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A New Bath for the Electrodeposition of Aluminium. IV. The Electrochemical Behaviour of the Rotating Aluminium Disc Electrode in Pure LiAlH₄/THF-Toluene Solutions

W. A. Badawy*) and N. Hilal

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

Chemical Kinetics / Electrochemistry / Electrodeposition / Electrodissolution / Surfaces

The electrochemical behaviour of the rotating aluminium disc electrode in $LiAlH_4$ /tetrahydrofuran (THF)-toluene solutions was studied. The kinetic parameters controlling the electrode process were investigated. The effect of concentration of $LiAlH_4$, the speed of rotation of the rotating disc electrode, and the temperature on the current density-potential behaviour of the aluminium electrode during the anodic and cathodic polarization was analyzed. The results were compared with those obtained for pur AlCl₃ or AlCl₃ + $LiAlH_4/THF$ toluene solutions.

1. Introduction

In a series of publications the electrochemical deposition of aluminium from the tetrahydrofuran-hydride bath was extensively studied [1-3]. Generally, the electrodeposition of aluminium from aqueous solutions is impossible, due to its too negative deposition potential [4]. Most investigations were directed to the aluminium deposition from water free melts [5,6] or organic non-aqueous electrolytes [7-12]. Recently, the electrodeposition of aluminium from an electrolytic bath containing AlCl₁ and LiAlH₄ dissolved in THF, THF-benzene or THF-toluene was extensively studied [13-15]. The kinetics and mechanism of the cathodic deposition as well as the anodic dissolution of aluminium in these solutions were discussed. The deposition of aluminium from the AlCl₃-LiAlH₄ solutions is a continuous process and the obtained aluminium layers are very pure, fine crystalline, nonporous, silver white and adherent to the substrate surface [16-19]. In our last publication [3] we reported on the electrochemical behaviour of the aluminium electrode in pure AlCl₃/THF-toluene solutions. The results showed that the presence of LiAlH₄ in the solution was very important for the electrodeposition of aluminium from these non-aqueous organic solutions. To complete the picture it was important to study the mechanism

Present address: Freie Universität Berlin, Institut für Physikalische Chemie. Takustraße 3, D-1000 Berlin 33. of the anodic and cathodic processes taking place at the rotating aluminium disc in solutions of $LiAlH_4/THF$ -toluene free from $AlCl_3$ or other aluminium salts.

2. Experimental

A standard potentiostatic circuit was used to trace the current density-potential behaviour of the aluminium disc. It consists 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 M 720). The electrolytic cell 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/AgNO3-acetonitrile or Hg/ Hg₂(CH₃COO)₂ electrode was attached to the test cell through a salt bridge with a Luggin-cappilary placed almost adjacent to the working electrode. Materials and solutions were prepared as described previously [2]. All preparations and measurements were carried out under purified nitrogen gas. Copper catalyst and molecular sieves were used to remove the last traces of oxygen and humidity from the nitrogen gas [14]. The composition of the solution was determined volumetrically [1].

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^{*)} Author to whom all correspondence should be addressed.

3. Results

3.1. Equilibrium Potential Measurements

Fig. 1 illustrates the variation of the equilibrium potential of the rotating aluminium disc electrode (E_h) referred to the normal hydrogen electrode (NHE) with the concentration of LiAlH₄ in the THF/toluene mixture. As shown in the figure, the plot of E_h vs. log C_{LiAlH_4} gave a straight line of slope 0.9 V/decade. This too positive value may be attributed to a decrease of the concentration of free ions in the solution as the concentration of LiAlH₄ increases which is in good agreement with the results of conductivity measurements of LiAlH₄ in THF, THF-benzene, and THF-toluene solutions [15].



Variation of the equilibrium potential of the aluminium disc electrode (E_h) with the concentration of LiAlH₄ in the THF-toluene solvent mixture (C_{1,VHI_4}) at 298 K



Current density-potential curves of the rotating aluminium disc during cathodic polarization in LiAlH₄/THF-toluene solutions of different concentrations. Scan rate 4 mV s⁻¹, rotation speed 1000 rpm, temperatur 298 K. (○) 0.21, (●) 0.45, (□) 0.58, (■) 0.79 mol dm⁻³

3.2. Polarization Measurements

The current density-potential behaviour of the rotating aluminium disc was studied using a low scan rate of 4 mV s⁻¹. The effect of the concentration of LiAlH₄ ($C_{\text{LiAlH_4}}$), the speed of rotation of the rotating aluminium disc (ω), and the temperature on the electrochemical behaviour of the aluminium disc in LiAlH₄/THF-toluene solutions (20 volume% THF) was studied. All experiments were carried out under purified nitrogen gas and with IR-compensation.



