Electrochemical Behavior of AlCl₃ In Propylene Carbonate at Room Temperature

By G. Manoli, Y. Chryssoulakis & C. Tsintavis

The electrochemical behavior of AlCl₃ in propylene carbonate at 25 °C was studied by triangular sweep voltammetry with platinum electrodes. The overall mechanism is in agreement with the well-known E_rC_i reaction scheme:

$$\mathbf{O} + \mathbf{n}\mathbf{e}^{-} \stackrel{\mathbf{k}_{1}}{\underset{\mathbf{k}_{-1}}{\rightleftharpoons}} \mathbf{R}$$
$$\mathbf{R} \stackrel{\mathbf{k}_{f}}{\longrightarrow} \mathbf{Z}$$

with O: Al(III), where the electrochemical step reflects a quasi-reversible behavior and the following chemical reaction shows a first-order rate. The apparent electron transfer coefficient αn_{α} (where α is the transfer coefficient, and n_{α} is the number of electrons exchanged in the rate determining step) is evaluated at 0.24 ± 0.055 by semi-integration of the voltammetric E = f(I) curves. The first-order rate constant of the chemical step was calculated and found to be $k_f \cong 5$ /sec. The absence of aluminum deposited on the cathode was confirmed by scanning electron microscopy on electrodes that were polarized at E = -0.65 V/RE for as many as eight hr.

As an epilogue to the framework of a research program for aluminum plating of electrodes^{1.4} in organic electrolytes (dimethylsulfoxide, n-butylpyridinium chloride, propylene carbonate) at room temperature, the study of the electrochemical behavior of AlCl₃ in propylene carbonate (PC) at 25 °C was undertaken.

In the case of dimethylsulfoxide, the results obtained were not reproducible, so no reaction mechanism has been proposed. Voltammetric and chronopotentiometric data showed the contribution of both adsorption and diffusion to the kinetic scheme, as well as the solubility of the reduction product.^{1,2} Concerning the electrochemical reduction of AlCl₃ in acidic AlCl₃-n-butylpyridinium chloride, it was proven that it occurs via a quasi-reversible reaction with αn_{α} between 0.45 and 0.7.^{3,4}

In this study, the electrochemical reduction of aluminum in propylene carbonate using Pt electrodes has been investigated using triangular sweep voltammetry. Semi-integral analysis was used to calculate the number of electrons exchanged during the electrochemical reaction. Finally, a reaction mechanism was proposed, taking into consideration the characteristic criteria proposed by Nicholson *et al.*,⁵ as well as comparing experimental voltamperometric curves with theoretical ones calculated for the proposed reaction scheme.





Fig. 1c—Voltammograms at a Pt electrode in PC, TEAP 10² M, AlCl₃ 0.067 M, q = 25 °C for various scan rates. Scan rate, V/ sec: (7) 0.50, (8) 0.80, (9) 1.00.

Experimental Procedure Chemicals

The propylene carbonate was a commercially available reagent grade, stored in a dark column with molecular sieves under high-purity dried argon. The AlCl₃ was further sublimated,⁶ while tetraethyl ammonium perchlorate (TEAP) was used as electrolyte salt. AlCl₃ and TEAP were dissolved in the PC solution in a glove box under dried argon.

Electrodes and Cell

All of the voltammetric work employed a platinum working electrode, $S = 0.785 \text{ mm}^2$, made from a Pt 5N wire sealed inside a glass tube. The reference electrode was Ag/AgClO₄, 0.01 M, as described by Kirowa-Eisner *et al.*⁷ All potentials reported in this study are measured vs. this reference electrode. The counter electrode was a pure aluminum 5N foil, $S = 2 \text{ cm}^2$. The electrolysis cell has been previously described.¹ Oxygen was removed by flushing the solution with dried argon for 10 min prior to each series of measurements, and the argon blanket was maintained over the solution throughout the experiment.

Instrumentation

Electrical signals were delivered by a potentiostat. The curves were recorded using either an X-Y recorder or a digital oscilloscope.



