Role of indium in promoting anodic dissolution of Al–In alloys in non-aqueous electrolyte

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Exploratory work on the anodic dissolution behaviour of aluminium and aluminium binary alloys in electrolytes in non-aqueous organic solvents is reported. Commonly used electrolytes for non-aqueous battery systems were selected on the basis of their conductivities and activities for anodic dissolution of Al and Al-alloy anodes. It is found that Al–In alloy electrodes exhibit an exceptionally active anodic dissolution behaviour in a 1 M solution of $AlCl_3$ in anhydrous acetonitrile. The steady-state Tafel polarization plots for dissolution of pure Al, Al–Sn, Al–Ga and Al–In alloy anodes are compared, and a.c. impedance spectra for an Al–In alloy anode in 1 M solution of $AlCl_3$ in CH_3CN are evaluated and discussed. The In component, like Ga or Hg, interferes with passivation of Al during its anodic dissolution and thus promotes an "active" condition on the metal surface leading to relatively high anodic dissolution current-densities at substantially negative electrode potentials.

1. Introduction

One of the major problems restricting the development of aqueous Al-battery systems and their wider use is that substantial evolution of hydrogen gas arises concurrently with the anodic dissolution of the aluminium. This reduces the electrochemical energy efficiency and also gives rise to a large discrepancy between the theoretical and practical open-circuit voltages of the aluminium anode [1, 2]. Ideally, it is desirable to achieve the most negative open-circuit potential for the aluminium anode. However, the concurrent hydrogen gas evolution rate can be exponentially enhanced with increased negative electrode potential in aqueous solution, a phenomenon related to the so-called negative difference effect at aluminium. An even more important factor in the use of aluminium in aqueous electrolytes is that complex oxide films are formed irreversibly and passivate the aluminium anode, preventing its active dissolution and depressing its open-circuit potential (o.c.p.) [1, 3].

The possibility of developing a non-aqueous aluminium rechargeable battery is attractive as it would have few of the disadvantages of lithium rechargeable systems yet have an equivalent weight of the anode material (of 9), close to that of Li (of 7). Therefore, in the present work, as part of a programme of research on the electrochemistry of aluminium and its alloys in non-aqueous, aprotic media, we report investigations on the anodic electrochemical behaviour of aluminium in non-aqueous electrolytes where the passivation effects familiar in aqueous media may be eliminated or minimized. Although a number of novel developments have been made recently [4, 5] in molten salt systems involving aluminium, surprisingly little work is found in the literature on the behaviour of aluminium in non-aqueous electrolyte systems,

except in one of our previous papers [6] and references quoted therein.

In aqueous medium, it has been found that treatment of Al with traces of Hg or Ga, or the use of Al–Ga alloys [7, 8], greatly activates the process of aluminium anodic dissolution. Similar effects have been observed with Al–Sn and especially Al–In alloys [9, 10].

In the present work, the anodic behaviour of Al–In alloys containing small percentages of In has been evaluated in acetonitrile solution, 1 M in $AlCl_3$; high rates of anodic dissolution of aluminium can be achieved without the passivation effects that arise in aqueous medium and without the complication of simultaneous hydrogen evolution.

Electrolyte systems in non-aqueous organic solvents have a number of advantages, including favorable low temperature properties. The lithium battery electrolyte systems are good examples.

It has been reported that some binary [7] and ternary [2] aluminium alloys have the special property of suppressing the hydrogen evolution reaction and exhibiting much more negative o.c.p.'s in aqueous solution than does pure aluminium itself. Workers in the USSR [11] have investigated the anodic and corrosion behaviour of Al and that of an active Al–Mg–Hg-alloy in water, formamide and methanol solutions. Among the systems studied, the hydrogen evolution reaction was still involved to some significant extent due to the "active hydrogen" in certain functional groups of the molecules of the organic solvents employed.

The present paper reports exploratory work on binary Al–In, Al–Ga and Al–Sn alloy anodes in $AlCl_3$ in two non-aqueous organic solvents which have no 'active' hydrogen in the solvent-molecule structures. The anodic behaviour of some exceptionally active

Table 1. The Al and Al-alloy electrodes used in the present work

Electrode	wt %	at %
Al	99.999	
Al–Ga	0.26	0.12
Al–Sn	0.12	0.03
Al–In	0.037	0.009
	0.074	0.018
	0.16	0.042
	0.20	0.055
	0.40	0.13

Al–In alloy anodes in acetonitrile, 1 M in $AlCl_3$, was especially examined.

2. Experimental details

2.1. Electrodes

All aluminium alloys were supplied in rod form (radius 7 mm) by Alcan International Ltd, Banbury Laboratories [8]. The alloys had been prepared with high purity (99.995%) aluminium as the primary component and were heat-treated at 600° C for more than 1 h, followed by a cold water quench. The alloying components had been added in amounts ranging from 0.037–0.4 wt % (see Table 1). The maximum solubilities of indium, tin and gallium in aluminium are 0.17, 0.2 and 9 wt %, respectively. The Al–In (0.2 wt %) and Al–In (0.4 wt %) are two phase alloys. In the following sections of the paper, unless otherwise specified, only weight percent (wt %) composition figures will be shown.

The alloy rods were mounted inside close fitting glass tubes by means of epoxy resin. Before each set of experiments, the electrodes were cut by a diamond saw which created a fresh and smooth electrode surface (area $0.38 \, cm^2$), covered, almost certainly with a thin, air-formed oxide film. Pure aluminium (99.999%) and indium (Grade 1) were supplied by Johnson Matthey (England).

The reference electrode was an Ag/AgCl electrode in the same solution under study, [6]. Several identical Ag/AgCl reference electrodes were prepared and used. The potential of the reference electrode was monitored and compared with that of various freshly prepared ones. If the potential of a used Ag/AgCl reference electrode shifted by more than a few millivolts from the normally reproducible, steady value, it was replaced by a freshly prepared one. It was found, however, that the Ag/AgCl reference electrodes were quite stable in the system $AlCl_3$ + CH_3CN over a number of days.

