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A new bath for the electrodeposition of aluminium. III. The electrochemical behaviour of the rotating aluminium disc electrode in pure $AlCl_3$/THF-toluene solutions

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The electrochemical behaviour of the rotating aluminium disc electrode in $AlCl_3$/tetrahydrofuran-toluene solution was studied. The kinetic parameters controlling the electrode processes were investigated. The effect of the concentration of $AlCl_3$, the speed of rotation of the rotating disc electrode and the temperature on the cathodic and anodic current density was analysed. The results were compared with those for $AlCl_3$–$LiAlH_4$/THF-toluene solutions.

1. Introduction

The increased world market price of many metals such as Sn, Zn and Ni together with the excellent properties of aluminium, e.g. surface hardness, abrasion, corrosion resistance and dye-absorption properties greatly increases the importance of aluminium for galvanization techniques.

Due to the high negative deposition potential of aluminium from aqueous solution (−1.66 V vs normal hydrogen electrode-NHE) [1], its deposition from aqueous solutions is impossible. Many investigations have been directed towards the deposition of the metal from water-free melts of aluminium salts [2, 3]. Great attention has been paid to the deposition of aluminium from organic non-aqueous electrolytes [4–10]. Recently, the deposition of aluminium from an electrolytic bath containing $AlCl_3$ and $LiAlH_4$ dissolved in THF, THF-benzene or THF-toluene solvents was extensively studied [10–13]. The kinetics and mechanism of the cathodic deposition and anodic dissolution of aluminium in these solutions were thoroughly discussed. Also, the cathodic deposition of aluminium from these solutions is a continuous process, and the aluminium deposits obtained are very pure, finely crystalline, non-porous, silver white in colour and adherent to the substrate surface [15–17]. It is important to study the electrochemical behaviour of the aluminium electrode in solutions containing only one salt component in the mixed solvent THF-toluene. The aim of this investigation is to study the polarization phenomena and the mechanism of the anodic and cathodic processes taking place at the rotating disc aluminium electrode in solutions of $AlCl_3$/THF-toluene mixed solvent.

2. Experimental details

The current density-potential measurements were carried out potentiodynamically. The circuit used consisted of a multifunction potentiostat (FHI GO 50-17) provided with an interruption unit to compensate and to measure the ohmic overpotential accompanying the electrode processes, and a digital voltmeter to trace the open-circuit potential between the working electrode and the reference electrode. The interruption of the current was controlled by means of an oscilloscope (Tektronix INC Type 564). The current density-potential curves were recorded using an X–Y recorder (JJPL 50). The open-circuit potential measurements were controlled using a high impedance valve voltmeter (Elpo type M720). The cell used was a double walled all-glass cell provided with a light Teflon stopper of suitable openings for the working-, counter-, reference-electrode, and gas in- and out-lets. The working electrode was either a rotating aluminium or aluminized platinum disc. The counter electrode was made from 99.999% pure aluminium plate. The reference electrode, whether aluminized platinum sheet, aluminium spiral, $Ag/AgNO_3$-acetonitrile or $Hg/Hg_2(CH_3COO)_2$ electrode, was attached to the test cell through a salt bridge with a Luggin capillary placed almost adjacent to the working electrode. Materials and solutions were prepared as described previously [12]. All preparations and measurements were carried out under purified nitrogen gas. Copper catalyst and

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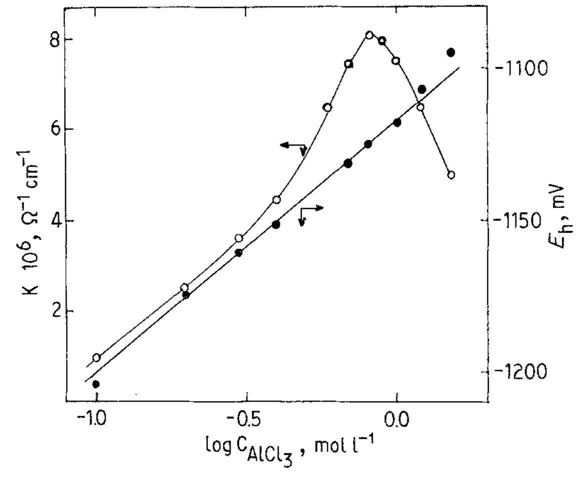

Fig. 1. Variation of the equilibrium potential of the aluminium disc E_h (●) and the conductivity of the solution k (○) with the concentration of aluminium chloride (C_{AlCl_3}) in the $AlCl_3$/THF-toluene solutions at 298 K.

molecular sieves were used to remove the last traces of oxygen and moisture from the inert gas [11]. The composition of solution was determined volumetrically as described elsewhere [15–18]. 0.1 M Tetrabutylammonium perchlorate in THF-toluene was used as supporting electrolyte.

