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Organic electrolytes for corrosion testing of aluminium and Al–Li binary alloys

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The electrochemical behavior of high purity aluminium and Al-Li alloy has been investigated in various organic environments. Various lithium- and aluminium-compatible solvents were considered before selecting propylene carbonate (PC) and tetrahydrofuran (THF) with addition of either chloride or perchlorate ions. THF finally proved to be the most suitable solvent for these tests. The aluminium dissolution reaction in a THF environment is fast and reversible. The Al/Al(III) couple can therefore be used as a reference electrode. Aluminium salts can be reduced by lithium, making the Li/Li^+ couple unsuitable for the reference electrode. The voltammograms obtained show voltage characteristics (protective potential E_p and breakdown potential E_b) similar to those found in aqueous environments. The voltage variations recorded by potentiometric measurements could be associated with changes in the alloy surface state.

1. Introduction

Electrochemical investigations aimed at determining the characteristics of aluminium or its alloys mainly use aqueous electrolytes. Several methods exist.

1.1. *Aqueous environments*

The properties of aluminium in aqueous environments are determined by measuring its protective potential E_p (or pitting potential) and breakdown potential E_b in electrolytes containing chemically aggressive ions such as chlorides. The following three methods may be used to measure these values.

(1) Potentiokinetic method: a linear voltammetric scan is made in the anodic domain until a dissolution current is observed followed by a return scan. The E_b values determined in this way depend on several variables including the scan rate. This method is no longer used [2–5].

(2) Quasi-stationary method: constant potential jumps are applied and the corresponding currents recorded after identical times. The values of E_p and E_b are different and closer together than those obtained using the previous method.

(3) Stationary method: as in the previous method, potential steps during oxidation are applied, but this time the current is measured after return to equilibrium. Pessall and Liu [6] have recommended another method to characterize the behavior of metals and alloys in chloride environments. The critical pitting potential E_p is determined after scratching the electrode surface. This technique offers the advantage of providing a potential value dependent on the composition or structure of the metal or electrolyte but independent of superficial oxide contribution.

1.1.1. Alloys. For Al–Cu, Al–Zn and Al–Mg alloys in a chloride environment, Galvele *et al.* [7, 8] have shown that the pitting potential E_p varies with the types of alloy constituents used and their contents. For example, with Al–Cu alloy E_p increases significantly with copper content (up to a limiting value of 5%). However, the alloy thermal treatment (quenching, annealing, etc) has only a slight influence on the E_p values. Maximum differences are around 0.1 V [7]. This is, however, sufficient to show the structure changes taking place in the alloy composition. During the slow cooling of an Al–Cu alloy, the excess insoluble copper precipitates in the form of Al_2Cu, leading to low copper content zones in the grain boundaries [9, 10].

For Al–Zn alloys, measurements made in chloride environments have shown that E_p decreases as the zinc content increases up to 4% and then remains constant.

With Al–Mg alloys, E_p is not affected by the Mg content and remains the same as in pure aluminium. These alloys are, however, affected by an intergranular corrosion phenomenon marked by preferential dissolution of the most electropositive phase or element.

The addition of Ga (0.2%) to pure aluminium leads to intense pitting and corrosion at the grain boundaries. The addition of P (0.2%) to this alloy reduces the corrosion rate due to the formation of intermetallic compounds and their dissolution in the lattice [11].

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1.1.2. Al–Li alloy. These alloys are of considerable interest in aeronautics due to their enhanced elasticity (6%) and reduced density (3%) [12]. In aqueous environments they corrode actively, accompanied by the production of hydrogen and the alkalization of the environment up to a pH of 11.3 [13]. The pH of the solution is controlled by the transfer of lithium, or of the most lithium-rich phase in solution, according to the reaction

$$\langle \mathrm{Li} \rangle + \mathrm{H_2O} \longleftrightarrow \mathrm{LiOH} + \mathrm{H^+}$$

Precipitation of the delta phase (AlLi) within the grain boundaries has a detrimental effect on corrosion [14, 15].

In chloride/carbonate/bicarbonate solutions, passivation of these alloys occurs through precipitation of a lithium aluminate $LiAlO_2$ [16]. In aqueous environments, crack initiation in Al–Li–Cu–Mg alloys is strongly dependent on the copper content in the alloy. For copper contents less than 2%, crack initiation does not take place for total or alternating immersion/emergence in saline electrolytes [17].

