JOURNAL OF APPLIED ELECTROCHEMISTRY 17 (1987) 857–867

Electrochemical study of aluminium ion reduction in acidic $AlCl_3$–n-butyl-pyridinium chloride melts

YANNIS CHRYSSOULAKIS[1], JEAN-CLAUDE POIGNET[2], GEORGIA MANOLI[1]

[1]*Laboratory of Physical Chemistry and Applied Electrochemistry, National Technical University of Athens, 42 Patission Street, 10682 Athens, Greece*

[2] *Centre de Recherche en Electrochimie Minérale et en Génie des Procédés, INPG–ENSEEG, CNRS–Unité Associée 1212, Domaine Universitaire BP 75, 38402 St Martin d'Heres, France*

Received 20 August 1986; revised 15 December 1986

Electrochemical reduction of $AlCl_3$ dissolved in acidic $AlCl_3$–n-butyl-pyridinium chloride melt was studied by linear sweep voltammetry and chronopotentiometry at tungsten and platinum electrodes, in the $Al_2Cl_7^-$ concentration range 0.3 to 0.5 M between 30 and 60° C. $Al_2Cl_7^-$ bulk reduction was preceded by a nucleation (tungsten) or alloy formation phenomenon (platinum). The overall results agree rather well with the mechanism:

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

$$4Al_2Cl_7^- + 3e \rightleftharpoons Al + 7AlCl_4^-$$

The electrochemical reaction appeared quasi-reversible. Calculated values of the product of the transfer coefficient by the number of the electron exchanged in the rate determining step were in the range 0.45 to 0.7. Diffusion coefficients for $Al_2Cl_7^-$ were calculated.

1. Introduction

Within the framework of a research programme for low-temperature aluminium plating electrolytes [1, 2] we undertook the electrochemical study of the reduction of aluminium ions in $AlCl_3$–BPC (n-butyl-pyridinium chloride) molten mixtures between 30 and 60° C.

The electrochemical behaviour of aluminium in these electrolytes has already been investigated by Robinson and Osteryoung [3] and more recently by Qui-Xian-Quin and Skyllas-Kazakos [4]. A comprehensive review of the physicochemical properties of these electrolytes has been given by Hussey [5]. The 1 : 1 melt contains BP^+, $AlCl_4^-$, $Al_2Cl_7^-$ and Cl^- ions. The equilibrium constant, k, for the reaction

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

determined potentiometrically by Gale and Osteryoung [6] and Schoebrechts and Gilbert [7] is $\simeq 3 \times 10^{-14}$ at 30° C. At this temperature the Cl^- and $Al_2Cl_7^-$ ion concentrations lie in the range 10^{-6} to 10^{-7} M, whereas the BP^+ and $AlCl_4^-$ ion concentrations, calculated using the value of the melt density [8], are 4 M.

Any $AlCl_3$ added to the 1 : 1 melt complexes with $AlCl_4^-$ to $Al_2Cl_7^-$, whereas the Cl^- ion concentration becomes extremely small (10^{-13}–10^{-14} M). In the composition range between the 1 : 1 and 2 : 1 melts, BP^+ and $AlCl_4^-$ are major components and the $Al_2Cl_7^-$ concentration can vary from about 10^{-7} to 3 M (for the 2 : 1 melt). In the vicinity of the 2 : 1 composition the $AlCl_4^-$ concentration becomes very small and beyond this composition $Al_3Cl_{10}^-$ ions are known to exist [9].

Robinson and Osteryoung [3], using linear sweep voltammetry and chronopotentiometry at tungsten, platinum and vitreous carbon electrodes in the 6×10^{-3} to 0.32 M $Al_2Cl_7^-$ concentration range, proposed a mechanism involving the diffusion-controlled reduction of $Al_2Cl_7^-$ ions preceded by an aluminium nucleation phenomenon. Qui-Xian-Quin and Skyllas-Kazakos [4], using chronopotentiometry at platinum and vitreous carbon electrodes in the 0.28 to 1 M $Al_2Cl_7^-$ concentration range, suggested an $Al_2Cl_7^-$ reduction step complicated by a catalytic mechanism. We present here a linear sweep voltammetric study, with a few chronopotentiometric experiments at tungsten and platinum electrodes in the 0.3–0.5 M $Al_2Cl_7^-$ concentration range, beyond which the $Al_2Cl_7^-$ content would be too high for the general laws of voltammetry and chronopotentiometry to be applicable.

2. Experimental details

2.1. *Preparation of BPC and $AlCl_3$*

The n-butyl-pyridinium chloride was synthesized from pyridine (Fluka puriss.) and butylchloride (Fluka puriss.), reacted at 60–80° C for several hours. The salt was recrystallized twice and the precipitation was completed by ethyl acetate addition. The product was then washed with ethyl acetate and finally dried under a hot argon flux. $AlCl_3$ was a Prolabo RP product further sublimated. Weighings, salt mixing and electrochemical determinations were performed inside a glove box under an argon atmosphere. The molten mixtures were colourless but became slightly brown after a few hours.

The *IR* spectrum of the 1 : 1 melt was identical to that published by Gale and Osteryoung [10].