3. Results

3.1. *Conductivity and equilibrium potential measurements*

The equilibrium potential of aluminium electrode in $AlCl_3$/THF-toluene solutions of different concentrations was found to increase with the concentration of $AlCl_3$. A plot of E_h vs log C_{AlCl_3} gave a straight line of slope 80 mV dec^{-1}. This positive value may be attributed to a decrease of the concentration of free ions as the concentration of $AlCl_3$ increases. The results of conductivity measurements were in good agreement with the equilibrium potential measurements. The relation between both the conductivity of solution (k) and the equilibrium potential of the aluminium electrode (E_h) and the concentration of $AlCl_3$ in THF-toluene mixed solvent is illustrated in Fig. 1.

3.2. *Polarization measurements*

The potentiodynamic current density-potential curves were measured with a low scan rate, namely, 1 mV sec^{-1}. The effect of concentration of $AlCl_3$, the speed of the rotating aluminium disc electrode, and the temperature on the current density-potential behaviour of the aluminium electrode in $AlCl_3$/THF-toluene solutions (20 vol % THF) was studied. The measurements were carried out with IR-compensation. For comparison, some measurements were carried out with and without IR-compensation. All experiments were carried out under purified nitrogen gas.

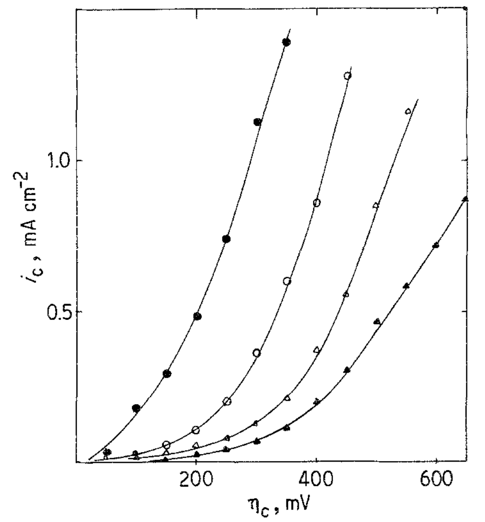

Fig. 2. Current density-potential curves of the aluminium disc electrode during cathodic polarization in $AlCl_3$/THF-toluene solutions of different aluminium chloride concentrations (C_{AlCl_3}) at 298 K and a scan rate of 1 mV sec^{-1} without rotation. (●) 1.0; (○) 0.8; (△) 0.7; and (▲) 0.4 mol l^{-1}.

3.2.1. *Effect of $AlCl_3$ concentration.* Figs 2 and 3 illustrate the current density-potential behaviour of the aluminium electrode in solutions of $AlCl_3$/THF-toluene of different concentration. The measurements were carried out at 298 K and under stationary conditions, i.e. without rotation. In both the cathodic curves (Fig. 2) and the anodic curves (Fig. 3) the overpotential accompanying the electrode processes decreased as the concentration of $AlCl_3$ increased.

In the case of anodic polarization and at high overpotentials (η_a > 100 mV) the curves are almost parallel. The relation between i_a and η_a is more or less linear and no Tafel behaviour could be obtained. On the other hand, the cathodic current density-potential curves (Fig. 2) showed a Tafel behaviour at overpotentials more negative than −60 mV. The Tafel

