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Anodic polarization of aluminium in organic electrolytes

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The polarization characteristics of aluminium anodes have been studied in various organic electrolytes containing aluminium chloride. The small amount of oxide present on the metal was dissolved by an anodic pre-treatment. The charge transfer number of the overall reaction was three. The current density supported by the electrolytes decreased in the order nitromethane > acetonitrile > propylene carbonate, formamide > tetrahydrofuran. The rest potential increased in the order formamide < propylene carbonate < tetrahydrofuran < acetonitrile < nitromethane.

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1. Introduction

Interest in high energy batteries [1–4] has increased in recent years and the lithium anode [5–9] has considerable potentialities in this context. Batteries using lithium anodes have usually utilized a non-aqueous electrolyte and cathodes of metal halides [4, 7, 9–12], sulphide [13], oxide [4, 14] or active organic materials [15–18].

On the other hand aluminium anodes react less vigorously with water and also have a high standard electrochemical potential, 1·66 V (versus NHE) at 25°C and the electrochemical equivalent of Al^{3+} is 8·994. For these reasons, batteries with aluminium anodes have good prospects in the field of high energy batteries, but non-aqueous electrolytes are required if the formation of a passive film on the electrode is to be avoided. The behaviour of an aluminium anode in acetonitrile and its mixed solvents, and the influence of the water content on the performance have been recently reported by Takada and Miyake [19]. In the present work, the performance of an aluminium anode has been investigated in various organic electrolytes and relations between the anode characteristics and some properties of the electrolytes, clarified.

2. Experimental technique

2.1 *Reagents*

Nitromethane (NM) was distilled twice in the presence of calcium chloride. The water content was measured, using Karl Fischer reagent, as being below 350 ppm. Acetonitrile (AN) was distilled twice in the presence of phosphorus pentoxide to a water content of below 120 ppm. Tetrahydrofuran was distilled over lithium aluminium hydride to give a water content of below 100 ppm. Propylene carbonate (PC), dehydrated through a column packed with 5A molecular sieve, was distilled under reduced pressure in the presence of calcium oxide, to a water content of below 50 ppm. Formamide (FA) was neutralized with sodium hydroxide and distilled, followed by distillation in the presence of sodium formate, both under reduced pressure.

2.2 *Electrolytic cell and operation*

The electrolytic cell, shown in Fig. 1, had a diameter of 4 cm and height 10 cm with a Teflon cap. The test electrode was a 1 × 1 × 0·04 cm aluminium plate (99·99% purity). Two counter electrodes, each 3 × 2 × 0·04 cm, were sited on each side of the test electrode. A silver chloride electrode was used as reference and its potential was checked against a saturated calomel electrode before and after measurements. The volume of the electrolyte solution, which was prepared by adding aluminium chloride to each organic solvent, was 50 ml. Nitrogen gas was bubbled into the solution before electrolysis and passed over the electrolyte surface during measurement.

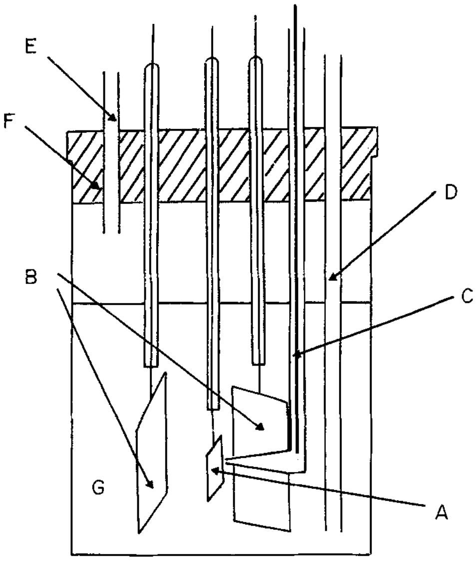

Fig. 1. Structure of cell.
A, Aluminium electrode B, Platinum counter electrodes
C, Reference electrode D, Nitrogen gas inlet
E, Nitrogen gas outlet F, Teflon cap
G, Electrolyte

Before making polarization measurements, the aluminium electrode was generally pre-electrolysed at 500 mV more positive than each initial rest potential for 10 min. Measurements were made, usually in the stationary state by using a potentiostat. For coulometric measurements, a current pulse generator and a digital coulometer were used.

3. Results and discussion

An aluminium electrode is covered with a thin oxide layer after the usual polishing with emery paper. The thickness of this oxide layer was estimated coulometrically using a square current pulse of 15 mA cm^{-2} of 0·3 ms width (Fig. 2).

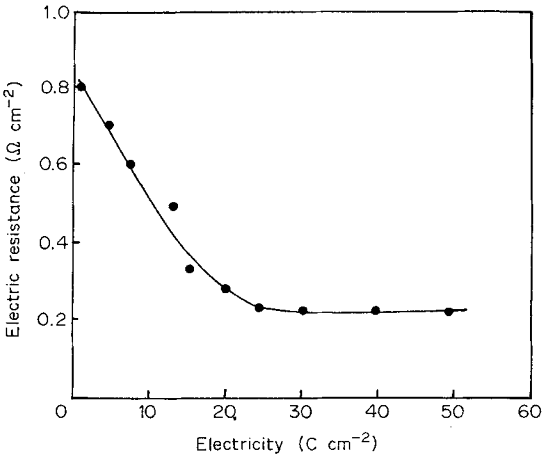

Fig. 2. Resistance versus charge under constant current. Current density: 10 mA cm^{-2}; electrolyte: AN+1 M $AlCl_3$, 30°C. (See text for explanation of abbreviation.)