2.2. *Electrodes*

The tungsten electrode ($S = 1.89 \times 10^{-2}\,cm^2$) was the cross-section of a tungsten wire embedded in a Pyrex tube and polished using alumina; the platinum electrode ($S = 0.22\,cm^2$) was a cylindrical wire, 0.5 mm in diameter; and the reference electrode was a pure aluminium Prolabo rod immersed in the 2 : 1 $AlCl_3$–BPC mixture.

Because of the rather low electrical conductivity of the melts ($\gamma \simeq 6 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ at 25° C for the 1 : 1 mixture [5]) we separated the reference compartment from the main compartment using a Luggin capillary reaching close to the working electrode, with one extremity closed by quartz wool.

2.3. *Instrumentation*

Electrical signals were delivered by a PAR model 176 potentiostat monitored by a PAR model 175 programmer. The curves were recorded using either a Nicolet digital oscilloscope or a Hewlett-Packard X–Y recorder.

3. Results and discussion

3.1. *Building-up of voltammograms*

Fig. 1 shows how the voltammograms at a

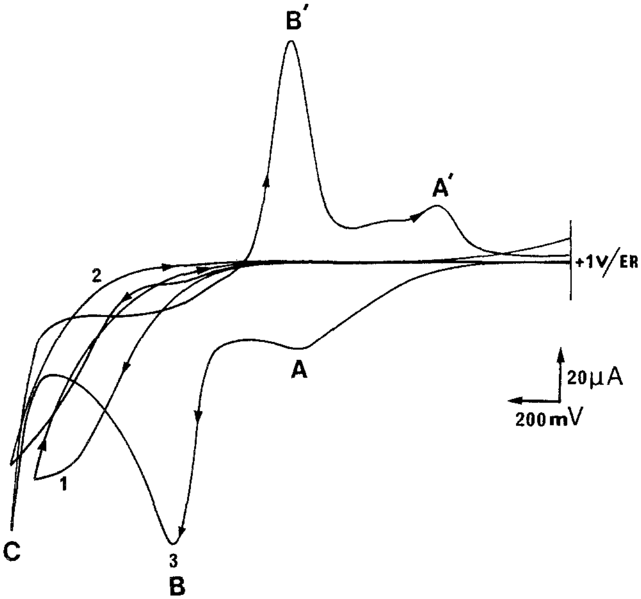

Fig. 1. Voltammograms obtained at the tungsten electrode for successive additions of small quantities of $AlCl_3$ to the 1 : 1 melt at 52° C. Scan rate, $0.2\,V\,s^{-1}$ $AlCl_3$ content increases from a few 10^{-2} M (curves 1 and 2) to 0.12 M (curve 3).

tungsten electrode changed qualitatively on addition of a few mg $AlCl_3$ to about 10 g of the 1 : 1 mixture at 30° C. For very small quantities of $Al_2Cl_7^-$ ions (a few 10^{-2} M $Al_2Cl_7^-$, curves 1 and 2, to 0.12 M, curve 3) only one reduction wave was observed, with no reoxidation peak. When the $Al_2Cl_7^-$ concentration reached a sufficient value (0.12 M, curve 3) the voltammogram began to exhibit two main reduction peaks labelled A and B (Fig. 1) situated at about 0 V and −0.480 V versus the aluminium reference electrode, respectively, and two corresponding reoxidation peaks B′ (at about −0.04 V) and A′ (at about +0.5 V). Wave C, at about −1 V, is the solvent reduction wave and care had to be taken to reverse the potential scanning before that wave, otherwise reaction products would modify the value of the electrode area.

3.2. *Comparison of voltammograms at tungsten and platinum electrodes (Fig. 2)*

Fig. 2 shows two voltammograms obtained at tungsten (curve 1) and platinum (curve 2) electrodes for an $Al_2Cl_7^-$ concentration of 0.39 M. For both electrodes the reduction peak intensities of wave A appeared independent of $Al_2Cl_7^-$ concentration and were small compared to the main reduction peak intensity (wave B). In agreement with Robinson and Osteryoung [3] we can say that peak B corresponds to the reduction of Al(III) ions. The shapes of waves B, when the slope varies abruptly, indicate that on both electrodes the reaction product has constant activity. Long-time electrolysis has been performed at the potential of peak B and it was found that the reaction product is aluminium. The corresponding reoxidation peaks B′ are therefore aluminium stripping peaks. The potential difference between the anodic and the cathodic peaks, $|Ep_a - Ep_c|$, which is about 0.3 V, indicates that the electrochemical process is not reversible.

The main difference between the two curves is that before peak B the current intensity rises slowly and continuously at the platinum electrode (and not at the tungsten electrode), which could mean some platinum–aluminium alloy formation [3]. Furthermore, aluminium deposition appears slightly more difficult on platinum than on tungsten (Ep_c is 50 mV more cathodic at platinum than at tungsten; Ep_a is 25 mV more anodic at platinum than at tungsten).