The counter electrode was a platinum gauze of area $\sim 10 \, cm^2$.

2.2. Electrolytes

High purity anhydrous acetonitrile (AN) (< 0.003% water) and propylene carbonate (PC) (< 0.013% water), (American Burdick and Jackson), were used as solvents. All anhydrous salts used as electrolytes

($AlCl_3$, $(C_2H_5)_4NCl$, LiBr and $LiClO_4$) were vacuum dried for a prolonged time at 80° C. Solutions were prepared in a nitrogen-containing dry glove box. It was demonstrated [6] by NMR spectroscopy that no free water (< 1 p.p.m.) was present in the solutions of 0.33 M $AlCl_3$ in CH_3CN; since anhydrous $AlCl_3$ is a strong internal desiccating agent in a solution, i.e. any free water tends to become complexed, the free solvent fraction is very dry on account of a gettering effect of the $AlCl_3$.

2.3. Cell

An all-glass 3-compartment cell was used. The Ag/AgCl reference electrode was mounted in a tube in the working compartment provided with a Luggin capillary positioned very close to the aluminium alloy electrodes. The cell was separated from the atmosphere by means of ground-glass joints and bubblers in the conventional way. Before each measurement, purified [12] dry nitrogen was bubbled through the solution for at least 45 min.

All measurements were carried out at room temperature (296 K) unless specified.

2.4. Instrumental description

D.c. polarization curves were recorded using a PAR model 273 potentiostat controlled by a PAR software package M270 through an IBM-AT computer. The potential sweep-rate employed for recording polarization curves was $1 \, mV \, s^{-1}$.

The first two or three polarization curves taken on a freshly prepared aluminium or aluminium alloy electrode were usually not entirely reproducible and such data were discarded since complex oxide films had probably been formed during the electrode preparation procedures. Only the reproducible quasi steady-state polarization curves are reported here.

A.c. impedance spectra were recorded using a Solartron Model 1255 frequency response analyser in conjunction with the PAR 273 potentiostat, controlled by the software package ZPLOT (Scribner Associates Inc.). All d.c. data reported were IR_s-corrected, the solution resistance, R_s, having been measured by both a.c. impedance and current-interruption methods; typically this R_s value was of the order of 15 Ω for 1 M $AlCl_3$ in CH_3CN, i.e. rather larger than values commonly encountered in aqueous solutions of moderate concentration. Hence, the IR_s-correction procedure is important for these non-aqueous solution experiments, especially at the high current-densities realized at some of the Al–In electrode alloys.

2.5. Conductance measurements

A specially designed all-glass cell having 2 compartments connected by a capillary of length 3 cm and inside diameter 0.7 mm was used for the conductance measurements and employed two platinized platinum gauze electrodes. The cell constant ("L/A") was

Table 2. Resistivity and conductivity of the electrolytes used (at 298 K)

Solute	Solvent	Resistivity ρ $(\Omega\,cm)$	Conductivity κ $(\Omega^{-1}\,cm^{-1})$
1 M AlCl₃	AN	31.5	3.17×10^{-2}
0.33 M AlCl₃	AN	58.8	1.70×10^{-2}
0.3 M AlCl₃ + 1.0 M LiClO₄	AN	31.1	3.21×10^{-2}
1 M AlCl₃	PC	156	6.41×10^{-3}
0.3 M (C₂H₅)₄NCl	PC	281	3.56×10^{-3}

* PC = Propylene carbonate, AN = Acetonitrile (κ = 1.28 × $10^{-2}\,\Omega^{-1}\,cm^{-1}$ for 0.1 M aq. KCl at 298 K).

$848\,cm^{-1}$, as determined by calibration using a standard 0.10 M aq. KCl solution. All conductance measurements were carried at 298 K by means of the a.c. impedance equipment described above.

The ESCA results were obtained on a M-probe, Surface Science Instrument. Ion etching was carried out with argon ions (4.5 kV). The sample specimens were prepared by cutting about 2 mm pieces from the tips of the electrodes using a diamond saw. Then the sample specimens were ultrasonically cleaned in baths of distilled water and methanol successively. The same procedure was used for preparation of specimens for SEM examination.

3. Results and discussion

3.1. *Conductivities of electrolytes*

The conductivity of the electrolyte is one of the most important factors to be considered in evaluation of a non-aqueous battery system. Table 1 lists the values of specific resistivity and conductivity of some systems examined.

Acetonitrile (AN) is an excellent solvent for many polar or ionized organic compounds and for some inorganic salts, and is resistant to both oxidation and reduction over a wide potential range. Its dielectric constant of 37 permits reasonably high equivalent conductivities to be realized. Propylene carbonate (PC) is also a commonly used solvent for Li batteries, and has a low vapour pressure and relatively low toxicity. However, the conductivity of AlCl₃ electrolyte, at the same concentration (1 M), is five times lower in PC than in AN (see Table 2). Other commonly used solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO) do not provide sufficient solubility or conductivity for some organic or most inorganic halide salts. It was found that DMF reacts with AlCl₃ to form an insoluble complex compound. It is essential, for active dissolution of aluminium, that the electrolyte contains one or more "aggressive" anions, in particular, halide ions or hydroxyl ion [1].

The 1 M AlCl₃ in AN has a reasonably good specific conductivity, $3.17 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ (Table 2) which is similar to the value for 0.3 M aqueous KCl solution at 298 K.

LiClO₄ is an excellent supporting solute for a number of Li-battery systems. Unfortunately, it seems that ClO₄⁻ can react with aluminium to form an oxide

film which prevents its active dissolution. (See Fig. 1). Figure 1 shows the quasi steady-state polarization curves for aluminium dissolution in solutions of (1) 1 M AlCl₃ in AN; (2) 0.3 M AlCl₃ + 1.M LiClO₄ in AN and (3) 0.3 M (C₂H₅)₄NCl in PC. Although the conductivities of the solutions for curves 1 and 2 (Fig. 1) are similar, curve 2 corresponds to a much higher polarization. Systems with LiClO₄ supporting electrolyte require an extra two volts in order to drive the dissolution of aluminium at a rate of, say, $i = 10\,mA\,cm^{-2}$. A much higher Tafel slope and observation of 'pitting dissolution' at about 2.0 V for curve 2 indicated the formation of a strongly passive film on the aluminium electrode surface [1]. Similarly, the passive film is also formed in the solution of (C₂H₅)₄NCl in PC (curve 3).

