$, pH 3 solution in the presence of different concentrations of $Zn^{2+}$, at $v = 0.001\ V\,s^{-1}$. The electrode was previously cathodized at −1.50 V for 10 min. Curves: (a) 0.01 M $Zn^{2+}$ and (b) 0.1 M $Zn^{2+}$.

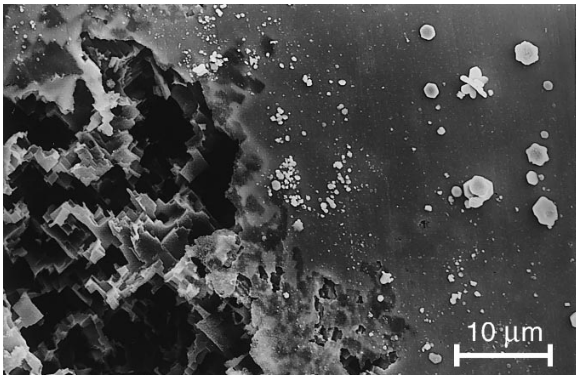

Fig. 10. SEM micrograph of Al surface after potentiodynamic polarization at $v = 0.001\ V\,s^{-1}$ in a 0.5 M $Cl^-$ + 0.01 M $Zn^{2+}$, pH 3 solution, between −1.50 V and −0.63 V and potential holding at $E_\tau = -0.63$ V for 2 min.

electroxidation (peaks II′ and II). The two couples are clearly distinguished.

The voltammogram of Zn initiated at −1.50 V in 0.5 M $Cl^-$, pH 3 solution in the presence of different $In^{3+}$ concentrations, shows increasing cathodic current for increasing $In^{3+}$ concentration (Fig. 12). As the potential changes in the anodic direction the cathodic current also decreases and, finally, at potentials more positive than about −1.40 V, the cathodic current increases again (as was found for Al in the same solution [5]). When the potential exceeds −1.15 V, there is a sharp increase in the anodic current associated with the Zn dissolution.

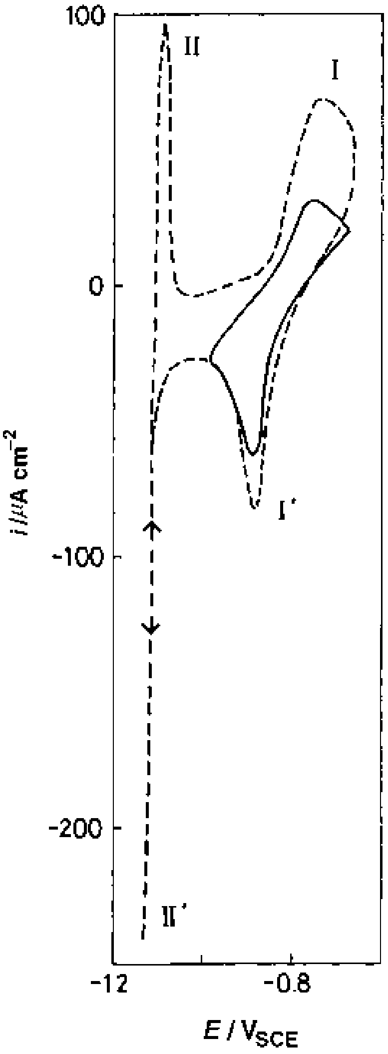

Fig. 11. Potentiodynamic polarization curve of In in 0.5 M $Cl^-$ + 0.1 M $Zn^{2+}$, pH 5.3 solution, at $v = 0.001\ V\,s^{-1}$. (–): $-1.0\ V \le E_{sweep} \le -0.66\ V$; (– – –): $-1.15\ V \le E_{sweep} \le -0.66\ V$.

## 4. Discussion

### 4.1. *Cathodization of Al in the presence of $In^{3+}$ and $Zn^{2+}$*

The typical *i/t* response during cathodic polarization of the Al electrode at −1.50 V in chloride solution containing $In^{3+}$ is shown in Fig. 1, curve (a). After the current decay, the current density was found to rise again. This behaviour is mainly attributed to the dissolution and/or hydration of the Al oxide due to the local pH increase produced by hydrogen evolution, which increases the active area. This does not seem to be the case found in Fig. 7, when only $Zn^{2+}$ is present in the chloride solution. The cathodic current

