

## THE CYCLING BEHAVIOUR AND STABILITY OF THE LITHIUM ELECTRODE IN PROPYLENE CARBONATE AND ACETONITRILE ELECTROLYTES

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### Summary

The conductivity and chemical stability with lithium of various electrolytes containing propylene carbonate (PC) and acetonitrile (AN) were determined. Addition of AN improved the conductivity of  $\text{LiClO}_4/\text{PC}$  and  $\text{LiAsF}_6/\text{PC}$  electrolytes, and the  $\text{LiAsF}_6/\text{PC-AN}$  electrolyte showed remarkable chemical stability in contact with lithium. The lithium cycling efficiency was determined on nickel and aluminium substrates in the various electrolytes over a range of current density. While the efficiencies observed on nickel substrates were very poor for all AN-containing electrolytes, efficiencies approaching those for electrolytes containing only PC were obtained with the  $\text{LiAsF}_6/\text{PC-AN}$  electrolyte at low current densities ( $\sim 1 \text{ mA cm}^{-2}$ ) on aluminium substrates. It was concluded that the  $\text{LiAsF}_6/\text{PC-AN}$  electrolyte had generally favourable characteristics and may prove suitable for primary battery applications.

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### Introduction

The poor cycling performance of the lithium electrode remains a major factor limiting the development of secondary lithium/organic-electrolyte batteries. The two most common approaches to the problem now involve the development of more suitable organic electrolytes and the use of lithium alloy electrodes with improved cycling characteristics.

Electrolytes containing only PC (e.g.,  $\text{LiClO}_4/\text{PC}$ ) are regarded as unsatisfactory for secondary lithium batteries because of poor lithium cycling efficiencies [1 - 5]. There is now substantial evidence regarding the

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role of film formation in the failure of lithium electrodes [2, 5, 6]. Two of the more successful electrolytes identified over the past five years are  $\text{LiClO}_4/\text{dioxolane}$  [7] and  $\text{LiAsF}_6/2\text{-methyltetrahydrofuran}$  [8, 9]. The former electrolyte, however, is associated with an explosion hazard [10] while the latter has a relatively low conductivity.

The addition of low viscosity and/or high dielectric constant components to electrolytes is often used to improve conductivity. Mixed electrolytes such as  $\text{LiClO}_4/\text{PC-DME}$  [11] and  $\text{LiBr/PC-AN}$  [12] have been developed for primary batteries. Electrolytes containing AN do not appear to have been considered for secondary battery applications because of the reactivity of AN with lithium. However, with the development of improved electrolytes containing  $\text{LiAsF}_6$  and the use of alloy electrodes such as  $\text{Li-Al}$  [13 - 15], it was felt that PC-AN mixtures should be assessed with respect to the cycling of the lithium electrode.

The investigation involved short-term and long-term lithium plating/stripping experiments on nickel and aluminium substrates, as well as conductivity measurements and preliminary chemical stability studies. The behaviour of electrolytes containing  $\text{LiClO}_4$  (PC, PC-AN and AN) was evaluated initially to assess the influence of AN, and then compared against the corresponding electrolytes containing  $\text{LiAsF}_6$ .

## Experimental

Propylene carbonate (Aldrich Chemical Company, USA, 99%) was first dried with 4A molecular sieves and then vacuum distilled at  $\sim 5$  Torr with a reflux ratio of  $\sim 5:1$ . Technical grade AN was distilled from  $\text{KMnO}_4$ , dried over calcium hydride for a week, and then triply distilled from calcium hydride. Lithium hexafluoroarsenate (USS Agrichemicals, electrochemical grade) and lithium perchlorate (ICN, 99.8% pure) were vacuum dried overnight at  $\sim 200^\circ\text{C}$  and then used without further purification. Electrolyte preparation, cell assembly, and testing were conducted in an argon filled glove box (Vacuum Atmospheres Company, USA, Model HE-43) equipped with a gas purification train (Model HE-493).

The cell employed for cycling experiments was of similar design to that described by Rauh and Brummer [2]. The working electrode consisted of either an AR nickel or aluminium foil disc mounted in a Teflon holder to expose a known surface area ( $\sim 0.2\text{ cm}^2$ ). In PC electrolytes the counter electrode was constructed by pressing lithium metal ribbon (Alfa, m3N5, 0.38 mm thick) onto expanded nickel mesh (Exmet 5Ni7-4/0), while in AN-containing electrolytes an aluminium or lithium-aluminium foil counter electrode was employed. The reference electrode consisted of a strip of lithium foil supported on nickel mesh inside a fritted compartment normally filled with 1M  $\text{LiClO}_4/\text{PC}$  or 1M  $\text{LiAsF}_6/\text{PC}$  as appropriate.