Current density-potential behaviour of the rotating aluminium disc electrode during anodic polarization in LiAlH₄/THF-toluene solutions of different concentrations. $v = 4 \text{ mV s}^{-1}$, $\omega = 1000 \text{ rpm}$, T = 298 K.

(\bigcirc) 0.21, (\bigcirc) 0.45, (\square) 0.58, (\blacksquare) 0.79 mol dm⁻³

3.2.1. Effect of LiAlH₄ Concentration

To study the effect of the LiAlH₄ concentration on the current density-potential behaviour of the aluminium electrode during the cathodic and anodic processes, a series of solutions of different LiAlH₄ concentrations (C_{LiAlH_4}) ranging from 0.2 to 0.8 mol dm⁻³ were prepared. The current density-potential curves for the cathodic and anodic branches at 298 K, with a rotation speed of 1000 rpm and a scan rate of 4 mV s⁻¹ are illustrated in Figs. 2 and 3, respectively. The general trend in both anodic and cathodic processes is the decrease of the overpotential with the increase of the LiAlH₄ concentration. Neither the anodic nor the cathodic process could show a Tafel behaviour at high overpotential ($|\eta| \ge 60$ mV). In the vicinity of the equilibrium potential ($|\eta| < 50$ mV, Eq. (1) can be used for the calculation of the exchange current density (i_0) of the corresponding process

$$i| = |i_0| \frac{nF}{RT} |\eta| \tag{1}$$

from which the so-called charge transfer resistance, $R_{\rm ct}$, for the cathodic or the anodic process can be also calculated according to Eq. (2)

$$R_{\rm ct} = \frac{RT}{F} \frac{1}{ni_0}.$$
 (2)

 R_{ct} is a convenient index of kinetic facility [20]. The analysis of the current density-potential curves of Figs. 2 and 3 according to Eq. (1) are presented in Fig. 4A. The variation

of the anodic and cathodic exchange current densities is shown in Fig. 4B. The exchange current density increases as the concentration of LiAlH₄ increases whereas the charge transfer resistance decreases (cf. Table 1).

Table 1 Variation of the exchange current density and the charge transfer resistance during anodic and cathodic polarization of the rotating aluminium disc electrode in LiAlH₄/THF-toluene at different concentrations. Scan rate 4 mV s^{-1} , speed of rotation 1000 rpm, at 298 K

C _{LiAiH4} mol dm ³	charge transfer resistance Ω		exchange current density mA cm ⁻²	
	R _{ct(a)}	$R_{cl(c)}$	(<i>ni</i> ₀) _a	(<i>ni</i> ₀) _c
0.21	801.0	801.0	0.032	0.032
0.45	441.9	441.9	0.058	0.058
0.58	235.1	294.6	0.109	0.087
0.79	137.8	105.0	0.186	0.244



- (A) Linear approximation of the Butler-Volume equation for the anodic and cathodic polarization of the rotating aluminium disc electrode in LiAlH₄/THF-toluene solutions of different concentrations. $v = 4 \text{ mV s}^{-1}$, $\omega = 1000 \text{ rpm}$, T = 298 K.
- (B) Variation of the cathodic (○) and anodic (●) exchange current densities with the concentration of LiAlH₄ in the THF/toluene solvent

3.2.2. Effect of the Speed of Rotation of the Rotating Disc Electrode on the Current Density-Potential Behaviour

The current density-potential behaviour of the rotating aluminium disc during cathodic polarization in 0.45 mol dm⁻³ LiAlH₄/THF-toluene solution at 298 K and different speeds of rotation is presented in Fig. 5. For comparison, the current density-potential curve obtained without rotation is also presented. It is clear that the rotation of the rotating disc electrode decreases the overpotential and facilitates the charge transfer at the electrode/electrolyte interface. The relation between the measured current density and the speed of rotation at constant overpotential is presented in Fig. 6. At the three different overpotentials, namely +100, -200 and -300 mV, a linear relation between $1/i_c$ and $\omega^{-1/2}$ was obtained. For a rotating disc, a deviation of a plot of i vs. ω^{12} from a straight line that intersects the origin suggests some kinetic steps involved in the electron transfer reaction [21]. The disc current (i_D) in this case is given by Eq. (3)