Therefore, 1 M AlCl₃ in anhydrous AN was chosen as the most satisfactory electrolyte for the experiments described below.

3.2. *Dissolution of Al from binary alloys (Al–In, Al–Ga, Al–Sn)*

Figure 2 shows Tafel relations for anodic dissolution of pure aluminium and the above aluminium alloys [Al–Sn (0.12%); Al–Ga (0.26%) and Al–In (0.20%)] in 1 M AlCl₃ (AN). It is seen from this figure that the Al–In alloy anodes exhibit exceptionally active dissolution under anodic polarization at $i = 50\,mA\,cm^{-2}$, $E = -0.7\,V$, with respect to Ag/AgCl which is about 800 mV lower than that for a pure aluminium anode at
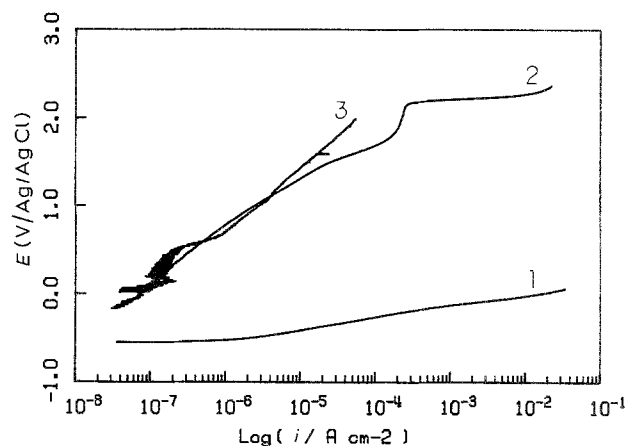

Fig. 1. Polarization curves for anodic dissolution of Al (99.999%) in solutions (1) of 1 M AlCl₃ in AN; (2) 0.3 M AlCl₃ + 1.0 M LiClO₄ in AN; and (3) 0.3 M (C₂H₅)₄NCl in PC (all at 296 K).
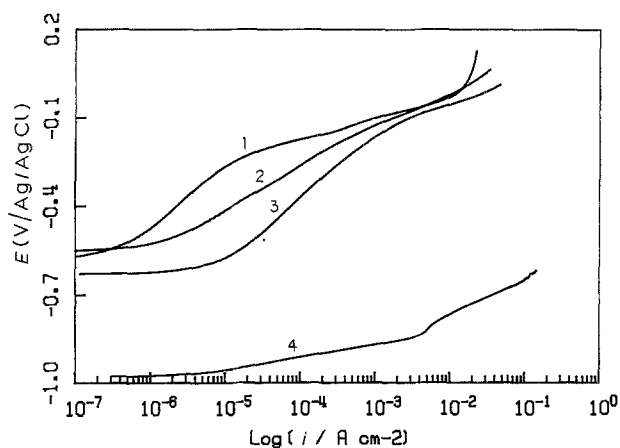
Fig. 2. Polarization curves for anodic dissolution of (1) Al–Sn (0.12%), (2) Al (99.999%), (3) Al–Ga (0.26%), and (4) Al–In (0.2%) in 1 M AlCl₃ in AN (all at 296 K).

the same current-density. Also, the rest potential for the Al–In anodes is shifted to potentials that are about 400 mV more negative, i.e. to about −1.0 V with respect to Ag/AgCl.

Surprisingly, the alloying elements gallium and tin which, are found to have a strong effect, favorable to the polarization behaviour of Al anodes in aqueous solutions [7, 8], have little effect on the aluminium electrodes in the non-aqueous AlCl₃/AN solution (Fig. 2).

3.3. The effects of concentration of the alloying In component

3.3.1. Tafel plots. Figure 3 shows the Tafel relations for (1) anodic dissolution of Al (99.999%) and for three Al–In alloys: (2) 0.037, (3) 0.074, (4) 0.2 wt % of In in 1 M AlCl₃ (AN) electrolyte solution. Figure 3a and b show the behaviour for ascending (from low i to high i) and descending (from high i to low i) changes of current-density, respectively.

It was found that an activation-passivation-reactivation phenomenon is involved in the Al–In alloy anode dissolution reaction. The extent of activation is found to depend on the concentration of the In component in the alloy. At 0.2% of In, Al–In electrodes

even dissolve anodically at $i = 0.2$ A cm⁻² without any indication of passivation.

For Tafel relations measured in the ascending direction (Fig. 3a), over the low current-density range, Al–In alloy anodes exhibit much more negative potentials than does the pure Al (curve 1) under similar conditions. However, when the polarization current is increased and a polarization potential of about −0.6 V is reached, the Al–In (0.037%) (curve 2) and Al–In (0.074%) (curve 3) alloys begin to exhibit passivation behaviour and the two curves then tend to become coincident with the Tafel line for anodic polarization of the pure Al electrode. For the Al–In (0.2%) electrode, the potential always remains lower than the critical value (−0.6 V), even at $i = 0.2$ A cm⁻², and no passivation is observed.

The critical potential value also applies to the Tafel lines measured in the descending directions of potential change (Fig. 3b), when the anodic dissolution reaction has started from more positive potentials; thus curve 2 (Al–In, 0.037%) and curve 3 (Al–In, 0.074%) merge into curve 1 for pure aluminium. As polarization potentials become more negative than −0.6 V, the Al–In alloy electrodes (curves 2 and 3) become activated and much higher currents then arise even for decreasing overpotentials. Similarly, for the Al–In (0.2%) electrode (curve 4), since the potential remains always more negative than −0.6 V, exceptionally active dissolution behaviour (*cf.* [8]) is observed. The small inflection seen in the polarization lines at about −0.85 V for electrodes exhibiting high anodic activity (for example, curves 3 and 4 in Fig. 3a) seem to correspond to incipient passivation which, however, is not completed in the manner seen in curves 2 and 3 of Fig. 3b.

