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A new bath for the electrodeposition of aluminium. I. Conductivity measurements

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The conductivity of mixed hydrides of aluminium chloride and lithium–aluminium hydride in a mixed solvent of tetrahydrofuran (THF) and toluene was measured with respect to the total concentration of aluminium and also to the molar ratio of $LiAlH_4$ to $AlCl_3$. The values obtained were compared with those of the THF–benzene mixed solvent and those of the NBS (National Bureau of Standards) bath – $AlCl_3$ and $LiAlH_4$ in dithyl ether. The results showed that a solution of $AlCl_3$ and $LiAlH_4$ with a molar ratio of 3 : 1, respectively, in THF–toluene (80 vol % toluene) with a total concentration of aluminium of about $1.0\,mol\,l^{-1}$, has a suitable conductivity for the electrodeposition and dissolution of aluminium. In addition to its low price, the electrolytic bath obtained has low volatility and relatively good stability with respect to the other baths studied.

1. Introduction

The electrochemical deposition of aluminium from aqueous solutions is practically impossible because of the high negative deposition potential of aluminium (− 1.66 V versus SHE) [1]. The deposition of aluminium from non-aqueous electrolytes, e.g. water-free melts of aluminium salts [2, 3] or organic non-aqueous electrolytes [4, 5] is well established.

One of the best known electrolytic baths for aluminium deposition is the hydride bath which consists of $AlCl_3$ and $LiAlH_4$ dissolved in tetrahydrofuran (THF) [6, 7] or THF–benzene mixtures [8, 9]. Aluminium deposition from this bath is a continuous process [10] and the cathodic films are very pure, fine crystalline, non-porous silver-white in colour and adherent to the substrate surface [11–13].Unfortunately, benzene is a very poisonous and carcinogenic compound [14, 15]. One of the aims of this work is to choose another hydrocarbon which can be mixed with THF and to study the properties of the new bath so formed. From the economic point of view, toluene is cheaper than benzene [16, 17] and has suitable properties as a main component in the THF–toluene mixed solvent. The problem in non-aqueous solution electrochemistry is the low conductivity of the solutions. This paper describes experiments aimed at investigating the conductivity of $AlCl_3$, $LiAlH_4$ and mixtures of both in THF and THF–toluene mixtures in order to select the optimum bath composition for the electrodeposition of aluminium and also its electrodissolution.

2. Experimental details

Tetrahydrofuran was kept over $LiAlH_4$ for 24 h, refluxed for about 8 h and then distilled. Toluene was kept over sodium for at least 24 h, refluxed for several hours and then distilled. Sublimated $AlCl_3$ was dissolved in THF–toluene mixture with cooling in an ice–salt mixture. Solutions of $LiAlH_4$ were prepared by refluxing an excess amount of $LiAlH_4$ in THF for about 8 h. The resulting solution was then decanted and filtered. The composition of the prepared solution was determined volumetrically as described previously [18].

For the conductivity measurements an all-glass conductivity cell with two platinized platinium sheets (geometric area of each = $0.25\,cm^2$) as electrodes and gas inlets and outlets was used. The conductivity of the solutions were measured by means of a SYBROM/Barnstead

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PM-70CB Conductivity Bridge. The cell constant was measured using a standard KCl solution of specific conductivity $\kappa = 0.0128\,\Omega^{-1}\,cm^{-1}$. The preparation of the solutions and also all measurements were carried out under nitrogen, which was first subjected to a standard purification process [19] to eliminate O_2 and humidity.

3. Results and discussion

Many authors have reported that solvents of low base strength such as THF should, in general, favour coordination disproportionation of metal halides [20–22]. The presence of $LiAlH_4$ with $AlCl_3$ in these solutions leads to the formation of aluminium dichlorohydride and aluminium chlorohydride depending on the molar ratio of $AlCl_3$ to $LiAlH_4$.