Because of the different values of electrode

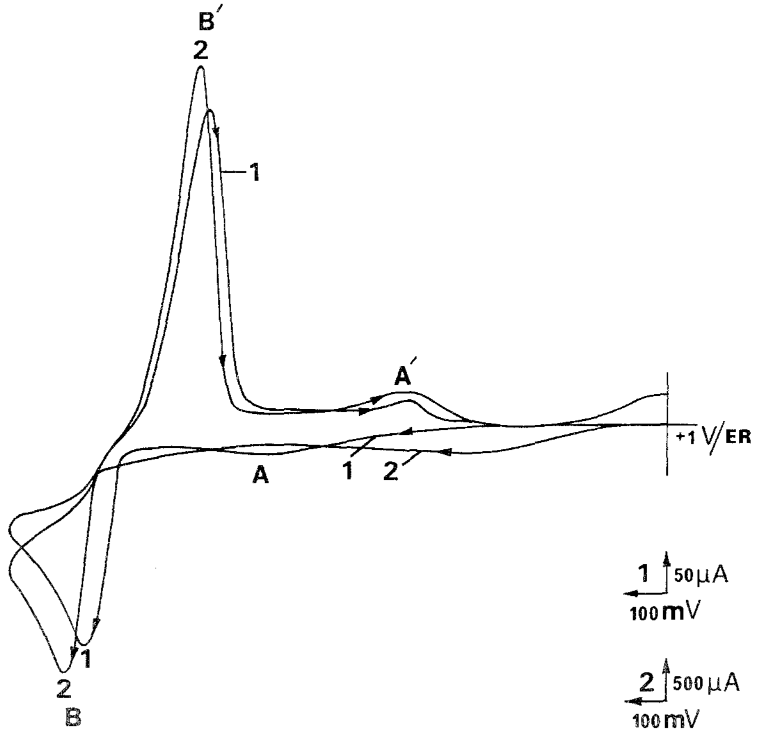

Fig. 2. Comparison of voltammograms at the tungsten electrode (curve 1) and the platinum electrode (curve 2) at 52° C. Scan rate, 0.2 V s^{-1}; $Al_2Cl_7^-$ concentration, 0.39 M.

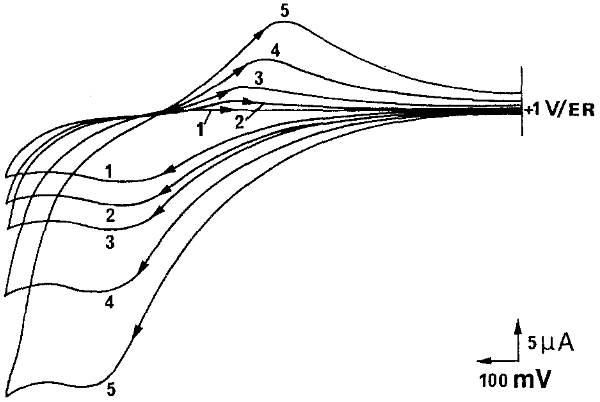

Fig. 3. Voltammograms at the tungsten electrode in the region of the first peak, at 52° C. Scan rates ($V s^{-1}$): curve 1, 0.05; curve 2, 0.1; curve 3, 0.2; curve 4, 0.5; curve 5, 1.0. $Al_2Cl_7^-$ concentration, 0.39 M.

area, the current intensities are about ten times larger at the platinum than at the tungsten electrode. It is therefore clear from Fig. 2 that ohmic drop contributes very little to the shape of the voltammograms.

3.3. *Analysis of peaks A/A′*

3.3.1. Tungsten electrode. Fig. 3 shows different voltammograms for various values of the scan rate. The current intensities of the reduction peak are proportional to $v^{1/2}$ rather than v as was observed by Robinson and Osteryoung [3], who proposed an underpotential reduction of aluminium with some surface layer formation prior to bulk aluminium deposition. We have no explanation as to how such a process could be diffusion controlled.

3.3.2. Platinum electrode. In agreement with the above authors, we observe that along wave A (Fig. 2) the current intensity rises continuously with no distinct peak. Such a wave may be ascribed to platinum–aluminium alloy formation. The wave that starts from about 0.9 V versus the aluminium reference electrode is probably due to the reduction of residual HCl.

3.4. *Analysis of aluminium bulk deposition peaks B*

Fig. 4a and b shows voltammograms for different values of scan rate for platinum and tungsten electrodes. For both electrodes the ratio $i_p/v^{1/2}$ (Table 1) decreases slightly when the scan rate increases, which could be consistent with a CE or catalytic mechanism, or due to quasi-reversible charge transfer [11]. In the present case the very low value of the Cl^- ion concentration precludes single reduction reaction such as:

$$Al_2Cl_7^- + 6e \rightleftharpoons 2Al + 7Cl^- \qquad (2)$$

or

$$AlCl_4^- + 3e \rightleftharpoons Al + 4Cl^- \qquad (3)$$

Such reactions would produce a large increase in Cl^- ion concentration at the electrode surface, make the electrolyte locally basic and hence the current densities extremely low, because the Al(III)/Al equilibrium potential is less than −1 V versus the aluminium reference electrode in basic melts. We must therefore assume the interference of a Cl^- consuming chemical reaction such as:

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^- \qquad (4)$$

Consequently it is reasonable to suggest, after other authors [3, 4], an electrochemical reaction in which Cl^- ions do not take part:

$$4Al_2Cl_7^- + 3e \rightleftharpoons 7AlCl_4^- + Al \qquad (5)$$

We propose an overall mechanism involving Reactions 4 and 5 for the electrochemical reduction of $Al_2Cl_7^-$ ions in the present experimental conditions. The $AlCl_4^-$ concentration is only a few times larger than that of the $Al_2Cl_7^-$ ions. Therefore, variations of $AlCl_4^-$ activity may affect the shape of the voltammograms or chronopotentiograms.