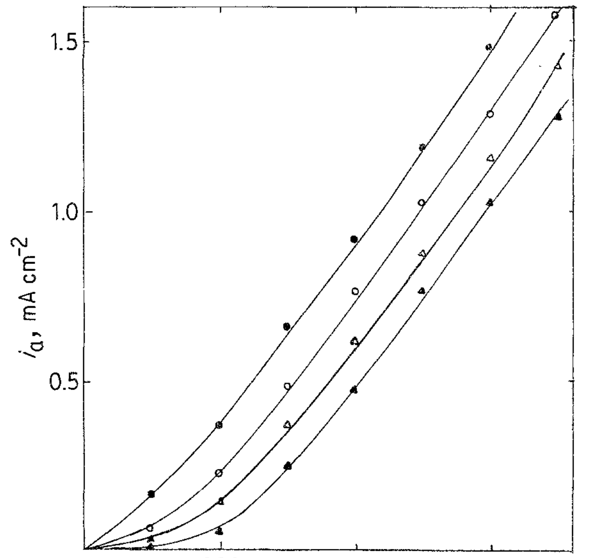

Fig. 3. Current density-potential behaviour of the aluminium disc electrode during anodic polarization in $AlCl_3$/THF-toluene solutions of different aluminium chloride concentrations (C_{AlCl_3}) at 298 K and a scan rate of 1 mV sec^{-1} without rotation. (●) 1.0; (○) 0.8; (△) 0.7; and (▲) 0.4 mol l^{-1}.

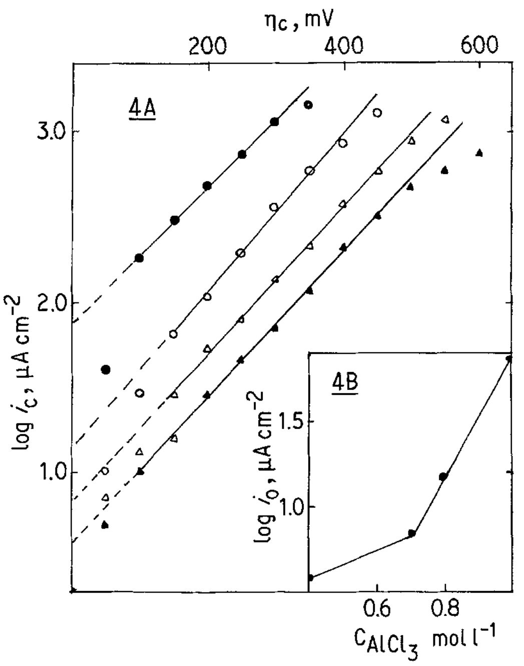

Fig. 4. (A) Tafel plots of the aluminium disc electrode in $AlCl_3$/THF-toluene solutions of different aluminium chloride concentration (C_{AlCl_3}). Scan rate 1 mV sec^{-1}, without rotation at 298 K. (●) 1.0; (○) 0.8; (△) 0.7, and (▲) 0.4 mol l^{-1}; (B) Relation between log i_0 (exchange current density) and concentration of $AlCl_3$.

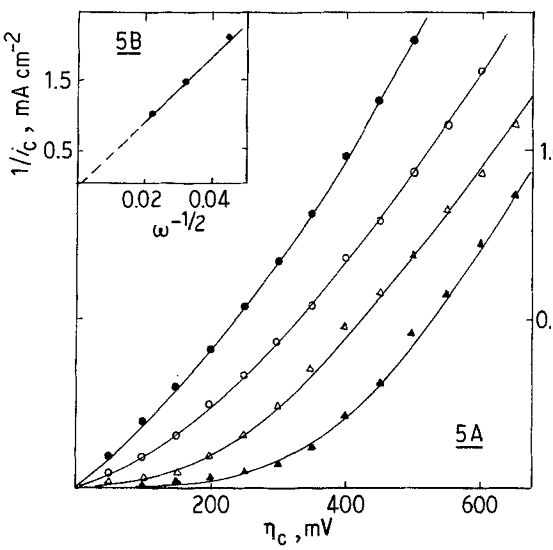

Fig. 5. (A) Current density-potential behaviour of the rotating aluminium disc electrode at constant concentration of $AlCl_3$ (C_{AlCl_3} = 0.4 mol l^{-1}) and different speeds of rotation (ω). Scan rate 1 mV sec^{-1}; 298 K; (▲) stationary, (△) 500, (○) 1000 and (●) 2000 r.p.m. (revolutions per min.); (B) Relation between 1/i_c and $\omega^{-1/2}$ at −400 mV.

plots obtained at different C_{AlCl_3} are presented in Fig. 4A. The kinetic parameters controlling the electrode process were calculated in the same way as described in Part II [13]. The Tafel lines are almost parallel with a slope (b) of ~230 mV dec^{-1}. The large value of b may be due to a very slow charge transfer process. The exchange current density increases as the concentration of aluminium chloride increases and the relation between log i_0 and C_{AlCl_3} is illustrated in Fig. 4B. The extrapolated values of i_0 are always less than 0.1 mA cm^{-2}.