It is also found that the Tafel lines for the Al–In (0.16%) alloy lie close to curve (4) in Fig. 3, (see Fig. 5) and the Tafel lines for Al–In (0.4%) are almost the same as that for Al–In (0.2%) (not shown here). The maximum solubility of indium in aluminium is 0.17%. Therefore, it appears that it is the soluble indium which contributes to the super-activation rather than second phases.
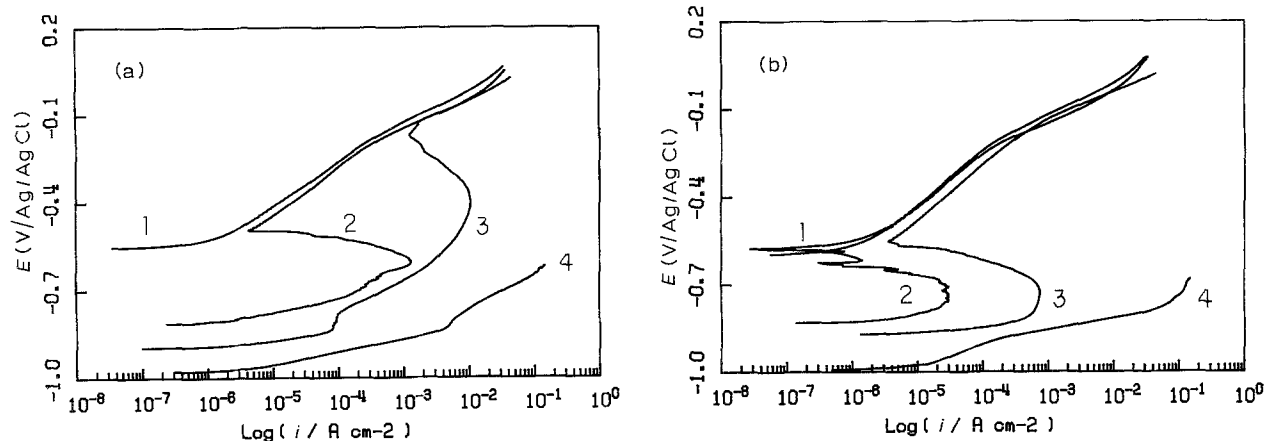

Fig. 3. Polarization curves for anodic dissolution of (1) Al (99.999%); (2) Al–In (0.037%); (3) Al–In (0.074%); and (4) Al–In (0.2%) in 1 M AlCl₃ in AN (all at 296 K). (a) and (b) show results of measurements in ascending and descending directions of potential change, respectively.
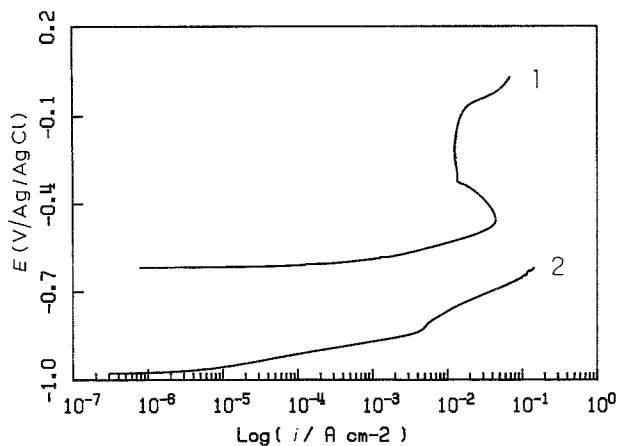
Fig. 4. *i-E* plots for anodic polarization of (1) pure In metal and (2) the Al-In (0.2%) alloy in 1 M AlCl$_3$ in AN (296 K).

The critical potential value of -0.6 V seems related to the anodic behaviour of the metal In in 1 M AlCl$_3$ (AN). Figure 4 shows Tafel lines for pure In (curve 1) and the Al-In (0.2%) alloy (curve 2) in 1 M AlCl$_3$ (AN). It is seen from Fig. 4 that anodic dissolution of the In electrode commences at about -0.6 V but a passivation process arises at about -0.4 V.

Therefore, one of the explanations for the critical potential of the activation effect in dissolution of the Al-In alloys is that that effect arises from In only, in the metallic form. When dissolution of In begins (or oxide films and/or complex compounds with solvent are formed), the In component loses its activating power. In other words, for exceptionally active dissolution of Al-In alloys to be maintained, only aluminium must be dissolving, i.e. In has to be kept unreacted at the alloy surface.

3.3.2. ESCA results. ESCA analysis results support the above explanation. For a freshly cut, unused Al-In (0.16 wt % or 0.042 at %) alloy surface, even after 5 min of ion sputtering, no In is observable by means of the ESCA technique, i.e. the surface concentration of In is lower than the detection level of the ESCA instrument. However, after the Al-In (0.16 wt %) alloy electrodes had been anodically polarized by means of potential sweeps taken between -1.0 and -0.6 V, and the total charge passed was equivalent to removal of an aluminium layer having a thickness of about 55 μm, significant amounts of In ($>$ 1 wt %) could be

Table 3. ESCA results on a previously polarized Al-In (0.04 at %) electrode

Atom %	O	C	Al	In	Cl
No sputtering	34.8	40.1	18.3	0.22	1.35
10 s sputtering	39.4	25.1	31.7	0.30	0.88
300 s sputtering	30.7	20.2	43.6	0.38	–

detected at the electrode surface by means of ESCA (see Table 3).