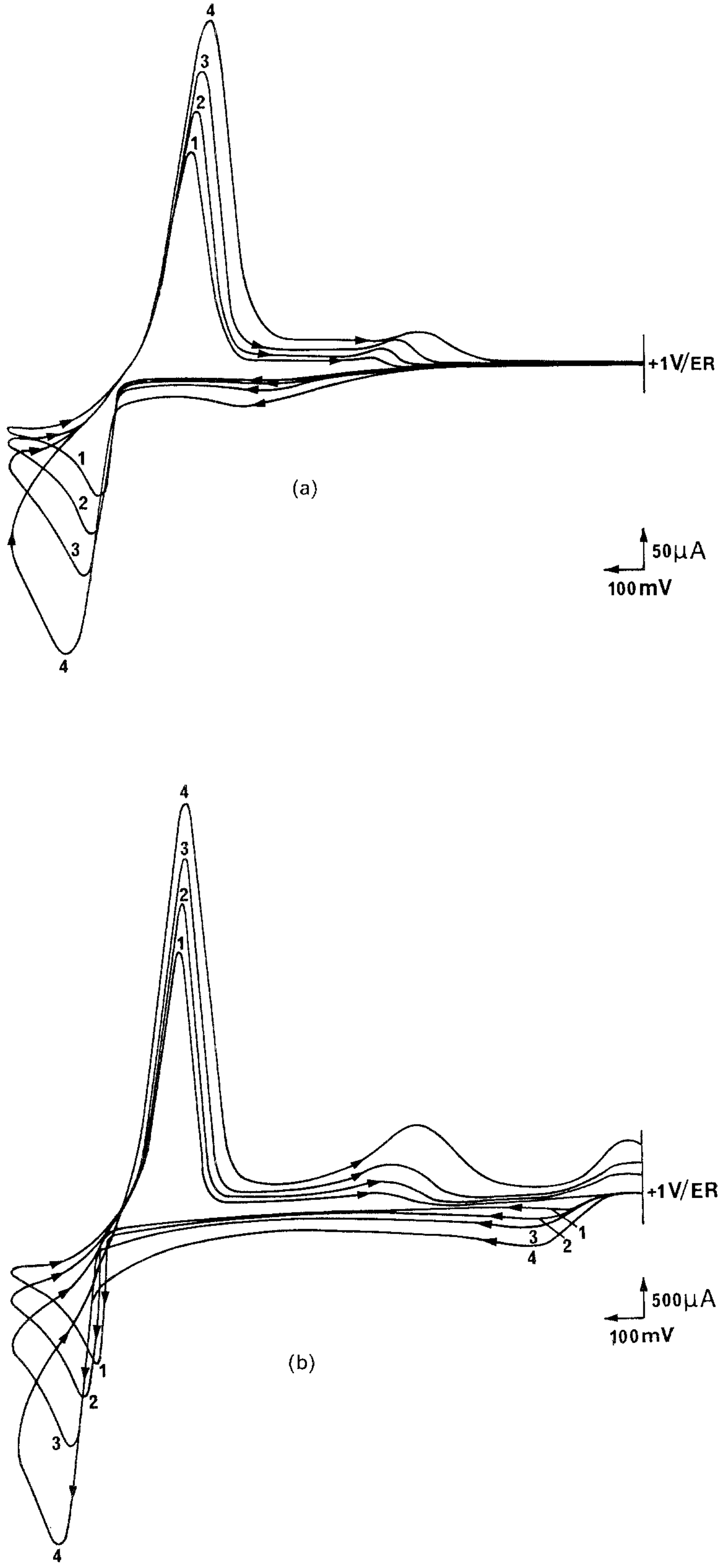

Fig. 4. Voltammograms at the tungsten electrode (Fig. 4a) and platinum electrode (Fig. 4b) at 52° C. Scan rates (V s^{-1}): curve 1, 0.05; curve 2, 0.1; curve 3, 0.2; curve 4, 0.5. $Al_2Cl_7^-$ concentration, 0.39 M.

Table 1. Values of i_{p_c}, i_{p_a}, $i_{p_c}/v^{1/2}$, i_{p_a}/i_{p_c}, Ep_c, Ep_a, $|Ep_c - Ep_a|$, $|Ep_{c/2} - Ep_c|$ *for various values of the scan rate, at 52° C, at tungsten and platinum electrodes.* $Al_2Cl_7^-$ *concentration, 0.39 M*