3.2.2. Effect of the speed of rotation. The current density-potential behaviour of the rotating aluminium disc during cathodic polarization in 0.4 mol l^{-1} $AlCl_3$/THF-toluene solution at different speeds of rotation is presented in Fig. 5A. At the same polarization potential the current density increases as the speed of rotation increases. The relation between the measured current density and the speed of rotation at a constant overpotential is illustrated in Fig. 5B. A plot of 1/i_c vs $\omega^{-1/2}$ at a given value of η gives a straight line. This line can be extrapolated to $\omega^{-1/2} = 0$ to yield 1/i_k, where i_k is the current density in the absence of any mass transfer effects. Determination of i_k at different values of η allows determination of the kinetic parameters controlling the electrode process [19]. This procedure has many applications, a typical one of which is the determination of the kinetic parameters controlling the reduction of O_2 to HO_2^- at gold electrodes in alkaline solutions [20]. At potentials in the limiting current region of the current density-potential curve, the plot of 1/i vs $\omega^{-1/2}$ gives straight line that intersects the origin. In this case the electron transfer is rapid [19]. If the rate of the electron transfer is sufficiently slow to act as a limiting factor, the straight line intersects the 1/i axis at 1/i_k which suggests some kinetic step involved in the electron transfer reaction.

During anodic polarization, the speed of rotation of the rotating aluminium disc did not show any effect on the current density-potential curves. This means that the anodic process is not influenced by mass transfer effects [21], whereas the cathodic process is controlled by both charge transfer and diffusion mechanisms.

3.2.3. Effect of temperature. The effect of temperature on the current density-potential behaviour of the aluminium electrode during cathodic polarization in a solution of 0.85 mol l^{-1} $AlCl_3$ in the THF-toluene is illustrated in Fig. 6. As the temperature increases the overpotential accompanying the cathodic process decreases. At overpotentials more negative than −60 mV Tafel behaviour was obtained (Fig. 7). The exchange current densities extrapolated from the cathodic Tafel lines increase as the temperature increases. A plot of log i_{oc} versus 1/T gives a straight line obeying the familiar Arrhenius equation [22]. From the slope of this line (Fig. 7B) the activation energy of the cathodic process was calculated according to:

$$\frac{d \log i_{oc}}{d\, 1/T} = \frac{-E}{2.303\, R} \qquad (1)$$

The calculated value was in the region of 80 kJ mol^{-1}. The temperature variation over the range of our measurements did not show a significant effect on the anodic current density-potential curves.

4. Discussion

Conductivity and equilibrium potential measurements indicate that $AlCl_3$ undergoes limited disproportionation in the THF-toluene solvent [23]. The dispropor-

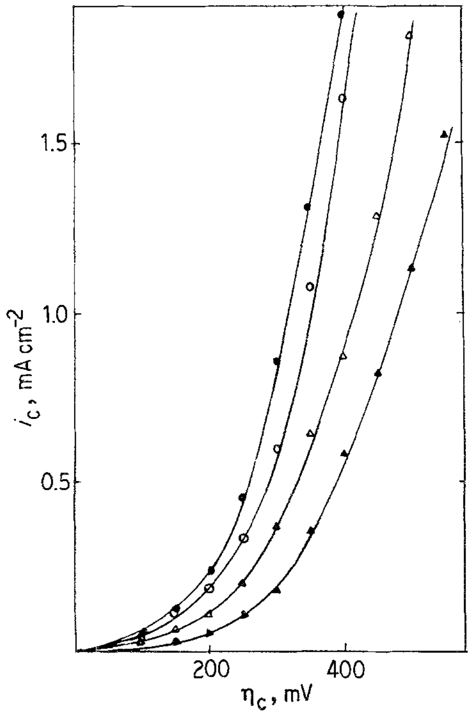

Fig. 6. Effect of temperature on the current density-potential behaviour of the aluminium disc electrode during cathodic polarization in 0.8 mol l^{-1} AlCl$_3$/THF-toluene solution. Scan rate 1 mV sec^{-1}, without rotation. (▲) 293; (△) 298; (○) 303, and (●) 308 K.