1.2. *Non-aqueous environments*

The electrochemical behavior of aluminium has also been investigated in non-aqueous environments. Tamura *et al.* [18] have measured the rest potential of aluminium in nitromethane (NM), acetonitrile (AN), propylene carbonate (PC), formamide (FA) and tetrahydrofuran (THF) non-aqueous environments containing 1 M aluminium chloride. The rest potentials increase in the order FA < PC < THF < AC < NM. This was interpreted as being due to the solvation energy of the aluminium cation. Similarly, for electrochemical polarization measurements, the current density increased in the order THF < FA < PC < AC < NM.

In another domain, potential measurements carried out in a $CH_3OH + CCl_4$ environment containing $CuCl_2$ have been used to test corrosion on Al–Cu alloys [19]. There is a gradual modification of the metallurgical state of the alloy resulting in a transition of the type of corrosion from intergranular corrosion to pitting. During attack, copper is deposited at the alloy surface, resulting in a major potential variation of -300 to -1100 mV.

1.3. *Fused salt environments*

Fused salt environments have also been investigated [20, 21] in electrochemical studies of very reactive aluminium alloys. Outside the classical fused salt investigations, only the study by Osteryoung *et al.* [22] is devoted to low-temperature fused salt environments. These authors examined the deposition or dissolution of aluminium based on aluminium chloride and *n*-butyl pyridine containing benzene.

In the present study, we focus on the characterization, by electrochemical methods, of aluminium alloys containing highly electropositive additives. Their reactivity in aqueous environments limits the study of these electrodes. We conducted this work in the presence of an organic solvent and selected an electrolyte which could be used to classify the properties of the alloys.

Table 1. Electrode material compositions

	Li	*Si*	*Cu*	*Fe*	*Mg*
High purity Al Impurities (ppm)	–	17	50	12	10
Al–Li (ppm)	2%	17	50	12	10

2. Experimental details

2.1. *Electrolytic cell*

The electrochemical part of the test cell included three electrodes. The working electrode was a high purity aluminium or Al–Li alloy disk with an active area of 1 cm^2. The electrode material compositions are given in Table 1. The aluminium was first subjected to ultrasonic cleaning in an acetone bath.

The reference electrode was either a high purity aluminium or lithium disk with a diameter of 6 mm. The auxiliary electrode was a stainless steel concentric ring with outside and inside diameters of 16 mm and 12 mm, respectively. The reference and auxiliary electrodes faced the working electrode. They were separated by a paper separator saturated with the organic liquid electrolyte. The products were obtained from Merck (THF, PC) or Fluka (AN). The salts were dried at 120° C in a dynamic vacuum before use. The cell was assembled in a glove box swept by a flow of purified argon (water content less than 5 ppm) and was maintained in an argon atmosphere for the duration of the electrochemical tests, within a sealed glass vessel.

2.2. *Electrical apparatus*

A Tacussel type 40-1X potentiostat linked with a Servovit control system and a Sefram TGM 101 recorder was used for the voltammetry scans. A Tacussel Minisis 8000 millivoltmeter connected to a Sefram Servotrace recorder was used for the potentiometric measurements.

3. Results

3.1. *Choice of electrolytes*

Investigations into the electrochemical behavior of aluminium in non-aqueous environments have been oriented mainly towards: (i) thin layer deposition of aluminium [22]; (ii) anodes for electrochemical batteries [18]. We have carried out similar investigations with the aim of proposing an organic electrolyte for use in characterizing aluminium and its alloys (mainly with lithium).

Table 2. Choice of solvents

		Solvent				
		THF	*PC*	*DMF*	*AN*	*Toluene*
Stability	Al	yes	yes	yes	yes	yes
	Li	yes	yes	no	no	–

3.1.1. Choice of organic solvents. This electrolyte must be compatible with the aluminium and its additives and must solubilize the salts of the latter. Solvents considered include acetonitrile (AN), tetrahydrofuran (THF), propylene carbonate (PC), dimethylformamide (DMF) and toluene. The main results are given in Tables 2 and 3.

Lithium reacts rapidly with two of the organic solvents and the toluene solutions containing salts blacken rapidly. Insofar as we are focusing our interest on Al–Li alloys, DMF and AN can be eliminated from our choice of solvents. Similarly, toluene may be eliminated due to the low stability of the electrolytes.