With a ratio of 3 : 1

$$LiAlH_4 + 3AlCl_3 \longrightarrow LiCl + 4AlHCl_2 \quad (1)$$

With a ratio of 1 : 1

$$LiAlH_4 + AlCl_3 \longrightarrow LiCl + 2AlH_2Cl \quad (2)$$

The chlorohydrides formed undergo disproportionation leading to the formation of ionic species which are responsible for the increased conductivity of these solutions:

$$2AlHCl_2 \longrightarrow AlCl_2^+ + AlH_2Cl_2^- \quad (3)$$

$$2AlH_2Cl \longrightarrow AlH_2^+ + AlH_2Cl_2^- \quad (4)$$

The LiCl formed may also react with aluminium chlorohydrides giving rise to ionic species:

$$LiCl + AlHCl_2 \longrightarrow LiAlHCl_3 \longrightarrow Li^+ + AlHCl_3^- \quad (5)$$

$$LiCl + AlH_2Cl \longrightarrow LiAlH_2Cl_2 \longrightarrow Li^+ + AlH_2Cl_2^- \quad (6)$$

Table 1 illustrates the reported [23] and the measured conductivities of the pure organic solvents used in our measurements.

The conductivity of benzene or toluene increases with addition of THF. A solution of 20% THF and 80% toluene has a conductivity comparable with that of pure THF itself and is better than that of toluene (cf. Table 1). A mixture of 20% THF and 80% toluene (vol %) seems to be a suitable solvent for preparing the $LiAlH_4$–$AlCl_3$ bath. The bath is less volatile and less inflammable than the pure THF or NBS bath and its conductivity depends on both the concentration of the solution and the molar ratio of $LiAlH_4$ to $AlCl_3$. Fig. 1 shows the variation of the specific conductivity of $AlCl_3$ and $LiAlH_4$ solutions in pure THF. Although the conductivity is higher than the corresponding conductivity of solutions of similar concentration in THF–benzene or THF–toluene mixtures, the solubility of $AlCl_3$ in pure THF is less than its

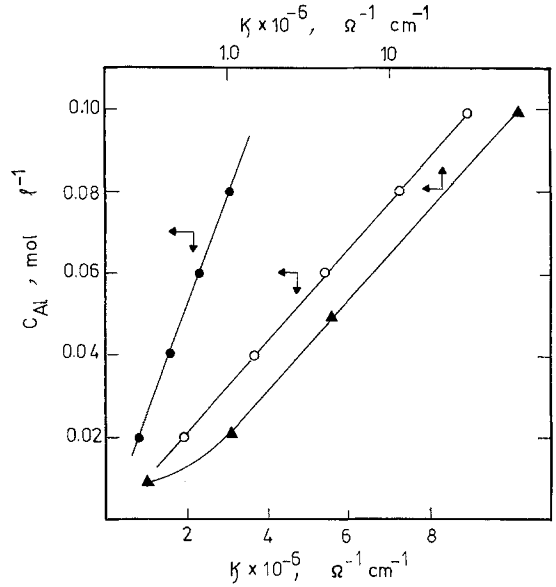

Fig. 1. Variation of the specific conductivity of $AlCl_3$ and $LiAlH_4$ solutions in THF with concentration. ●, prepared from 0.2 M $AlCl_3$ solution; ○, from 0.1 M $AlCl_3$ solution; ▲, from $LiAlH_4$ in THF.

Table 1. Conductivity of benzene, THF, toluene and their mixtures

Liquid	*Reported κ* $(\Omega^{-1}\,cm^{-1})$	*Measured κ* $(\Omega^{-1}\,cm^{-1})$
Benzene	7.6×10^{-8}	4.6×10^{-8}
Toluene	$< 10^{-14}$	5.4×10^{-9}
THF	–	8.4×10^{-8}
80% toluene, 20% THF	–	5.6×10^{-8}
80% benzene, 20% THF	–	7.5×10^{-8}
50% benzene, 50% THF	–	9.9×10^{-8}

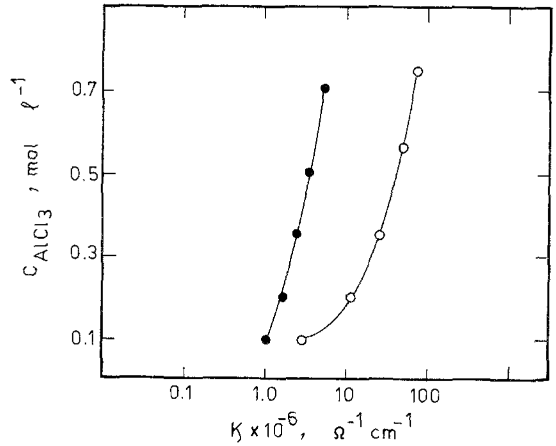

Fig. 2. Variation of the specific conductivity of $AlCl_3$ in THF–benzene and THF–toluene mixed solvents as a function of concentration. ●, $AlCl_3$ in THF–benzene; ○, $AlCl_3$ in THF–toluene.

solubility in THF–benzene [7] or THF–toluene. The general feature is the increase in the specific conductivity with increasing concentration of $AlCl_3$ or $LiAlH_4$ in THF.