Electrode	*Curve number*	i_{p_c} ($mA\ cm^{-2}$)	i_{p_a} ($mA\ cm^{-2}$)	v ($V s^{-1}$)	$v^{1/2}$ ($V^{1/2} s^{-1/2}$)	$i_{p_c}/v^{1/2}$ ($mA\ cm^{-2}\ V^{-1/2} s^{1/2}$)	i_{p_a}/i_{p_c}	$-Ep_c$ (*V*)	$-Ep_a$ (*V*)	$\|Ep_c - Ep_a\|$ (*V*)	$\|Ep_{c/2} - Ep_c\|$ (*V*)
Platinum	1	7.727	14.091	0.050	0.2236	34.557	1.824	0.39	0.13	0.26	0.030
	2	8.864	16.591	0.100	0.3162	28.033	1.872	0.41	0.12	0.29	0.040
	3	10.795	19.091	0.200	0.4472	24.139	1.768	0.44	0.12	0.32	0.048
	4	13.977	22.500	0.500	0.7071	19.767	1.610	0.48	0.11	0.37	0.065
Tungsten	1	7.407	12.434	0.050	0.2236	33.126	1.679	0.36	0.125	0.235	0.045
	2	9.524	15.079	0.100	0.3162	30.120	1.583	0.38	0.115	0.270	0.042
	3	12.169	17.725	0.200	0.4472	27.211	1.457	0.41	0.100	0.310	0.063
	4	15.873	21.164	0.500	0.7071	22.448	1.333	0.45	0.075	0.375	0.080

3.5. *Analysis of the $Al_2Cl_7^-$ reduction peaks by classical criteria [11]*

Table 1 gives the values of the quantities Ep_c, $|Ep_a - Ep_c|$ and $|Ep_c - Ep_{c/2}|$ for four values of the scan rate. The corresponding curves are plotted in Fig. 5a (tungsten electrode) and 5b (platinum electrode).

Extrapolation to $v = 0$ yields the following values, corrected for ohmic drop.

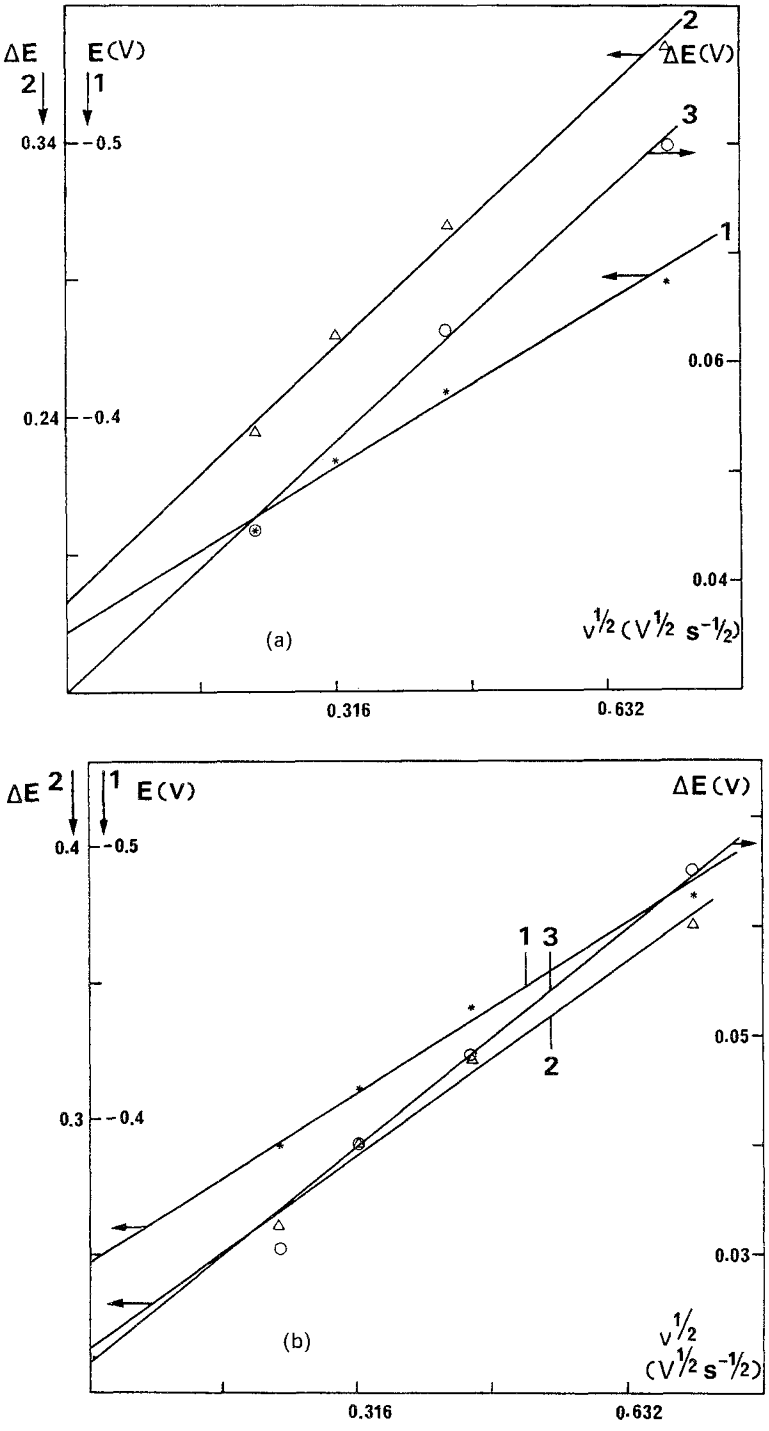

Fig. 5. Plots of Ep_c (curve 1), $|Ep_a - Ep_c|$ (curve 2) and $|Ep_c - Ep_{c/2}|$ (curve 3) as a function of $v^{1/2}$. (a) Tungsten electrode; (b) platinum electrode. $Al_2Cl_7^-$ concentration, 0.39 M at 52° C.