It is seen from Table 3 that the surface concentration of indium for the previously polarized Al-In (0.042 at %) alloy without sputtering is 0.22 at %, that is 5 times higher than the bulk indium concentration. After 10 s and 300 s of argon ion sputtering, the indium concentration even increased to 0.30 and 0.38 at %, respectively. These results indicate that the much higher concentration of indium on the surface was not due to surface contamination. The effect probably arises as a consequence of dissolution of aluminium, leaving an accumulation of the In component on the surface. However, the mechanism of the effects of the alloying element In is still unknown.

In Table 3, the surface carbon contents detected probably arise on account of contamination by organic solvents, since the amount of carbon is greatly reduced after 300 s sputtering. The oxygen contents are due to the formation of an oxide film on the surface during the preparation of the samples.

3.3.3. Rest potentials. The rest potentials (against Ag/AgCl) for Al-In alloys, and for pure Al and In electrodes in 1 M AlCl$_3$ (AN) are listed in Table 4. In our previous study [6] the rest potential of an Al electrode having a temporarily oxide-free surface, created by scraping the Al surface in the anhydrous non-aqueous solution, was found to be about -1.15 V with respect to Ag/AgCl. Here, the best o.c.p.'s realized for the Al-In (0.16 to 0.4%) alloys are evidently also quite negative and close to the above value (Table 4). The similarity of the rest potentials for Al-In alloy (0.16-0.40%) again provides strong evidence that the super-activation of Al-In alloy electrodes originates from the soluble indium rather than a second phase. (The maximum solubility of indium in aluminium is 0.17%.)

Table 4. The rest potentials (against Ag/AgCl) for Al-In alloys, pure Al and pure In electrodes in 1 M AlCl$_3$ (AN)

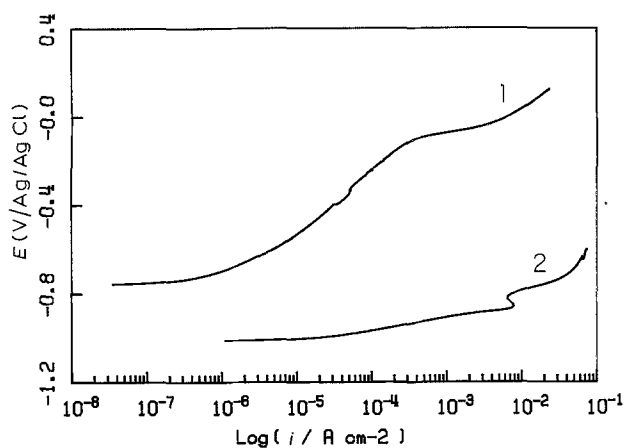| Electrode	$E(V)$ (for an electrode before dissolution reaction)	$E(V)$ (for an electrode under active anodic dissolution/conditions)
Al	-0.15	-0.64
In	-0.60	-0.58
Al-In (0.037%)	-0.27	-0.80
Al-In (0.074%)	-0.46	-0.89
Al-In (0.16%)	-0.81	-1.0
Al-In (0.2%)	-0.83	-1.0
Al-In (0.4%)	-0.91	-1.0

Fig. 5. *i-E* plots for anodic polarization of an Al–In (0.16%) anode in 1 M AlCl₃ in AN: (1) without bubbling of purified dry nitrogen (in presence of traces of oxygen); (2) with bubbling of purified dry nitrogen through solution for 20 ~ 40 min (displacing dissolved oxygen).

Fig. 6. *i-E* plots for anodic polarization of an Al–In (0.2%) alloy electrode in 0.6 M AlCl₃ in AN at four temperatures: (1) 293; (2) 268; (3) 253; and (4) 243 K.

3.3.4. Effects of traces of O_2 in the solution. The activity of the Al–In alloy electrodes is found to be sensitive to the presence of traces of oxygen in the solution, as illustrated by the results shown in Fig. 5 in which polarization curves for an Al–In (0.16%) electrode in 1 M AlCl₃ (AN) are plotted. Curve 1 in Fig. 5 was measured in the solution without bubbling of purified dry nitrogen (i.e. traces of oxygen were present) and is very similar to curve 1 in Fig. 3 for the pure aluminium electrode. The exceptional activity of the Al–In alloy electrode can be regained by bubbling purified dry nitrogen through the solution for 20–40 min to drive away traces of oxygen (see curve 2 in Fig. 5). This also suggests that the activation effect at Al–In alloys is associated with metallic indium which loses its exceptional activity when the In on the surface becomes itself oxidized (by oxygen, in this case).

Although the details of the mechanism of the activating effect of indium are unknown at the moment, it is unlikely that it can promote any chemical dissolution of passivating aluminium oxide films. Therefore the effect probably arises by the indium undermining any oxide film that is formed, allowing it to be displaced from the aluminium surface or promoting aluminium dissolution through a broken down film. Thus, the effect may be similar to that of a mercury drop placed on a scratched, dry aluminium surface which then burns in air.

3.3.5. Low temperature behaviour. It was found that Al–In alloy anodes exhibit good low temperature behaviour in AN (AlCl₃) solutions with respect to rapidity of anodic dissolution. Figure 6 shows Tafel lines for anodic polarization of an Al–In (0.2%) electrode in 0.6 M AlCl₃ in AN at four temperatures: (1) 293; (2) 268; (3) 253; and (4) 243 K, respectively.

Figure 6 demonstrates that the exceptionally active dissolution behaviour of the Al–In anode does not change appreciably as the temperature is lowered to 243 K. The polarization curves in Fig. 6 were *IR*ₛ
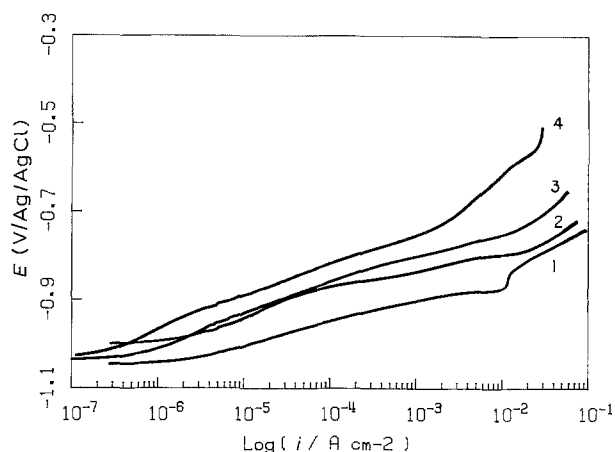
corrected; therefore, the effect of decrease of conductivity with lowering of temperature is excluded as a reason for the behaviour shown in Fig. 6.