Fig. 2 illustrates the variation of the conductivity of $AlCl_3$ solutions in THF–benzene or THF–toluene solvent with the concentration of $AlCl_3$. It is clear from the figure that the conductivity of the solutions is slightly higher or comparable with those shown in Fig. 1, although the concentration of $AlCl_3$ reached about 0.7 mol l^{-1} in such solvent mixtures. The conductivity of the solution shows a large increase on addition of $LiAlH_4$. In both solvent mixtures, and at a constant concentration of total aluminium of 0.7 mol l^{-1}, the conductivity of the solution increases markedly with increase of the molar ratio $LiAlH_4$ to $AlCl_3$ (cf. Fig. 3) up to a molar ratio of 1 : 1. Above this ratio the increase in the conductivity at this concentration is more or less insignificant. At a constant molar ratio of $LiAlH_4$ to $AlCl_3$ of 1 : 3 the conductivity of the solution increases as the total concentration of aluminium increases. From Figs 3 and 4 it is clear that the conductivity of the solution could be increased either by increasing the molar ratio of $LiAlH_4$ to $AlCl_3$ or by increasing the total concentration of aluminium in the solution.

To choose the optimum concentration of total aluminium and the optimum molar ratio of $LiAlH_4$ to $AlCl_3$, a series of experiments were carried out. The results are collectively illustrated in Fig. 5. Curve a represents the variation of the specific conductivity with increasing concentration of $AlCl_3$ and $LiAlH_4$ at constant molar ratio $LiAlH_4$ to $AlCl_3$ of 2 : 3, while curve b represents the same relation but for solutions of constant molar ratio of 3 : 2, respectively. Aside from the differences at low concentrations the two curves seem to be parallel. The curve for higher ratio of $LiAlH_4$ (curve b) shows higher conductivity values. Curve c illustrates the effect of increased concentration of aluminium at a constant $LiAlH_4$ concentration of 0.4 mol l^{-1} on the specific conductivity of the solution. The

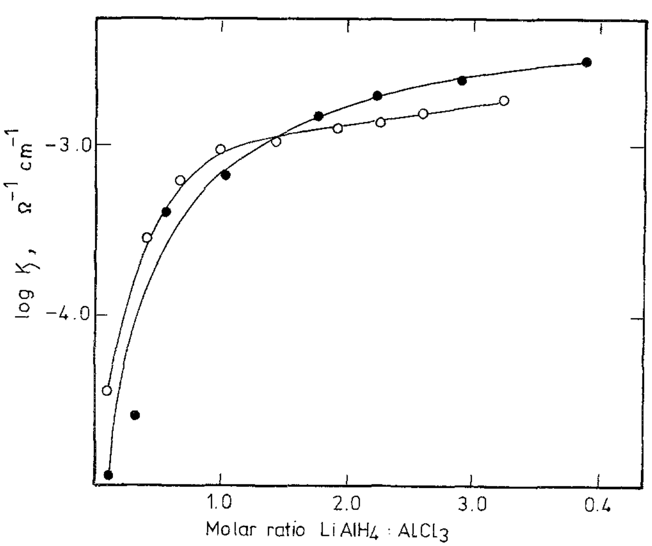

Fig. 3. Effect of the molar ratio of $LiAlH_4$ to $AlCl_3$ on the specific conductivity of the solution at a total concentration of aluminium of 0.7 M in THF–benzene (●) and in THF–toluene (○) mixed solvents (20 vol % THF).

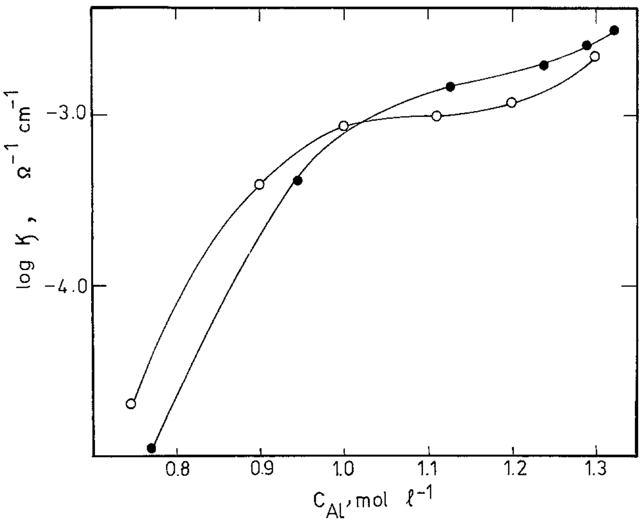

Fig. 4. Effect of increased total concentration of aluminium on the specific conductivity of the solution at a constant molar ratio of $LiAlH_4$ to $AlCl_3$ of 1:3 in THF–benzene (●) and in THF–toluene (○) mixed solvents (20 vol % THF).