$$i_{\rm D} = nFAk_{\rm f}C_0 \tag{3}$$

where k_f is a constant at a given overpotential

$$k_{\rm f} = k_0 \exp\left[-\alpha n F \eta / R T\right] \tag{4}$$

where k_0 is the rate constant at $\eta = 0$, α the charge transfer coefficient, *n* the number of transferred electrons, and η the overpotential. *F*, *R* and *T* have their usual meaning. *A* and C_0 of Eq. (3) are the disc electrode area (0.2 cm²) and the concentration at the electrode surface, respectively. The measured current *i* is given by Eq. (5)

$$i = nFAk_{\rm f}C_0^* \left| 1 - \frac{i}{i_{\rm L}} \right| \tag{5}$$

where C_0^* is the bulk concentration and i_L is the limiting current density. If i_L is very large or under conditions of negligible mass transfer effects, the current density is given by

$$i_{\rm K} n F A k_{\rm f} C_0^* . \tag{6}$$

 $i_{\rm K}$ is the current density in the absence of mass transfer effects.

From Eqs. (5) and (6) one can write

$$\frac{1}{i} = \frac{1}{i_{\rm K}} + \frac{1}{i_{\rm L}}.$$
(7)

Since $i_{\rm L}$ is proportional to $\omega^{1/2}C$ [22,23] and $i_{\rm K}$ is not very large, a plot of 1/i vs. $1/\omega^{1/2}$ should be linear and can be extrapolated to $\omega^{1/2} = 0$ to obtain $1/i_{\rm K}$. Fig. 6 shows that the relation between i^{-1} and $\omega^{-1/2}$ in the range of our measurements is a linear one. The intercept of these plots may allow the determination of the kinetic parameters at each overpotential [21].



Current density-potential behaviour of the rotating aluminium disc electrode during cathodic polarization at constant concentration of LiAlH₄ ($C_{\text{LiAlH}_4} = 0.45 \text{ mol dm}^{-3}$) and different speeds of rotation (ω). Scan rate 4 mV s⁻¹, 298 K

(○) stationary, (●) 500, (□) 1000, (■) 1500, (△) 2500 rpm (revolution per min)



(O) $\eta_c = -100 \text{ mV}$, (\bullet) -200 mV, (\blacksquare) -300 mV

The straight lines of Fig. 6 were extrapolated to $\eta = 0$ and the corresponding values of $i_{\rm K}$ were calculated. From these values the rate constants $k_{\rm F}$ at -100, -200 and -300 V were calculated. These values are summarized in Table 2.

It is clear from Table 2 that the value of $i_{\rm K}$, i.e. the current density in absence of mass transfer effects, increases as the overpotential increases.

Table 2 Values of $i_{\rm K}$ and $k_{\rm F}$ at different overpotentials during the cathodic polarization of the rotating aluminium disc electrode in 0.45 mol dm-3 LiAlH₄/THFtoluene at different speeds of rotation and 298 K. Scan rate 4 mV s⁻¹

mV	$i_{\rm K} \ {\rm A} \ {\rm cm}^{-2}$	$(nk_{\rm F})~{\rm cm^{-2}~s^{-1}})$	
-100	1.6 · 10 ⁻³	3.68 · 10 ⁻⁸	
-200	$8.0 \cdot 10^{-3}$	1.84 · 10 ⁻⁷	
-300	$15.4 \cdot 10^{-3}$	$3.55 \cdot 10^{-7}$	

3.2.3. Effect of Temperature

The effect of temperature on the current density-potential behaviour of the rotating aluminium disc electrode during cathodic polarization in 0.45 mol dm⁻³ LiAlH₄/THF-toluene solution is illustrated in Fig. 7. It is clear from the different curves that the overpotential accompanying the cathodic process decreases as the temperature increases. In the range of our measurements and at overpotentials (η_c) more negative than -60 mV, no Tafel behaviour could be obtained. Analysis of these current density-potential curves ac-

Table 3 Variation of the exchange current density and the charge transfer resistance during cathodic polarization of the rotating aluminium disc electode in 0.45 mol dm⁻³ LiAlH₄/THF-toluene solution with the temperature. Scan rate 4 mV s⁻¹, speed of rotation 1500 rpm

T/K	$1/T K^{-1}$	$(i_0 n) \text{ mA cm}^{-2}$	$\log(i_0 n)$	$R_{\rm ct} \Omega$
293	$3.41 \cdot 10^{-3}$	0.044	-1.357	572.8
298	$3.36 \cdot 10^{-3}$	0.096	-1.018	267.0
303	$3.30 \cdot 10^{-3}$	0.124	-0.907	210.2
308	$3.25 \cdot 10^{-3}$	0.220	-0.658	120.4

cording to Eq. (1) is presented in Fig. 8A. The exchange current density increases as the temperature increases. On the other hand, the increase of temperature is accompanied by a decrease of the charge transfer resistance, R_{ct} (cf. Table 3).