The conductivity of 0.6 M AlCl₃ in AN was measured as a function as temperature and the results are shown in Fig. 7 which shows that conductivity of 0.6 M AlCl₃ in AN solution decreases apparently linearly with lowering of temperature but drops sharply at 223 K where the solution was found to have become frozen.

It was found that the electrochemical behaviour of the Al–In alloy anodes were very similar in 1 M AlCl₃ and 0.6 M AlCl₃ (AN) solutions, except that the *IR*ₛ-drop was, of course, rather greater in 0.6 M than in 1.0 M AlCl₃ (AN) solution.

3.3.6. Transient galvanostatic behaviour. Figure 8 shows galvanostatic anodic potential against time transients for an Al–In (0.16%) electrode in 0.6 M AlCl₃ (AN) polarized from zero current to three anodic current-densities: (1) 0.05; (2) 0.13; and (3) 0.26 A cm⁻². It is seen from Fig. 8 that the anode potentials are quite stable with time, and decline (only slightly) during the interval from $t = 0$ to $\simeq 20$ s. The curves in Fig. 8 suggest that the activation time for Al–In anode dissolution in AlCl₃ (AN) solution is negligibly short. It was reported [1] that "some time lag" was required for onset of superactivation of an Al–Ga (0.2%) in aqueous chloride solution but this is not observed in
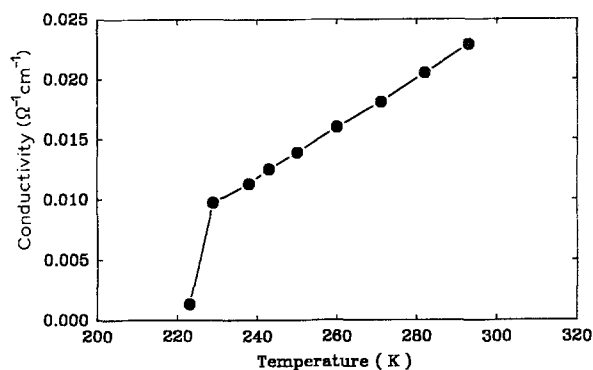

Fig. 7. Conductivity against temperature plot for 0.6 M AlCl₃ in AN electrolyte.

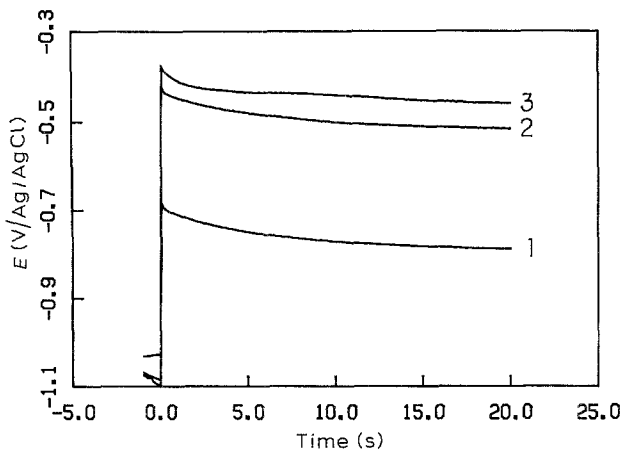Fig. 8. Galvanostatic transient anodic electrode potential against time plots for an Al–In (0.16%) electrode in 0.6 M AlCl₃ in AN for three current-densities: (1) 0.05; (2) 0.13; and (3) 0.26 A cm⁻².

the present case of a non-aqueous medium. This may be due to much thinner and simpler surface oxide films being present on the Al–In electrodes in the "anhydrous" AN (AlCl₃) solutions used in the present experiments, than in water, as indicated also by other aspects of the results reported in the present paper.

3.3.7. Surface morphology. Figure 9a and b show SEM pictures, at two magnifications, of the same location of the surface of an Al–In (0.2%) electrode

after it had been subject to polarization measurements by means of anodic sweeps taken between − 1.0 and − 0.6 V in 0.6 M AlCl₃ in AN solution. The total charge passed during the polarization measurements at the electrode shown in Fig. 9a and b was equivalent to removal of an aluminium layer having a thickness of about 60 μm. It is seen that the thickness of the aluminium layer removed during the experiment must have been much greater than the depths of the holes in the surface visible in Figs. 9a and b.

The morphology of the surface shown in Fig. 9a and b is different from that for pure aluminium electrodes used in the same solution; these have a much smoother surface with only some small pits as shown in our previous study [6]. It seems that the surface pattern in Fig. 9a was formed by dissolution of Al–In alloy in cubic-pit holes which overlap one another. Fig. 9b shows one of the cubic holes on the surface which has a much larger size (*ca.* 20 ×) than that observed on the surface of pure aluminium electrodes after anodic dissolution in aqueous KCl solutions, as shown in Fig. 9c (*cf.* [6]) for comparison.