A constant low resistance was observed after passing an anodic current corresponding to *c.* 25 mC cm^{-2}, and so the charge required for

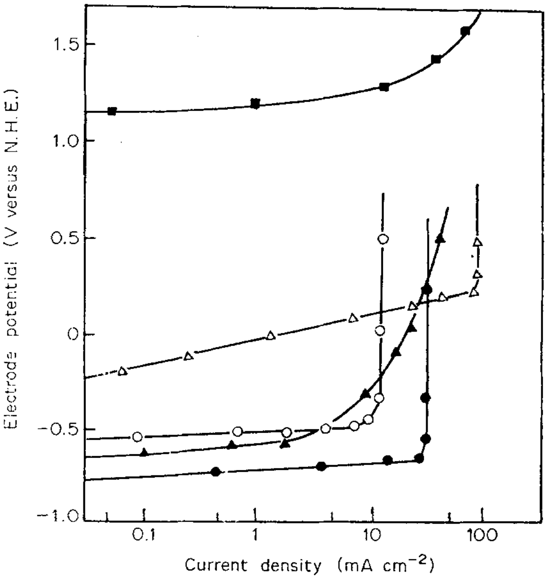

Fig. 3. Anodic polarization characteristics of Al electrodes in various electrolytes, -■-, NM+1 M $AlCl_3$; -△-, AN+1 M $AlCl_3$; -○-, THF+1 M $AlCl_3$; -▲-, PC+1 M $AlCl_3$; -●-, FA+sat. $AlCl_3$, 30°C.

Table 1. Dielectric constants and viscosities of organic solvents [4, 20], *and conductivities of the electrolyte measured*

Solvent	*Dielectric constant*	*Viscosity (cp)*	*Electrolyte*	*Conductivity* (Ω^{-1} cm^{-1}, 30°C)
Nitromethane (NM)	35·87 (30°C)	0·576 (30°C)	NM+1 M $AlCl_3$	$1{\cdot}59\times 10^{-2}$
Acetonitrile (AN)	37·5 (20°C)	0·325 (30°C)	AN+1 M $AlCl_3$	$2{\cdot}26\times 10^{-2}$
Tetrahydrofuran (THF)	7·58 (25°C)	0·460 (25°C)	THF+1 M $AlCl_3$	$1{\cdot}44\times 10^{-3}$
Propylene carbonate (PC)	64·4 (25°C)	2·503 (25°C)	PC+1 M $AlCl_3$	$7{\cdot}16\times 10^{-3}$
Formamide (FA)	111·0 (20°C)	3·302 (25°C)	FA+sat. $AlCl_3$	$8{\cdot}03\times 10^{-3}$

dissolution of the oxide layer was assumed to be this.

By means of coulometric measurements of the anodic dissolution of the aluminium at a potential of 300 mV positive versus NHE, the charge transfer number was calculated as 2·73 on the overall process. The charge transfer number should therefore be 3 and the overall reaction:

$$\mathrm{Al} \longrightarrow \mathrm{Al}^{3+} + 3e^-$$

The anodic polarization curves of aluminium in stationary measurements are shown in Fig. 3. The behaviour varied with electrolyte. The dielectric constants and viscosities of these solvents, and electric conductivities of the electrolyte containing aluminium chloride are shown in Table 1. Generally, the higher the dielectric constant and the lower the viscosity of the solvent, the higher the electric conductivity found. The order of increase in maximum current density was NM>AN>PC, FA>THF which almost corresponds to the order of the conductivities. For a low rest potential, the order was FA<PC< THF<AN<NM and this would be related to the solvation energy of the aluminium cation.

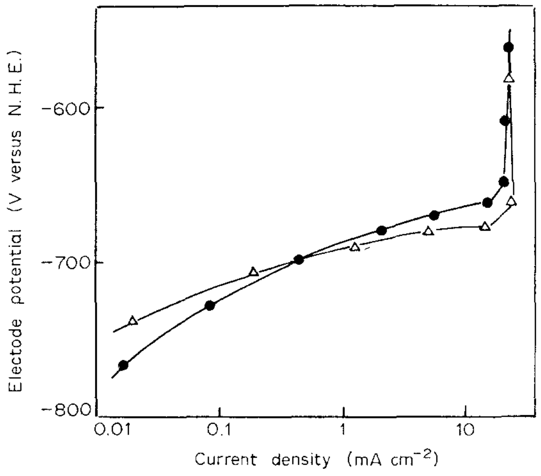

Fig. 4. Anodic polarization characteristics of pretreated Al. Electrolyte: FA+sat. $AlCl_3$, -●-, Al anodically pre-treated; -△-, Al cathodically plated, 30°C.

Fig. 4 shows the anodic polarization characteristics of aluminium electrodes anodically pre-treated and cathodically plated before measurement, in FA containing aluminium chloride. These two polarization curves are very similar, showing that aluminium has some prospects for application in secondary batteries.

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