addition of $AlCl_3$ to $LiAlH_4$ is accompanied by a gradual increase in the specific conductivity of the solution. Curve d of Fig. 5 illustrates the effect of increased concentration of aluminium at a constant concentration of $AlCl_3$ of 0.5 mol l^{-1} on the specific conductivity of the solution. It is clear that the addition of $LiAlH_4$ to the low conducting $AlCl_3$ results in a considerable increase in the conductivity of the solution. The increased conductivity with increasing concentration of $LiAlH_4$ can be attributed to the formation of both $AlHCl_2$ and AlH_2Cl which undergo disproportionation leading to the ionic species $AlCl_2^+$, $AlH_2Cl_2^-$ and AlH_2^+ (cf. Equations 1, 2, 3 and 4). These ionic species are responsible for the increased conductivity of the solution. At a constant molar ratio of $LiAlH_4$ to $AlCl_3$ any increase in the total concentration of aluminium leads to an increase in the concentration of the ionic species and, consequently, to

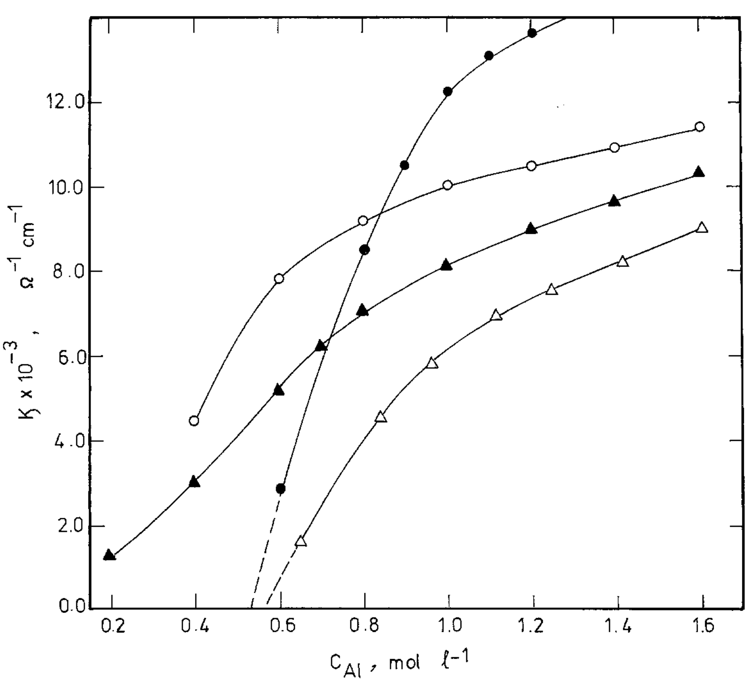

Fig. 5. Variation of the specific conductivity of $LiAlH_4$–$AlCl_3$ in THF–toluene with the total concentration of aluminium. △, Constant molar ratio $LiAlH_4$ to $AlCl_3$ of 2:3. ▲, Constant molar ratio $LiAlH_4$ to $AlCl_3$ of 3:2. ○, Constant concentration of $LiAlH_4$ of 0.4 M. ●, Constant concentration of $AlCl_3$ of 0.5 M.

an increase in the conductivity of the solution. The remarkable increase in the conductivity of the solution with increase of the concentration of $LiAlH_4$ at a constant concentration of $AlCl_3$ (Fig. 5d) may be attributed to the increased possibility for the formation of Li^+ according to Equations 5 and 6.

It may be concluded that a solution of total aluminium concentration of $1\,mol\,l^{-1}$ and a molar ratio of $LiAlH_4$ to $AlCl_3$ of 1:3 in a solvent of 20% THF–80% toluene (vol %) represent a very good bath for the electrodeposition and electrodissolution of aluminium. The kinetics and mechanism of these processes will be discussed in detail in part II.

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