Procedures

The peak currents during triangular voltammetry were measured using, two different procedures. The first was the graphic procedure, where the difference between the peak current and the current base line was measured. In the second procedure, the difference between the peak current and the decaying base line obtained by holding the potential value constant at the foot of the wave, was measured. The second method is generally accepted as more reliable, because it eliminates faradaic currents and permits measurement of the reverse wave peak current.^{8,9} In most cases, however, the two methods provided quasi-identical results. The peak potentials were measured directly, and the error limits are standard deviations of at least five different experiments.

Results & Discussion

Build-up of Voltammograms

The voltammograms obtained at a Pt electrode for a PC solution containing 10^{-2} M TEAP, 6.7 x 10^{-2} M AlCl₃ at 25 °C for various scan rates are presented in Fig. 1a, b, c. For a scan rate v = 0.01 V/sec, the voltammogram exhibits a cathodic

	Table 1
Experimental Values of E_{pc} , E_{pa} , $\left I_{pc}\right $, I_{pa} ,	$\left \left \mathbf{I}_{pa} / \mathbf{I}_{pc} \right , \log \left(\mathbf{I}_{pc} \right), \log v, \left \mathbf{I}_{pc} / v^{1/2} \right , \left \mathbf{I}_{pc} / v^{1/2} n^{3/2} \right \right $
$ \mathbf{E}_{pc/2} $, $ \mathbf{E}_{pc/2}/logv $, $ \mathbf{E}_{pa}-\mathbf{E}_{pc} $	for Various Values of the Scan Rate

Curve N°	v (V.s ⁻¹)	E _{pc} (V)	E _{pa} (V)	I _{pc} (µA)	$\stackrel{I_{pa}}{(\mu A)}$	$\left \mathbf{I}_{pa}/\mathbf{I}_{pc}\right $	$\log \mid \mathbf{I}_{_{\mathrm{pc}}} \mid$	logv	$\left \mathbf{I}_{\mathbf{pc}} \mathbf{V}^{1/2} \right $ $\mu \mathbf{A.s}^{1/2} \mathbf{.V}^{-1/2}$	$\begin{array}{ l_{pc}/V^{1/2}n^{3/2} \\ \mu A.s^{1/2}.V^{-1/2}\end{array}$	E _{pc/2} (V)	E _{pc/2} /logy (V)	$\begin{vmatrix} \mathbf{E}_{\mathbf{pa}} \mathbf{-} \mathbf{E}_{\mathbf{pc}} \\ (\mathbf{V}) \end{vmatrix}$
1	0.01	-0.52	-0.06	0.65	0.01	0.015	-6.187	-2.00	6.50	52.0	0.33	0.165	0.46
2	0.02	-0.54	0.22	0.84	0.07	0.083	-6.076	-1.70	5.96	47.7	0.36	0.212	0.32
3	0.05	-0.56	0.28	1.01	0.26	0.257	-5.996	-1.30	4.51	36.1	0.38	0.292	0.28
4	0.10	-0.58	0.26	1.35	0.56	0.415	-5.870	-1.00	4.27	34.4	0.42	0.420	0.32
5	0.20	-0.62	0.28	1.74	1.12	0.644	-5.759	-0.70	3.89	30.8	0.43	0.614	0.34
6	0.40	-0.66	0.28	2.26	2.04	0.903	-5.646	-0.40	3.58	26.6	0.45	1.125	0.38
7	0.50	-0.70	0.28	2.45	2.25	0.918	-5.611	-0.30	3.46	25.4	0.46	1.533	0.42
8	0.80	-0.72	0.28	2.80	3.15	1.125	-5.553	-0.10	3.13	23.3	0.47	4.700	0.42
9	1.00	-0.72	0.26	3.15	3.35	1.063	-5.502	-0.00	3.15	23.2	0.49	4.900	0.46

25 °C at Pt electrode; $[AlCl_3] = 0.067$ M; measurements performed using E = f(I) curves of Figs. 1a, 1b and 1c.