3.1.2. Choice of salts. For chloride utilization, initially, aluminium chloride is soluble in the solvents considered. This result is consistent with the results of previous studies [18]. In contrast, lithium chloride either precipitates in a toluene environment or is sparingly soluble in a PC environment. With such solvents, other salts must be envisaged (e.g. perchlorates, bromides)

3.2. *Electrochemical behavior of aluminium in a PC environment*

A voltammetric scan was carried out on the high purity aluminium in a PC environment containing aluminium chloride or lithium perchlorate. We used this electrolyte since it represents a basic electrolyte in organic environments.

Anodic dissolution of the aluminium occurs with low current density values until overvoltages of around 1.5 V are reached in the chloride environment, and aluminium deposition occurs during the return scan. The reduction of the salt limits the voltage domain (Fig. 1)

With perchlorate ions, the dissolution of aluminium requires a high potential (3 V/Li). The presence of lithium ions in the electrolyte is characterized by the lithium deposit cathodic limit and by the formation of Li–Al alloys during reoxidation (Fig. 2).

Table 3. Choice of salts

	Solvent				
	THF	*PC*	*DMF*	*AN*	*Toluene*
Solubility $AlCl_3$	yes	yes	yes	yes	yes
$LiCl$	yes	no	yes	–	no
$AlBr_3$	–	–	–	–	yes
$LiClO_4$	yes	yes	–	–	–
$Al(ClO_4)_3$	yes	yes	–	–	–

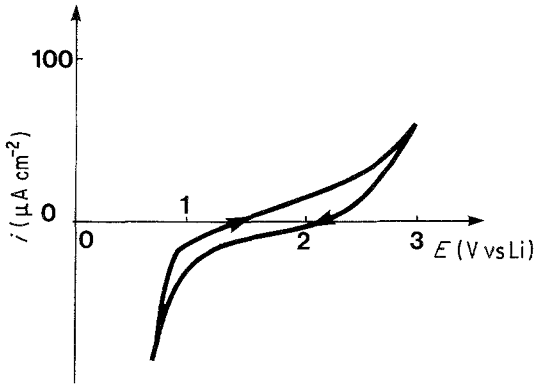

Fig. 1. Cyclic voltammogram. Electrode: aluminium; electrolyte: PC + $AlCl_3$ (0.9 M) + LiCl (0.1 M); scan rate: 0.6 V min^{-1}.

In conclusion, with PC the aluminium dissolution kinetics are limited in the presence of chloride ions and require a high overvoltage in the presence of perchlorate ions.

3.3. *Electrochemical behavior of aluminium in a THF environment*

A linear voltammetric scan was carried out on the high purity aluminium with lithium chloride or aluminium chloride dissolved in the THF. The dissolution reaction is very fast and reversible in the voltage range investigated (Fig. 3). This electrolyte was chosen due to the rapid kinetics observed with aluminium. Note however that this solvent is highly volatile and that the cell life is limited by the drying of the separator paper.

3.4. *Choice of a reference electrode*

In the presence of aluminium or aluminium salt, electrochemical tests using the Li/Li^+ couple as the reference electrode must take into account the possible redeposition of the least electropositive element. We observed that the potential of an aluminium electrode in a THF solution (containing LiCl + $AlCl_3$) behaved differently depending on the nature of the

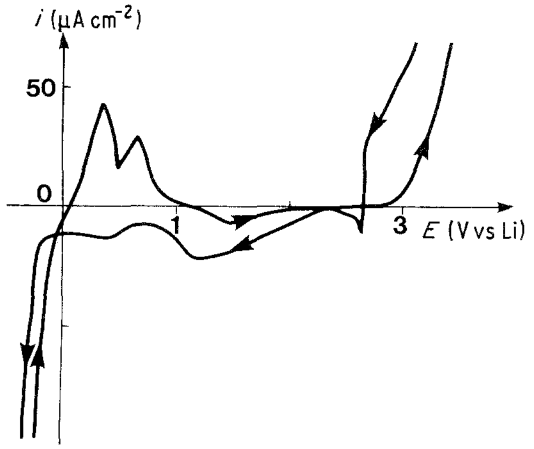

Fig. 2. Cyclic voltammogram. Electrode: aluminium; electrolyte: PC + $LiClO_4$ (0.8 M); scan rate: 0.6 V min^{-1}.