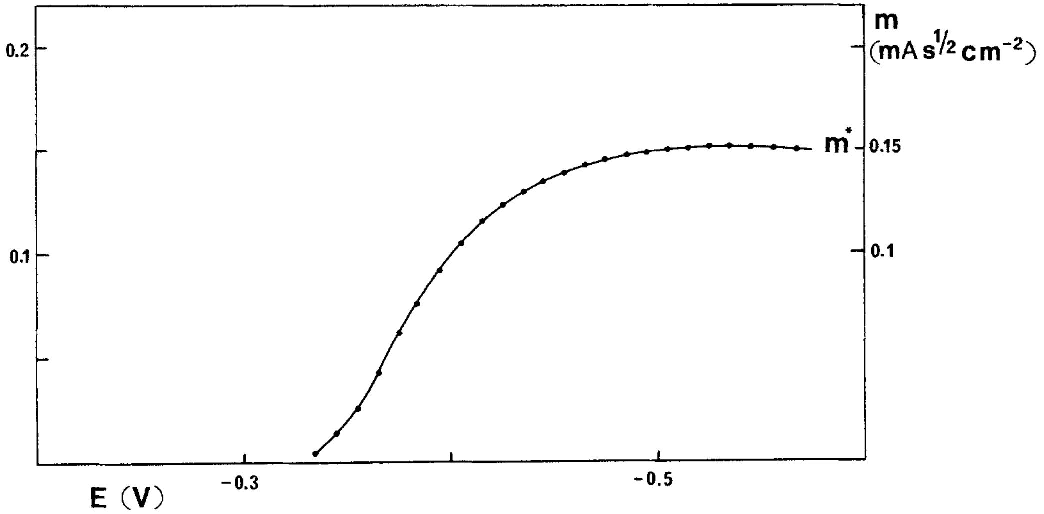

Fig. 6. Convolution analysis of $Al_2Cl_7^-$ bulk reduction peak at the tungsten electrode: $m(E)$ plot at 52° C. Scan rate, 0.2 V s^{-1}; $Al_2Cl_7^-$ concentration, 0.39 M.

Platinum electrode:

$Ep_c = -0.347\,V$

$|Ep_a - Ep_c| = 0.216\,V$

$|Ep_c - Ep_{c/2}| = 0.020\,V$

Tungsten electrode:

$Ep_c = -0.322\,V$

$|Ep_a - Ep_c| = 0.173\,V$

$|Ep_c - Ep_{c/2}| = 0.030\,V$

At both electrodes, the values of $|Ep_a - Ep_c|$ indicate that the reaction is of the quasi-reversible type (in the reversible case the values of $|Ep_a - Ep_c|$ would be about 0.02 V). From the values of $|Ep_c - Ep_{c/2}|$, with the gross approximation of the 'reversible insoluble' case, we can calculate that $an_a \simeq 0.7$ for the tungsten electrode, and $an_a \simeq 1$ for the platinum electrode, where a is the cathodic transfer coefficient and n_a is the number of electrons exchanged in the rate-determining step. The correct values, since the process is not reversible, are probably lower.

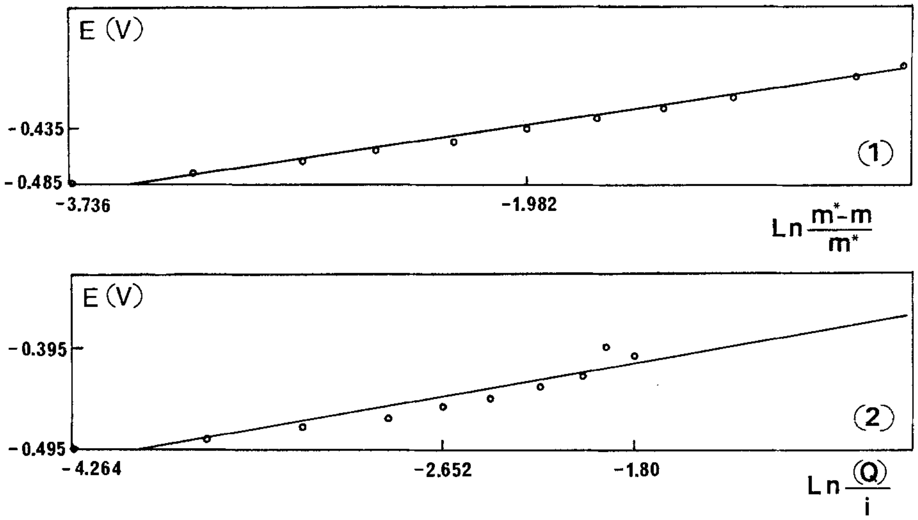

Fig. 7. E–m variations at 52° C. $Al_2Cl_7^-$ concentration, 0.39 M. (1) $E = f(\ln m^* - m/m^*)$ (reversible insoluble case). (2) $E = f(\ln Q/i)$; $Q = m^* - m[1 + \exp nF(E - E_{1/2})/RT]$.