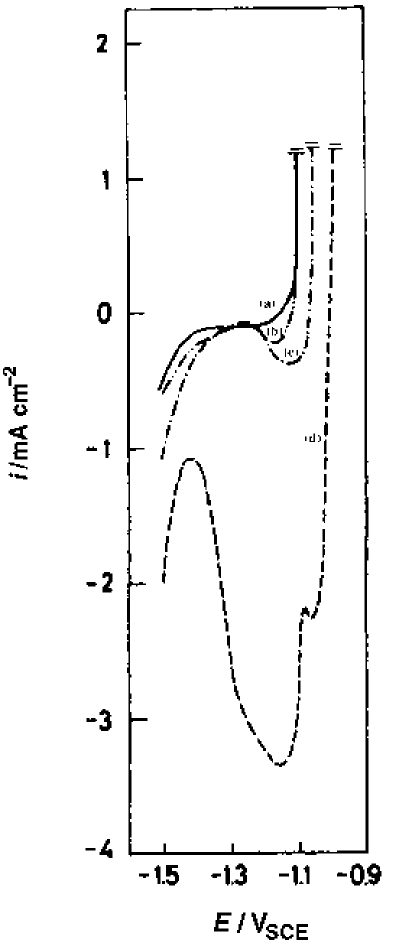

Fig. 12. Potentiodynamic polarization curves of Zn in 0.5 M $Cl^-$, pH 3 solution in the presence of different concentrations of $In^{3+}$, at $v = 0.001\ V\,s^{-1}$. The electrode was previously cathodized at −1.50 V for 10 min. Curves: (a) without $In^{3+}$; (b) 0.001 M $In^{3+}$; (c) 0.01 M $In^{3+}$ and (d) 0.05 M $In^{3+}$.

did not increase when the Al electrode was polarized at −1.50 V. In this case, adsorption of $Zn^{2+}$ on the Al surface may occur and this surface blockage may contribute to the decrease in hydrogen current as suggested by O'Keefe [13, 14]. Therefore, the current associated with proton reduction is smaller than that obtained for $Zn^{2+}$-free solution, and the cathodic current measured is associated principally with the deposition of Zn on the Al electrode.

The substantial difference in the deposition characteristics (Figs 2 and 8) is an indication that the deposition of In was more difficult than that of Zn, in spite of the latter being thermodynamically less favoured, as pointed out by Breslin [4]. The difficulty of In deposition may be due to (i) the specific Zn ion adsorption is probably more pronounced than that of In ions, and (ii) indium complexes in chloride media are more stable. Equilibrium constants for chloroindium species are at least three orders of magnitude greater than those of zinc [15, 16].

When starting the voltammograms in the cathodic direction in a chloride solution containing $In^{3+}$, In deposition started at −1.60 V [5], while the initiation of metal deposition is significantly shifted in the anodic direction (400 mV) for a solution containing only $Zn^{2+}$.

It is interesting to note that when only $Zn^{2+}$ is present in the chloride solution, a significant amount of elemental Zn is found on the surface of the electrode (Fig. 8), but when $In^{3+}$ and $Zn^{2+}$ are present, a predominant deposit of elemental In is found (84 wt% In and 16 wt% Zn) (Fig. 3). The presence of $Zn^{2+}$ promotes the In deposition, since for the case of added $In^{3+}$ alone, the surface examination showed smaller and fewer deposits in number (Fig. 2), compared to those obtained from both ions (Fig. 3). The addition of $Zn^{2+}$ substantially changed the amount of deposited In and modified the structure of the deposit.

The role of Zn on increasing the amount of deposited In can be explained as follows. Probably, in the early stages of cathodization, adsorption of $Zn^{2+}$ on the Al electrode mainly occurs, compared to that of $H^+$ and $In^{3+}$ adsorption. As soon as conditions on the electrode surface allow a critical content of deposited Zn, preferred In deposition on freshly nucleated Zn is initiated, denoting a lower overpotential for In deposition on Zn than on Al.

The shape of the curves at −1.50 V (Fig. 1, curves (b) and (c)) indicates that dissolution and/or hydration of the oxide has occurred, and this can be attributed to a pH increase. $In^+$ has been postulated as an intermediate during the electroreduction of In in an acid media [17, 18], and can be oxidized by hydrogen ions, increasing the pH [15]. This increase in pH explains the shape of the curves.

### 4.2. *Al activation in the presence of* $In^{3+}$ *and* $Zn^{2+}$

The Al surface attack developed in $Cl^-$ solution containing both $In^{3+}$ and $Zn^{2+}$ is very similar to that produced by $In^{3+}$ alone and that obtained from Al–In alloys. The attacked areas (Fig. 5(a)) show wide cavities and In particles within and above them, as identified by X-ray analysis (Fig. 5(b) and (c)). In contrast, the morphology of the pits on Al–1% Zn or Al in 0.5 M $Cl^-$ + 0.01 M $Zn^{2+}$ (Fig. 10) showed etched shapes with crystallographic planes, like those on pure Al. These pits become very irregular, probably tunnel-like [19, 20].