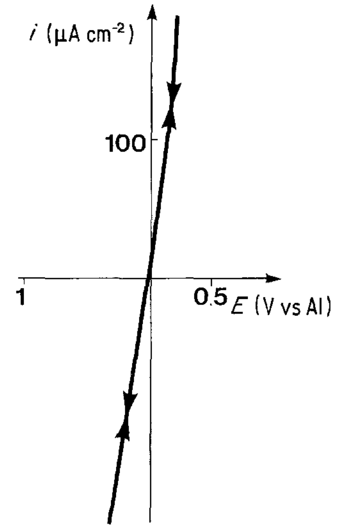

Fig. 3. Cyclic voltammogram. Electrode: aluminium; electrolyte: THF + $AlCl_3$ (0.9 M) + LiCl (0.1 M); scan rate $v = 1\,V\,min^{-1}$.

reference electrode (i.e. Al or Li). A lithium reference electrode may be covered by an aluminium deposit.

Concerning the reversibility of aluminium in the proposed electrolytes, we limited our test to THF containing aluminium chloride. The results of micropolarization near the rest potential (Fig. 4) allow us to propose aluminium as a reference electrode for THF environments. Note that the use of aluminium as a reference electrode for PC environments is not possible due to the excessively slow dissolution reaction. There is a difference of 2 V between oxidation and reduction.

3.5. *Rest potential variations*

The rest potential variations with time were recorded for aluminium in the following electrolytes: THF + 0.1 M $AlCl_3$; THF + 0.1 M $Al(ClO_4)_3$; THF + 0.05 M $Al(ClO_4)_3$ + 0.15 M $LiCF_3SO_3$; THF + 0.9 M $AlCl_3$ + 0.1 M LiCl. In these tests, the rest potentials obtained with the different ions Cl^-, ClO_4^- and $CF_3SO_3^-$ (Fig. 5) can be compared. They are all in the neighborhood of the reference electrode (Al) potential, with only slight differences caused by the anions or cations. The test duration is limited to 2 h due to the volatile nature of the solvent and the low quantity absorbed by the separator paper.

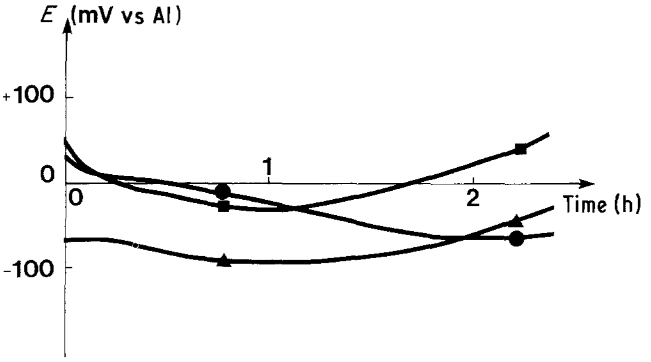

Fig. 5. Potential evolution with time. Electrode: aluminium; electrolyte: (▲) THF + $AlCl_3$ (0.1 M); (●) THF + $Al(ClO_4)_3$ (0.1 M); (■) THF + $Al(ClO_4)_3$ (0.05 M) + $LiCF_3SO_3$ (0.15 M).

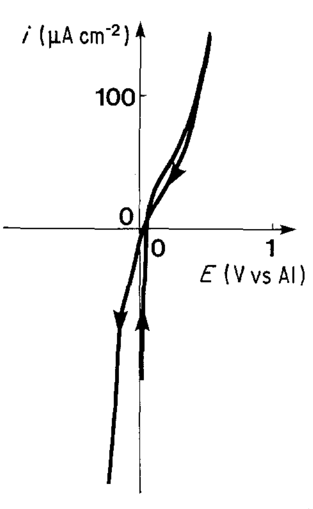

Fig. 4. Cyclic voltammogram. Electrode: aluminium; electrolyte: THF + $AlCl_3$ (0.9 M) + LiCl (0.1 M); scan rate $0.1\,V\,min^{-1}$.

3.6. *Voltammetric scans*

Voltammetric scans were carried out on the high purity aluminium in the above electrolytes. Two scan rates were used: a low rate ($10\,mV\,min^{-1}$), approaching stationary conditions, and a higher rate ($0.1\,V\,min^{-1}$), providing qualitative information on the electrode reaction kinetics.

For these two scan rates, the voltage characteristics observed on the voltammograms are similar to those obtained for aqueous environments. Table 4 gives the breakdown and protective potentials, E_b and E_p, respectively, obtained for these electrolytes.

The results shown in Table 4 are consistent with the general activity of these ions. As in aqueous environments the chloride ions provide the easiest dissolution of aluminium. They may be classed in the order $Cl^- > ClO_4^- > CF_3SO_3^-$.