It is interesting to note that a ripple pattern, with continuities across asperities and depressions, is seen clearly in Fig. 9b, and arises all over the surface; this may indicate that a layer structure had been formed during the anodic dissolution of the Al–In alloy, or that surface film cracking had occurred through stresses induced in the metal during the mechanical preparation of the alloy specimen.
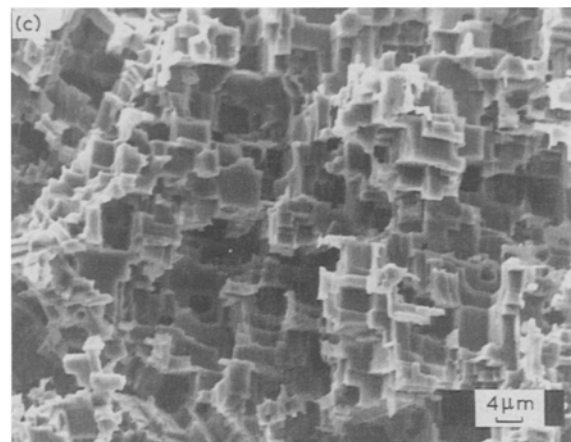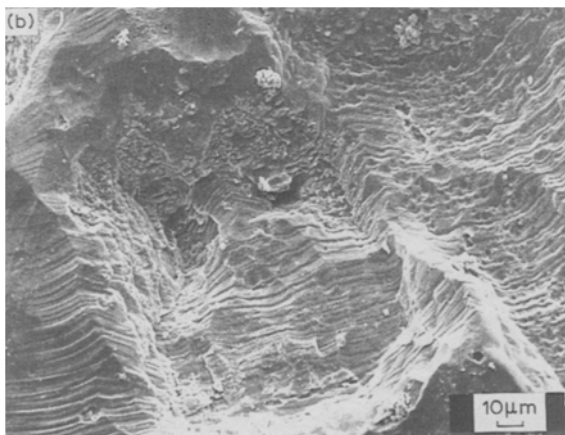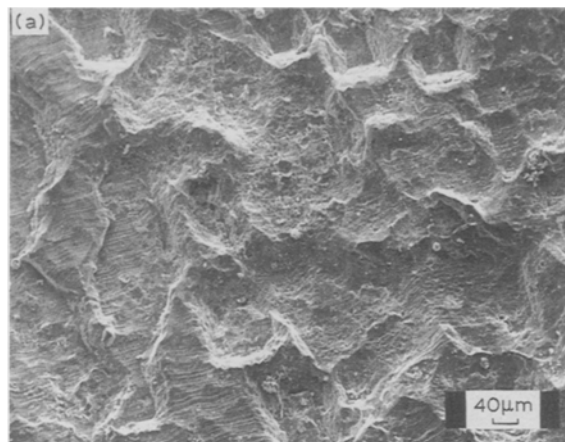

Fig. 9. SEM photographs, (a) and (b): for an Al–In (0.2%) electrode in 0.6 M AlCl₃ in AN solution; (c) for an Al (99.99%) electrode in 0.2 M KCl aqueous solution; which have been subjected to anodic polarization measurements.

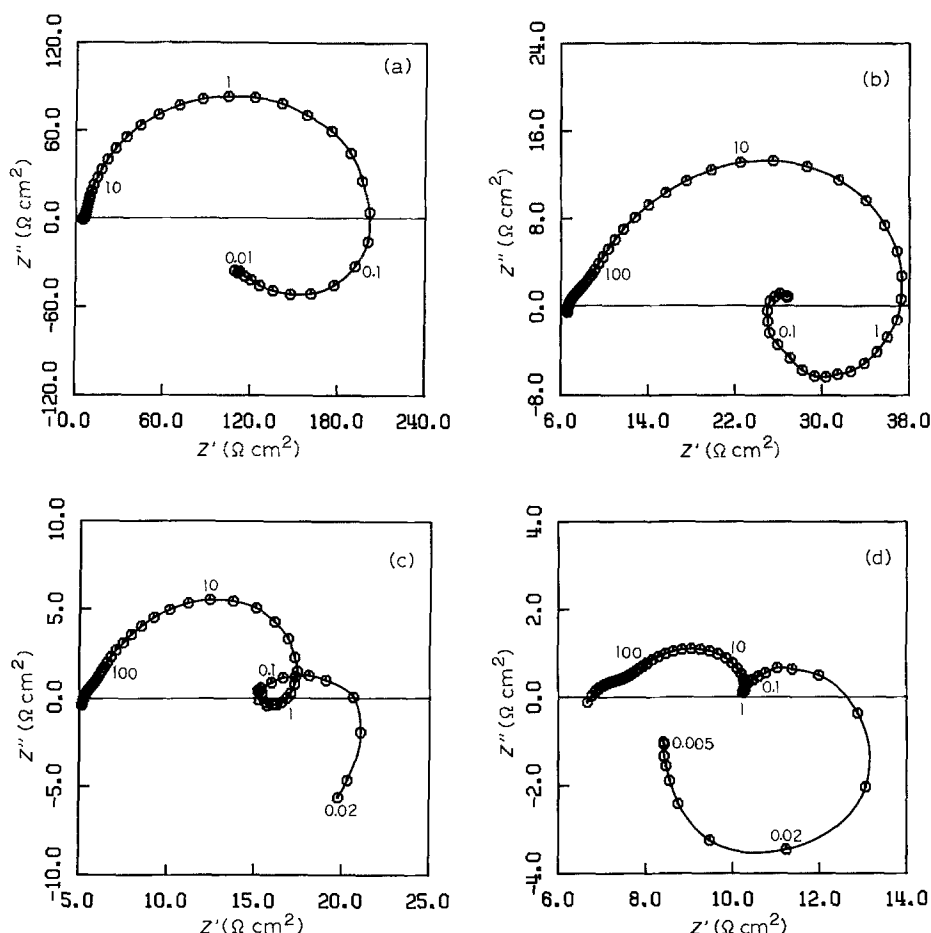Fig. 10. A.c. impedance complex plane (Z' against Z'') plots for an Al–In (0.2%) electrode in 1 M AlCl$_3$ in AN at: (a) $E = -0.95$ V, $i = 0.39$ mA cm^{-2}; (b) $E = -0.91$ V, $i = 1.9$ mA cm^{-2}; (c) $E = -0.82$ V, $i = 4.5$ mA cm^{-2}; and (d) $E = -0.78$ V, $i = 19.5$ mA cm^{-2}. The numbers indicate the respective frequencies (in hertz). (All at 296 K).