Free corrosion studies (open circuit potential against time profile) [4] demonstrated that simultaneous addition of $Zn^{2+}$ and $In^{3+}$ resulted in much lower induction periods to attain the active state compared to those obtained with only In salts. As soon as the active state is reached the active period lasts longer than that given by $In^{3+}$ alone [1]. In our work, the presence of both ions diminish the minimum $In^{3+}$ concentration required to produce activation. (Figure 4, curve (a) without $Zn^{2+}$, does not show activation while curves (b) and (c), with $Zn^{2+}$, do show activation.)

According to Fig. 5, where an active state was developed after a potential holding of $E_\tau = -1.05$ V in solutions containing both ions, only In could be detected on the pitted surface. This suggests that inside the cavity an In accumulation has been produced and preferential Zn dissolution occurred where the holding potential is anodic for the $Zn/Zn^{2+}$ couple.

Prior to the activation potential (Fig. 4, −1.15 V) and within the Al oxide cracks, more Zn can be deposited in metallic contact with Al by

$$2\text{Al} + 3\text{Zn}^{2+} \longrightarrow 2\text{Al}^{3+} + 3\text{Zn} \qquad (1)$$

As previously discussed, In deposition is easier on Zn than on Al, and the displacement reaction

$$3\text{Zn} + 2\text{In}^{3+} \longrightarrow 2\text{In} + 3\text{Zn}^{2+} \qquad (2)$$

can occur, promoting further In deposition. Reactions 1 and 2 explain the morphology and percentage element deposition found in Fig. 3. Also, comparing curve (a) with (c) or (d) at −1.10 V in Fig. 12, they show that In can be deposited simultaneously as Zn dissolves.

Active (Fig. 5) and passive (Fig. 6) states coexist at the same holding potential ($E_\tau = -1.05$ V), presenting surface areas with In and Zn deposits. Although only In was detected at the active cavities (Fig. 5), dendrites of 81 wt % In and 19 wt % Zn grew on cathodic impurities (Fig. 6). These did not promote Al attack.

As deposited Zn enters into metallic contact with Al, it promotes increasing local $\text{Cl}^-$ concentration because $\text{Cl}^-$ is specifically adsorbed on it [12], depolarizing its dissolution kinetics when −1.15 V is overcome (Fig. 12) or activating the Al electrode (Fig. 4). When Zn and/or In comes into metallic contact with cathodic impurities (Figs 6 and 8), it is surrounded by aluminium oxide which avoids direct contact of local $\text{Cl}^-$ concentration with bare Al, impeding its activation.

Furthermore, the $\text{Al}^{3+}$ hydrolysis reaction within an active pit is an exothermic reaction and this may produce a surface temperature high enough to promote In–Al phase formation [11]. The much lower mobility of Zn (compared to In) and its tendency to dissolve from the surface, explains the decreasing concentration of Zn at the interface [4]. Thus, Reactions 1 and 2 and the increasing local $\text{Cl}^-$ concentration produced, explain the activation of Al at −1.15 V.

For a chloride solution containing only $\text{Zn}^{2+}$, and after cathodic polarization, the potentiodynamic run in the anodic direction at 0.001 V s$^{-1}$ (Fig. 9) shows an anodic peak which characterizes the deposited Zn. At more positive potentials, the deposited Zn shifts the Al pitting potential in the anodic direction. Figure 10 shows an SEM of the Al electrode after subjection to polarization by anodic sweeps between −1.50 V and −0.63 V, and held at the last potential for 2 min. The dissolution of Zn is incomplete (some platelets remain) and crystallographic pits are observed. A similar effect has been reported by Khedr and Lashien [21], who found that $\text{Zn}^{2+}$, among other cations, caused an initial positive shift of the Al breakdown potential, indicating the inhibition of pitting corrosion. Further work on this issue is presently being carried out.

## 5. Conclusions

(i) In the early stages of cathodization, adsorption of $\text{Zn}^{2+}$ on the Al electrode prevails compared to that of $\text{H}^+$ and $\text{In}^{3+}$ adsorption. Once conditions on the electrode surface allow a critical content of deposited Zn, preferred In deposition on freshly nucleated Zn is initiated, denoting a lower overpotential for In deposition on Zn than on Al.

(ii) Prior to the activation potential and within the Al oxide cracks, Zn can be deposited in metallic contact with Al by a displacement reaction. This situation in turn also promotes further In deposition by a displacement reaction. Once the $\text{Zn/Zn}^{2+}$. $\text{Cl}^-$ potential is reached, Zn and Al oxidation take place, giving an active interface quasi free of Zn.

(iii) As deposited Zn and In enter into metallic contact with Al, they promote increasing local $\text{Cl}^-$ concentration depolarizing all anodic reactions and avoiding repassivation. This explains the activation of Al at −1.15 V.

## Acknowledgements

This research was financially supported by the Universidad Nacional del Sur (PGIC–UNS) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PID 3869/92).

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