Finally, the values of i_{p_a}/i_{p_c} (Table 1) are always larger than unity, as expected when the reaction product is insoluble.

3.6. *Evaluation of the diffusion coefficient of $Al_2Cl_7^-$ ions*

Plots of the cathodic peak intensity, Ip_c, versus the $Al_2Cl_7^-$ concentration (from 0.3 to 0.5 M) gave straight lines, which did not pass through the origin because the concentrations were slightly altered by unavoidable moisture inside the glove box; from the slope of these straight lines, using the 'reversible–insoluble' equation, the diffusion coefficient, $D_{Al_2Cl_7^-}$, at 52° C was calculated to be $2.5 \times 10^{-7} cm^2 s^{-1}$ at the tungsten electrode, and $2.3 \times 10^{-7} cm^2 s^{-1}$ at the platinum electrode. These values agree reasonably with the values given by Robinson and Osteryoung [3], which fall in the range 4.2×10^{-7} to $5.2 \times 10^{-7} cm^2 s^{-1}$ at 60° C. These values are reduced to between 3.2×10^{-7} and $4 \times 10^{-7} cm^2 s^{-1}$ at 52° C using an activation energy value of 29 kJ mol^{-1} estimated from [5].

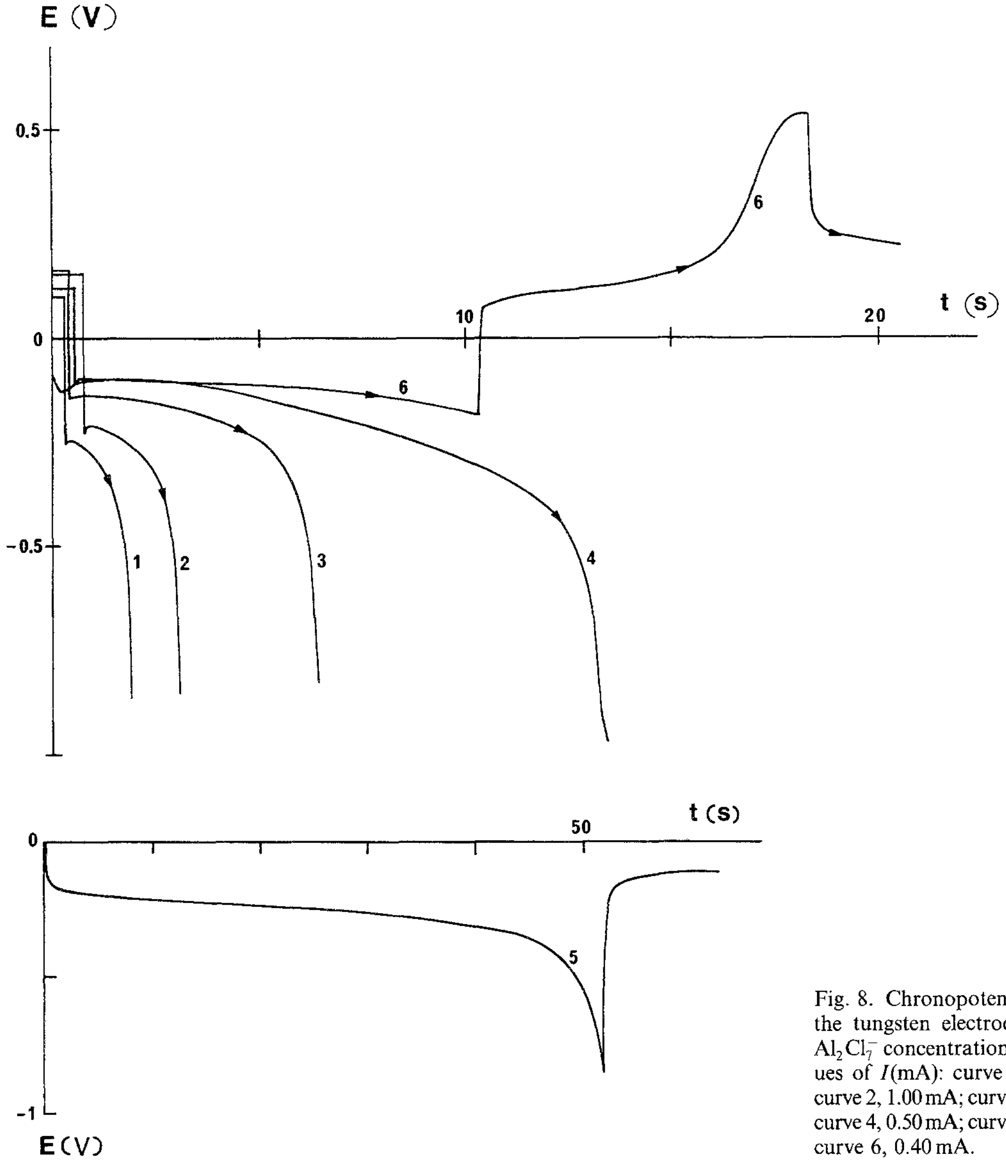

Fig. 8. Chronopotentiograms at the tungsten electrode at 30° C. $Al_2Cl_7^-$ concentration, 0.5 M. Values of I(mA): curve 1, 1.50 mA; curve 2, 1.00 mA; curve 3, 0.75 mA; curve 4, 0.50 mA; curve 5, 0.25 mA; curve 6, 0.40 mA.