3.4. A.c. impedance spectra for anodically polarized Al–In (0.2%) electrodes

Figure 10 shows a.c. impedance complex plane Z' against Z'' plots for an Al–In (0.2%) electrode in 1 M AlCl$_3$ (AN) under the following conditions: (a) $E = -0.95$ V, $i = 0.39$ mA cm^{-2}; (b) $E = -0.91$ V, $i = 1.90$ mA cm^{-2}; (c) $E = -0.82$ V, $i = 4.5$ mA cm^{-2}; and (d) $E = -0.78$ V, $i = 19.5$ mA cm^{-2} where the i's are the indicated anodic 'd.c.' current-densities passing.

Each impedance spectrum in Fig. 10 consists of two to four loops in the complex-plane, including, remarkably, one or two 'pseudo-inductive' loops in the fourth quadrant. According to our recent theoretical analysis [13], this behaviour can indicate that two or three reaction intermediates, formed in the reaction interphase, may be involved in the reaction mechanism. We have shown that pseudo-inductive loops of the kind arising in Fig. 9 can be generated by the complexity of the potential-function representing the dependence of the surface concentration of the intermediates [6] in the interphase on potential (cf. MacDonald, [14]).

A recent study of Chechirlian et al. [15] pointed out that, in low conductivity media, the pseudo-inductive effect arising in impedance measurements could be a consequence of capacitative coupling between the

working, reference and counter-electrodes. In their studies, the electrolyte resistance had to be rather high, in the range KΩ–MΩ, for such coupling effects to arise. However, in the present systems, the electrolyte resistance was negligibly low (see Table 2) so that the 'cell coupling' effect of [15] is unlikely to be the reason for the observation of the pseudo-inductive loops in the present results which, in any case can be accounted for, in principle, according to the kinetic treatment in [13].

3.5. Behaviour of Al–Ga alloy electrodes

In aqueous electrolytes, superactivation of aluminium (binary alloy) anodes by the alloying activators decreases in the order [1]: Sn > Ga > In. It is surprising that the alloying elements Sn and Ga have little effect on the anodic polarization behaviour of the Al electrode in AlCl$_3$/AN, as shown in Fig. 2.

However, a temporary activation effect of gallium in the Al–Ga anodes was observed. This effect was not observed for the Al–In anodes. When the Al–Ga electrode was kept in the 1 M AlCl$_3$ (AN) solution on open-circuit, the rest potential became 'increased' slowly in the negative potential direction with time and a corresponding increase of activity took place. For example, Fig. 11 shows polarization curves for an Al–Ga, (0.26%) anode that had been kept on open-
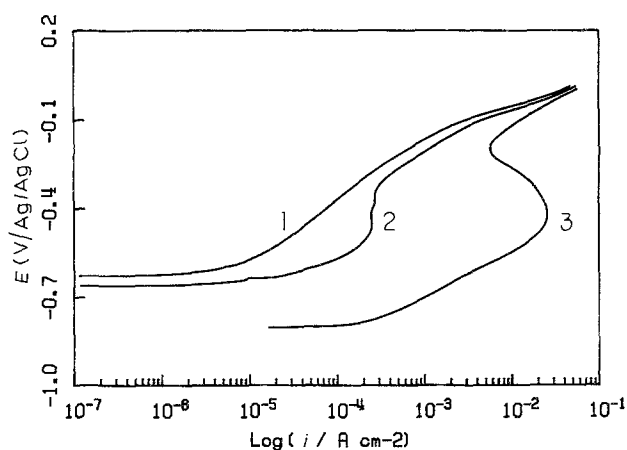
Fig. 11. *i-E* plots for anodic polarization of an Al-Ga (0.26%) anode after having been kept on open-circuit in 1 M AlCl₃ in AN solution for: (1) 1; (2) 100; and (3) 600 min (298 K).

circuit in 1 M AlCl₃ (AN) solution for (1) 1; (2) 100; and (3) 600 min. These results demonstrate that the longer the alloy is left on open-circuit, the better is the subsequent anodic activity of the Al-Ga anode in 1 M AlCl₃ (AN). However, this effect is only temporary: the Tafel data immediately after the measurements defining curves (2) and (3) in Fig. 11 fell on curve 1.

The temporary activation effect may be associated with a process of slow diffusion of Ga leading to its accumulation on the electrode surface, possibly forming a separate metal phase, as was indicated in the experiments by Tuck *et al.* [8, 16] on Al-Ga alloys in aqueous electrolytes. In the present work, the accumulated Ga on the surface may be removed by the continuing anodic polarization.

It was found that, at a higher temperature, 318 K, the temporary activation effect observed at the Al-Ga alloy on open-circuit became enhanced. This is consistent with an increase of the rate of gallium diffusion caused by the elevation of temperature.

4. Conclusions

1. An anhydrous solution of AlCl₃ (1 M) in CH₃CN provides an electrolyte having relatively high conductivity and excellent activity for anodic dissolution of aluminium and aluminium-alloys that is of interest for operation of an aluminium battery in non-aqueous medium.

2. Al-In alloy electrodes exhibit exceptionally active anodic dissolution performance with little polarization, in 1 M AlCl₃ in CH₃CN as solvent.

3. The activity of Al-In alloy anodes is found to depend on the concentration of the alloying element, indium. The best activity in 1 M AlCl₃ in CH₃CN solution for Al-In alloy anodes is attained at an indium concentration of 0.16–0.4 wt %.

4. The activation effect of the indium component seems to depend on it remaining in its metallic form on the alloy surface during anodic polarization. When the indium component starts itself to become oxidized or to dissolve, the Al-In alloy anodes lose their exceptional activity in dissolution.

5. Al-In alloy anodes exhibit good low temperature behaviour in AN (AlCl₃) solutions with respect to rapidity of anodic dissolution. The results of the transient galvanostatic experiments show that the activation time for Al-In anode dissolution in AN (AlCl₃) solution is negligibly short.

Acknowledgements

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