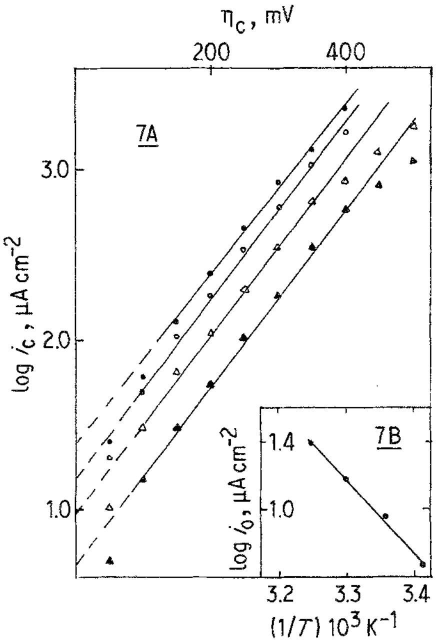

Fig. 7. (A) Tafel plots for the cathodic polarization of the aluminium disc electrode in 0.8 mol l^{-1} AlCl$_3$/THF-toluene at different temperatures. Scan rate 1 mV sec^{-1} without rotation. (▲) 293; (△) 298; (○) 303; and (●) 308 K; (B) log i_0 vs $1/T$ plot of the cathodic polarization of the aluminium disc electrode in 0.8 mol l^{-1} AlCl$_3$/THF-toluene solution.

tionation reaction may be represented by:

$$2AlCl_3 \rightleftharpoons AlCl_2^+ + AlCl_4^- \qquad (2)$$

$$2AlCl_3 \rightleftharpoons Al_2Cl_5^+ + Cl^- \qquad (3)$$

$$4AlCl_3 \rightleftharpoons Al^{3+} + 3AlCl_4^- \qquad (4)$$

The presence of such ions in the solution is responsible for its increased conductivity. At concentrations higher than 0.8 mol l^{-1} the conductivity of the solution decreases. This may be explained by the recombination of the disproportionated ionic species, i.e. the reaction is shifted towards the left with increasing AlCl$_3$ concentration. The ionic species present in the solution participate directly in the equilibrium process at the aluminium electrode. The increased equilibrium potential with increasing AlCl$_3$ concentration may be attributed to the presence of an equilibrium of the following type:

$$4AlCl_3 + 3e^- \rightleftharpoons Al + 3AlCl_4^- \qquad (5)$$

or

$$2AlCl_3 + 3e^- \rightleftharpoons Al + AlCl_4^- + 2Cl^- \qquad (6)$$

The value of the slope of the E_h vs log C_{AlCl_3} relation, Fig. 1, is not consistent with $n = 3$ for the total number of electrons in the potential determining electrode process. This observation may indicate that the electrode process is not a simple one and a mixed potential is expected. Consistent with this is the fact that the equilibrium potential changes with the speed of rotation of the rotating disc.

The results of polarization measurement show that the anodic and cathodic processes are quite different and have different mechanisms. The cathodic process is more affected by the different parameters such as the concentration of the solution, the speed of rotation of the electrode and the temperature, whereas the anodic process seems to be independent of these factors.

During cathodic polarization, the current density increases as the speed of rotation of the rotating disc increases, therefore a part of the overpotential accompanying the electrode process is of the diffusion type. This observation is quite similar to the result of AlBr$_3$-diethylether solutions [24]. The presence of traces of water, which is not absolutely impossible with the AlCl$_3$ solutions, may lead to a cathodic evolution of hydrogen which is accompanied by a hydrogen overpotential. The presence of traces of water leads to the formation of hydrogen ions according to

$$AlCl_3 + H_2O \longrightarrow AlCl_2OH + HCl \qquad (7)$$

$$HCl + AlCl_3 \longrightarrow H^+ + AlCl_4^- \qquad (8)$$

The hydrogen ions are cathodically discharged first and then the cathodic deposition of aluminium begins. The cathodic evolution of hydrogen was observed as very slow and small bubbles and was accompanied by the formation of a dark grey viscous deposit of colloidal aluminium. With increasing speed of rotation of the electrode the deposit formed as whiskers on the surface of the rotating aluminium disc. The high value of the Tafel slopes may be attributed to a very slow charge transfer process [25, 26]. It may be concluded that the pure solution of AlCl$_3$ in THF-toluene solvent is not suitable for the cathodic deposition of aluminium. Also, an anodic dissolution was not observed. Therefore, the presence of $LiAlH_4$ with $AlCl_3$ in the solution is very important for the production of pure, fine crystalline, non-porous silver white and adherent aluminium films on the cathode as discussed in Part II [13].

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