3.7. *Al-Li alloys*

The cyclic voltammetry tests were repeated for the Al-Li alloy in THF electrolyte containing chlorides. The results (Fig. 6) show the dissolution of the alloy. Rest potential measurements reveal surface changes on the alloy seemingly corresponding to the selective dissolution of lithium and superficial aluminium enrichment (Fig. 7). This hypothesis is supported by

Table 4. Breakdown and protective potentials for aluminium in organic environments (Al ref)

Electrolyte	$v = 10\,mV\,min^{-1}$	$v = 100\,mV\,min^{-1}$
THF + $AlCl_3$	$E_b = 96\,mV$	$E_b = 58\,mV$
	$E_p = 167\,mV$	$E_p = -19\,mV$
THF + $Al(ClO_4)_3$	$E_b = 154\,mV$	$E_b = 153\,mV$
	$E_p = 101\,mV$	$E_p = 314\,mV$
THF + $Al(ClO_4)_3$ + $LiCF_3SO_3$	$E_b = 1368\,mV$	$E_b = 963\,mV$
	$E_p = 727\,mV$	$E_p = 375\,mV$

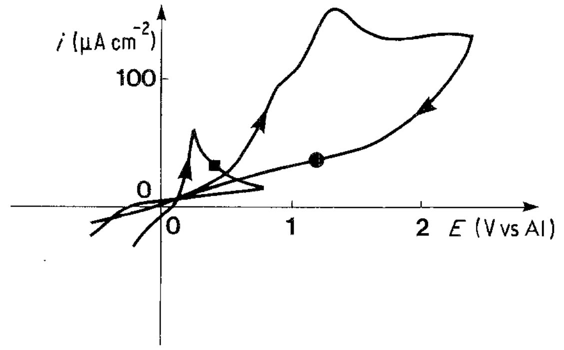

Fig. 6. Cyclic voltammogram. Electrode: Al–Li; electrolyte: THF + $AlCl_3$ (0.9 M) + LiCl (0.1 M); scan rate: (●) 1 V min^{-1}; (■) 10 mV min^{-1}.

the precipitation of LiCl for high currents as observed during the voltammetric scans.

4. Conclusion

The dissolution reaction of aluminium in organic environments has been investigated. The solvents considered were propylene carbonate (PC), tetrahydrofuran (THF), acetonitrile (AN), dimethylformamide (DMF) and toluene. Several of these solvents were eliminated from the investigation due to: (i) reactivity with alloy elements such as lithium (AN and DMF); (ii) reactivity with the salts (toluene); (iii) weak solvating power.

The electrolyte was rendered ion-conducting by the addition of chlorides (aluminium or lithium). The low solubility of lithium salts in propylene carbonate environments made tetrahydrofuran the best solvent for our tests. Other perchlorate or trifluoromethane sulfonate dissalts were then tested. The aluminium dissolution kinetics varied, as in aqueous environments, in the order $Cl^- > ClO_4^- > CF_3SO_3^-$.

Our results show that aluminium is a suitable reference electrode material since its dissolution reaction in a THF environment is fast and reversible. On the other hand, the Li/Li$^+$ couple cannot be used as a reference since the aluminium salts may be reduced by the lithium.

The electrochemical investigation methods used involved potentiometric measurements or voltammetric scans. The characteristics observed are comparable to those observed in aqueous environments insofar as passivity breakdown and protective potentials are concerned. In our case, the organic electrolyte did not modify the initial surface state of the alloy.

Now that the electrochemical behavior of aluminium and the binary alloy Al–Li in a THF environment containing chloride has been studied, the next step is to determine whether this electrolyte may be employed in a general manner with other aluminium alloys.

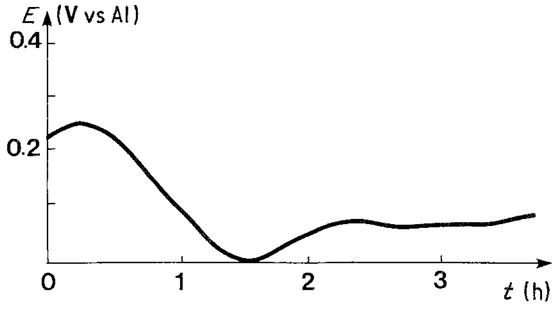

Fig. 7. Potential evolution with time. Electrode: Al–Li 1156; electrolyte: THF + $AlCl_3$ (0.9 M) + LiCl (0.1 M).

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