Fig. 3—Plot of $I_{n'}/v^{1/2}n^{3/2}$ as a function of v for the experimental data of Table 1.

Ser

Exchanged

electrons number

peak (A) at E = -0.52 V/RE, attributed to the reduction of aluminum cations. In fact, this cathodic peak is not observed when Al(III) ions are absent from the solvent, while its amplitude increases when the aluminum ion concentration is increased. When the scan rate increases, from 0.01 to 1 V/sec, the peak potential drifts negatively, reflecting the quasi-reversibility of the electrochemical reaction, or the influence of the ohmic drop resulting from the poor conductivity of the

solvent, or both. The exact measurement of the peak current and all the subsequent calculations are difficult, because a shoulder-type peak is observed at the foot of this cathodic peak, at a potential E = +0.14 V/RE. This shoulder is attributed to the reduction of protons that are present in the PC as traces of moisture. Moreover, a small cathodic shoulder B is observed at more negative potentials ($E \approx -1.358$ V/RE when v = 0.50 V/sec) (Fig. 2), depending on the reverse potential and the consecutive cycling. The exact nature of this electrochemical reaction is not yet determined. To avoid reduction of the solvent, observed at even more negative potentials, the potential was reversed at -1.7 V/RE (Fig. 1a, b, c) instead of -1.8 V/RE (Fig.2), and the solution was stirred between two different and consecutive measurements.



Fig.5: Plot of I_{pd}/I_{pc} as a function of v for the experimental data of Table 1.



Fig. 4—Plot of $\Delta E_{n/}/\Delta \log v$ as a function of v for the experimental data of Table 1.

Table 2									
Values of the Exchanged Electrons Number Calculated by									
Semi-Integration Of the Voltammetric Results for Different									
Scan Rates									
v (V/sec)	0.01	0.02	0.05	0.10	0.20	0.40	0.50	0.80	1.00

Comparison between two experimental curves obtained under the same experimental conditions (scan rate, temperature, composition of the plating solution) show a slight difference between the I values of these curves (Figs. 1 and 2). This fact is attributed to the difficulty of AlCl, dissolution in the solvent.

0.185 0.192 0.205 0.260 0.270 0.277 0.281 0.287 0.296

For 0.01 V/sec $\leq v \leq 0.5$ V/sec, this ratio remains always less than one, ranging from zero to one, reflecting the presence of a chemical step following the electrochemical reduction of the aluminum ions. For $v \ge 0.8$ V/sec, the ratio of the anodic peak current vs. the cathodic peak current, $|I_{pa}/I_{pc}|$ is greater than unity, but these measurements are not reliable because of the mechanical inertia of the X-Y recorder at high scan rates. When the applied scan rate values remain less than



Fig. 6—Convolution analysis curve and E-m(t) variation calculated for voltammogram No. 5 of Fig. 1b under assumption of an E_rC_i reaction scheme.

 $\begin{array}{c} \mbox{Table 3} \\ \mbox{Values of the Rate Constant } k_{f} \\ \mbox{CalculatedGraphically} \\ \mbox{From the Plot of } (E_{pc}-E_{1/2})n\, vs.\, \log\lambda \end{array}$

v (V/sec)	(E _{pc} - E _{1/2})n, mV	$log(k_{\rm f}/a)$	a(s)	k _f /sec
0.20	0.96	0.689	1.870	9.13
0.40	-9.60	0.294	3.739	7.36
0.50	-18.24	-0.112	4.674	3.61
0.80	-23.04	-0.435	7.478	2.75
1.00	-23.04	-0.435	9.348	3.43

0.01 V/sec, the anodic peak (A^{γ}) is completely absent from the voltammetric cycle (Fig. 2). The anodic peak appears at a potential E = +0.28 V/RE, and its intensity increases with scan rate (Table 1). The exact measurement of the anodic peak current is difficult, because an anodic shoulder-type peak (B^{γ}) appears at the foot of the wave before the anodic peak rises. This shoulder is attributed to reoxidation of the wave B (Fig. 2) and is, therefore, not accounted for. The above experimental observations led to adoption of the following E_iC_i type reaction mechanism (O corresponds to Al(III)):

$$O + ne^{-} \stackrel{k_{1}}{\underset{k_{-1}}{\rightleftharpoons}} R$$
$$\stackrel{k_{f}}{R \xrightarrow{}} Z$$