A plot of $\log i_0$ vs. 1/T gives a straight line obeying the familiar Arrhenius equation [23] (cf. Fig. 8B). The activation energy of the cathodic process was calculated from the slope of the line of Fig. 8B according to

$$\frac{d\log i_0}{d1/T} = \frac{-E^*}{2.303\,R}.$$
(8)

The calculated value was $E^* = 86.02 \text{ kJ mol}^{-1}$.



Effect of temperature on the current density-potential behaviour of the rotating aluminium disc electrode during cathodic polarization in 0.45 mol dm⁻³ LiAlH₄/THF-toluene solution. Scan rate 4 mV s⁻¹, ω = 1500 rpm. (○) 293, (●) 298, (□) 303, (■) 308 K



Fig. 8

- (A) Variation of the current density with the potential in the vicinity of the equilibrium potential during cathodic polarization of the rotating aluminium disc electrode in 0.45 mol dm⁻³ LiAlH₄/ THF-toluene solution at different temperatures. Scan rate 4 mV $s^{-1}, \omega = 1500$ rpm.
 - (○) 293, (●) 298, (□) 303, (■) 308 K.
- \log_{i_0} vs. 1/T plot of the cathodic polarization of the rotating **(B)** aluminium disc in 0.45 mol dm⁻³ LiAlH₄/THF-toluene solution

4. Discussion

LiAlH₄ solutions in THF or THF-toluene solvents have relatively high specific conductivity which may reach 0.01 Ω^{-1} cm⁻¹ [15]. This means that the solution contains ionic species which are responsible for its high conductance. These ionic species are formed due to the strong dissociation of the dimers or trimers present in the solution [24, 25]. This ionization process may be represented by Eq. (9):

$$(\text{LiAlH}_4)_3 \rightleftharpoons |\text{Li}(\text{LiAlH}_4)|^+ + |(\text{LiAlH}_4)\text{AlH}_4|^- . \tag{9}$$

The ionic species present in the solution participate directly in the equilibrium process at the aluminium electrode. The increased equilibrium potential with increasing LiAlH₄ concentration may be due to the presence of an equilibrium of the following type:

$$(\text{LiAlH}_4)_2 + e^- \rightleftharpoons \text{Al} + 2\text{LiH} + \text{H}_2 + \text{AlH}_4^- \tag{10}$$

$$(\text{LiA}|\text{H}_4)_3 + e^- \rightleftharpoons \text{Al} + 3\text{LiH} + \text{A}|\text{H}_3 + \text{H}_2 + \text{A}|\text{H}_4^-.$$
(11)

The high positive value of the slope of the $E_{\rm h}$ vs. log $C_{\rm LiAIH_4}$ plot is not consistent with a one electron step as a potential determining electrode process. This may show that the electrode process is a complicated one. The presence of LiH was identified as a greyish precipitate at the end of the measurements. During the measurements small bubbles of H₂ were also observed.

In LiAlH₄ solutions the cathodic and anodic processes are quite similar. The current density increases as the concentration of LiAlH₄ increases. The current densities accompanying the anodic or the cathodic process are very small with respect to those measured in the AlCl₃ + LiAlH₄/THFtoluene solutions [2]. During the cathodic process the electrodeposition of aluminium as a silver-white adherent layer was not observed. A greyish precipitate was formed not only at the bottom of the electrolytic cell but also on the electrode surface. This precipitate was found to contain LiH as well as Al metal.

The increase of the speed of rotation was accompanied by an increase in the current density or a decrease of the overpotential. The linear plot of 1/i vs. $\omega^{-1/2}$ (Fig. 6) shows that the cathodic process should be treated as a process of mixed control. The small values of the exchange currents may be attributed to a slow charge transfer process [26, 27]. The value of the rate constant k_F increases with the increase in the overpotential. Calculation of k_0 (the rate constant at $\eta = 0$) did not give the same value for each k_f which indicates that *n* cannot be treated as unity and the process as a whole is controlled with charge transfer and mass transport effects as well.

Conclusion

The cathodic deposition of aluminium as pure, fine crystalline and adherent aluminium layer from a $LiAlH_4/THF$ -toluene solution is impossible. The cathodic process which involves the deposition of a greyish, spongy aluminium deposit is a process of mixed control, i.e. mass transfer and charge transfer effects must be considered.

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