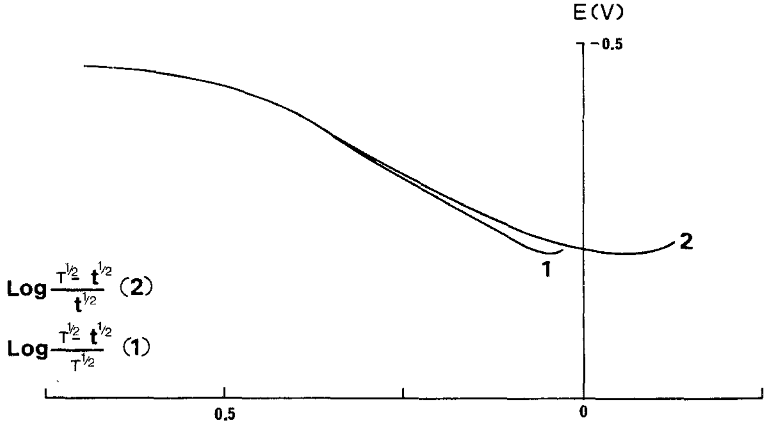

Fig. 9. Logarithmic analysis of the chronopotentiograms at the tungsten electrode at 30° C. Curve 1, insoluble case; curve 2, soluble case. $Al_2Cl_7^-$ concentration, 0.5 M.

3.7. *Convolution analysis of the $Al_2Cl_7^-$ reduction peak at the tungsten electrode*

Fig. 6 shows the plot of m (convolution transform of the $I(t)$ data) versus the electrode potential, E:

$$m(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} \, du$$

The shape of this curve, ending in a plateau, m^*, indicates that mass transfer can be considered as diffusion controlled.

A plot of E versus $\ln(m^* - m/m^*)$ and $\ln(Q/i)$ is given in Fig. 7. These two plots correspond respectively to the reversible insoluble case and the quasi-reversible case. The corresponding plots are not perfectly linear. From the slopes of the least squares fitted straight line it was calculated that $an_a = 0.78$ for the reversible insoluble case, and $an_a = 0.71$ for the quasi-reversible case.

3.8. *Chronopotentiometric determinations at the tungsten electrode*

A few chronopotentiograms obtained at 30° C (0.5 M $Al_2Cl_7^-$) are shown in Fig. 8. Most of the chronopotentiograms exhibit a nucleation phenomenon at their beginning.

In the transition time range investigated (from $\tau = 1.7$ s to $\tau = 50$ s) the product $I\tau^{1/2}$ was constant. Fig. 9 shows the plot of E versus $\log \tau^{1/2} - t^{1/2}/t^{1/2}$ and $\log \tau^{1/2} - t^{1/2}/\tau^{1/2}$ corresponding respectively to the cases of the soluble and insoluble product. The best straight line was obtained in the case of the insoluble product (curve 1), but the 'soluble' criterion cannot be completely ruled out. This can be ascribed to a partial soluble character because of $AlCl_4^-$ activity variations, as already mentioned in Section 3.4. From the slope of the straight line, it was calculated that $an_a = 0.45$. This value is in good agreement with the value of 0.46 given by Robinson and Osteryoung [3] and the value of 0.48 given by Qui-Xian-Quin and Skyllas-Kazakos [4].

The current reversal chronopotentiogram (Fig. 8, curve 6) shows that aluminium produced at the electrode undergoes some corrosion because the reoxidation time is less than the reduction time. This has been previously observed [3, 4].

References

[1] Y. Chryssoulakis, S. Kalogeropoulou, A. Protopappa and G. Manoli, *J. Appl. Electrochem.* **19** (1986) 196.

[2] Y. Chryssoulakis, J. C. Poignet and G. Manoli, *Métaux Corros. Ind.*, in press.

[3] J. Robinson and R. A. Osteryoung, *J. Electrochem. Soc.* **127** (1980) 122.

[4] Qui-Xian-Quin and M. Skyllas-Kazakos, *J. Electroanal. Chem.* **168** (1984) 193.

[5] C. L. Hussey, in 'Advances in Molten Salt Chemistry', Vol. 5 (edited by Gleb Mamantof), Elsevier (1983) p. 185.

[6] R. J. Gale and R. A. Osteryoung, *J. Electrochem. Soc.* **127** (1980) 2167.

[7] J. P. Schoebrechts and B. P. Gilbert, *ibid.* **128** (1981) 2679.

[8] R. A. Cappio, L. A. King, R. E. Lindstrom, J. C. Nardi and C. L. Hussey, *ibid.* **126** (1979) 1644.

[9] L. Heerman and W. D. Olieslager, Journées d'Etudes des Sels Fondus, Extended abstracts, Padova (1985).

[10] R. J. Gale and R. A. Osteryoung, *Inorg. Chem.* **19** (1980) 2240.

[11] Southampton Electrochemistry Group, in 'Instrumental Methods in Electrochemistry', Ellis Horwood (1985) p. 191.