The validity of the above assumption was first confirmed taking into consideration the fact that the shape of the theoretical curves: $I_{pc}/v^{1/2}n^{3/2} = f(v)$, $\Delta E_{p/2}/\Delta \log v = f(v)$ and $I_{pa}/I_{pc} = f(v)$, proposed by Nicholson *et al.*⁵ as characteristic criteria for the E_rC_1 mechanism, resembles one of our curves for the same kinetic scheme, using the experimental data presented in Table 1 (Figs. 3, 4 and 5).

Semi-Integral Analysis of the Voltammetric Curves To accurately calculate the number of the exchanged electrons during the electrochemical step, a convolution (semiintegral) analysis, proposed by Oldham¹⁰ and Imbeaux,¹¹ is also used. This method consists of studying the current function:

$$\mathbf{m}(\mathbf{t}) = \frac{1}{\sqrt{\pi}} \int_{0}^{\mathbf{t}} \frac{\mathbf{i}(\mathbf{u})d\mathbf{u}}{(\mathbf{t}-\mathbf{u})^{1/2}}$$

where i and t are the current density and time, respectively. This function, in the case of an $E_r C_i$ kinetic scheme, takes on a constant value equal to $m^* = nF(D_{ox})^{1/2}C_{ox}^{0}$, and the Nernst equation can be written as

$$\begin{split} E = E^0 + \frac{RT}{2nF} \; \ln k_{\rm f} + \frac{RT}{nF} \; \ln \left(\frac{m^* - m(t)}{I}\right) \\ E = f \left(\ln \frac{m^* - m}{I}\right) \end{split}$$

and m=f(E) functions are consequently studied for the nine voltamperometric curves reported in Table 1 and shown in Fig. 1a, b and c. These two plots are shown in Fig. 6 for curve No. 5 of Fig. 1b.



It was verified that

 $E=f\left(ln\frac{m^{*}-m}{I}\right)$

is always linear. Its slope is equal to RT/nF, from which the number of exchanged electrons, n, was calculated for several values of the scan rate v. The resulting values are reported in Table 2.

If Al⁺³ is supposed to be reduced to Al⁰ during a reversible electrochemical reaction, with no interference of kinetic complications, the value of the number of the exchanged electrons should be 3. In this case, the n values from all the voltamperometric curves, and for different scan rates, range between 0.185 and 0.296. This fact can be explained if it is assumed that: (a) a quasi-reversible behavior of the electrochemical reaction and/or (b) an important chemisorption of PC^{12,13} or TEAP¹⁴ on the platinum electrode, reported in the literature, is involved. Therefore, n becomes $\alpha_n = 0.24 \pm 0.055$, where α is the transfer coefficient and n_{α} the number of electrons exchanged in the rate determining step (*i.e.*, during the preceding electrochemical reaction).

Taking into consideration the above observations, the following mechanism is proposed:

$$\mathbf{O} + \mathbf{n}\mathbf{e}^{-} \underset{\mathbf{k}_{-1}}{\overset{\mathbf{k}_{1}}{\rightleftharpoons}} \mathbf{R}$$

(quasi-reversible electrochemical reaction)

$$\mathbf{R} \xrightarrow{\mathbf{k}_{\mathbf{f}}} \mathbf{Z}$$

(irreversible chemical reaction)

According to this mechanism, the product R of the quasireversible electrochemical reaction is removed from the



Fig. 8—Plot of $(E_{pc}-E_{1/2})n$ as a function of λ for an E_rC_i reaction scheme.

surface of the platinum electrode. This was confirmed by performing a long-duration electrolysis at constant E = -0.65 V/RE on platinum electrodes. After eight hr, no aluminum was detected on the electrode surface.

Comparison Between Experimental & Theoretical Voltammetric Curves

Describing the Al(III) Reduction

Comparison was made between the experimental voltamperometric curve taken with a Pt electrode for v = 0.4 V/sec when $[AlCl_3] = 0.067$ M at 25 °C and the theoretical curve describing an E_rC_i reaction mechanism, for $k_f/a = 1.6$;⁵ and $\alpha n_{\alpha} = 0.24$, where a = nFv/RT, is depicted in Fig. 7, taking into consideration that $(I_{pc})_{theor} = (I_{pc})_{exper}$ and $(E_{pc})_{theor} = (E_{pc})_{exper}$. The small difference between the theoretical and the experimental curves during the descending part of the cathodic peak is attributed to the progressive increase of the cathodic current of the experimental curve as a result of the electrochemical reaction following the Al(III) reduction.

Evaluation of the Half-Wave Potential E1/2

The $E_{1/2}$ value can be obtained from experimental data collected under reversible conditions, where the chemical reaction that follows does not interfere with the kinetic mechanism (*i.e.*, at high values of sweep rates). In this case, $|E_{pc}-E_{1/2}| = 1.109 \text{ RT/nF.}^8$ If this formula is applied to the experimental cathodic curve No. 9 (Fig. 1c) when v = 1 V/sec, n = 0.296 and $E_{pc} = -0.72 \text{ V/RE}$ at 25 °C, the value of $E_{1/2} = -0.624 \text{ V}$ is obtained .

Evaluation of the Rate Constant k_f

As already mentioned, theoretical curves describing an E_rC_i mechanism have been plotted by Nicholson and Shain⁵ for different values of λ , where $\lambda = k_r RT/nFv$.

For small values of λ , the chemical reaction that follows has little effect, while, for large values of λ , no oxidation current is observed during the anodic potential scanning, and the voltamperometric curve has the form of a curve describing an irreversible electrochemical reaction. For intermediate values of λ (0.1 < λ < 5), the rate constant k_f can be obtained by comparing experimental $|i_{pa}/i_{pc}|$ ratios with the working curve described by Nicholson and Shain,⁵ where this ratio is plotted as a function of log k_f τ , τ being the time elapsed between the polarographic half-wave potential (E_{1/2}) and the switching potential. Unfortunately, the $|I_{pa}/I_{pc}|$ ratio cannot be calculated with precision because of inaccuracy in the I_{pa} measurement of the experimental curves, which results from the presence of the anodic peak B['] during anodic scanning. Nevertheless, according to the same authors,⁵ k_f values can also be calculated graphically according to the function $(E_{pc}-E_{1/2})n = f(\log \lambda)$ (Fig. 8). The mean value of the rate constant k_p calculated using the experimental curves of Fig. 1a, b and c, related to the Al(III)/Al⁰ reduction for $E_{1/2} = -0.624$ V and n = 0.24, is 5.4 ±3/sec.

Findings

- From all the experimental results:
- 1. No Al is deposited from AlCl₃ in propylene carbonate at 25 °C.
- 2. From the calculated value of $|I_{pa}/I_{pc}| \le 1$, it is concluded that the electrochemical reduction is followed by a chemical step.
- 3. From the study of the theoretical curves, $I_{pc}/v^{1/2}n^{3/2} = f(v)$, $\Delta E_{p/2}/\Delta \log v = f(v)$ and $I_{pa}/I_{pc} = f(v)$, and from the semiintegral analysis, it is confirmed that the overall reaction consists of a quasi-reversible electrochemical reaction followed by a first-order chemical reaction.
- 4. Fitting of the theoretical and experimental curves gave further confirmation of the above mechanism.
- 5. The values of kf, αn_{α} and $E_{1/2}$ were calculated and found to be $k_f \approx 5/\text{sec}$, $\alpha n_{\alpha} = 0.24 \pm 0.055$ and $E_{1/2} = -0.624$ V.

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