Constant current was normally supplied from a cycling galvanostat that was specially designed and constructed in these laboratories. The working

electrode potential was recorded on a strip chart recorder *via* a voltage follower. A digital conductivity meter type G46 supplied by Automated Laboratory Equipment (Aust.) was used for the conductivity measurements. All solutions were 1M, mixtures were 50% v/v and experiments were carried out at room temperature ( $\sim 25^\circ\text{C}$ ).

## Results and discussion

### 1. Conductance

Table 1 gives the conductivity and the Walden product of the various electrolytes under consideration in this study. The conductivity of both 1M  $\text{LiClO}_4$  and 1M  $\text{LiAsF}_6$  in PC is increased by the addition of solvents with high dielectric constants (36 - 44) and low viscosity (0.3 - 0.4 cP) such as AN or dimethoxyethane (DME). Even though the  $\lambda$  values of the two lithium salts are  $\sim 6 - 8$  times higher in AN than in PC, the Walden product values ( $\lambda \times \eta$ ) are only slightly higher in AN than in PC. This suggests that the higher conductivities of these salts in AN are mainly due to the lower viscosity of AN than PC. In tetrahydrofuran (THF) and methylformate (MF) which have low dielectric constants, the Walden products of  $\text{LiClO}_4$  are significantly lower than their corresponding values in AN and PC which have relatively higher dielectric constants than THF and MF. Presumably ion-pairing in MF and THF which have low dielectric constants is much greater than in AN or PC.

In all solvents, 1M  $\text{LiAsF}_6$  is more conducting than 1M  $\text{LiClO}_4$ , but the difference is much greater in solvents with low dielectric constants such as THF and MF than in solvents with high dielectric constants such as PC. Table 1 also includes the ratio (Walden Product  $\text{LiAsF}_6$ /Walden Product  $\text{LiClO}_4$ ) in AN and MF. The magnitude of this ratio is significantly higher in MF which has a low dielectric constant than in AN which has a somewhat higher dielectric constant. This suggests that  $\text{LiAsF}_6$  is a stronger electrolyte than  $\text{LiClO}_4$  and that the mobility of the  $\text{AsF}_6^-$  ion is comparable with that of  $\text{ClO}_4^-$ .

### 2. Chemical stability

Lithium metal and Li/Al alloy (50 at.%) were placed separately in contact with a number of electrolytes and observed over a period of three weeks. The results are summarized in Table 2 and show that the use of  $\text{LiAsF}_6$  and PC allows AN to be used as a co-solvent for lithium electrodes.

The lithium metal was stable in electrolytes containing only PC. However, it tended to lose its metallic luster on long term storage. Besenhard and Eichinger [16] have suggested that even though lithium is thermodynamically unstable in PC, it shows little visual reactivity due to the formation of an  $\text{Li}_2\text{CO}_3$  film on the lithium. Lithium reacted with AN and PC-AN mixtures containing  $\text{LiClO}_4$ , but not if the solution contained  $\text{LiAsF}_6$ . Apparently the  $\text{LiAsF}_6$  forms a protective film on the lithium or in some other way interferes with the corrosion of lithium by AN.

TABLE 1

Molar conductance ( $\lambda$ ) and viscosity ( $\eta$ ) of 1M LiClO<sub>4</sub> and 1M LiAsF<sub>6</sub> in PC, AN, MF, THF, PC-AN (50% v/v) and PC-DME (50% v/v) Conductance values in ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) at 25 °C.

Solvent	Dielectric constant	Viscosity ( $\eta$ ) (cP)		LiClO <sub>4</sub>		LiAsF <sub>6</sub>		Ratio $\frac{(\lambda\eta)\text{LiAsF}_6}{(\lambda\eta)\text{LiClO}_4}$	
		Pure solvent	1M LiClO <sub>4</sub>	1M LiAsF <sub>6</sub>	$\lambda$	$\lambda\eta$	$\lambda$		$\lambda\eta$
PC	64.4 <sup>a</sup>	2.53 <sup>a</sup>	7.1 <sup>f</sup>	4.80 <sup>i</sup>	5.4	38.3	6.4	30.7	—
AN	35.9 <sup>a</sup>	0.341 <sup>a</sup>	0.66 <sup>g,h</sup>	0.85 <sup>i</sup>	32.9	21.7	50.0	42.5	1.9
MF	8.5 <sup>b</sup>	0.347 <sup>b</sup>	0.67 <sup>g</sup>	0.81 <sup>g,h</sup>	12.8	8.6	33.6	27.2	3.2
THF	7.6 <sup>a</sup>	0.46 <sup>a</sup>	1.02 <sup>f</sup>	—	3.4	3.5	13.7	—	—
PC-AN	> 35	1.10 <sup>i</sup>	—	2.20 <sup>i</sup>	15.5	—	21.8	48.0	—
PC-DME	42.5 <sup>d</sup>	1.0 <sup>d</sup>	—	—	12.7 <sup>d,e</sup>	—	16.2 <sup>c</sup>	—	—

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<sup>c</sup> Measured by Dr K. Cedzyska (Murdoch University).

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TABLE 2

Visual observations on the reaction of Li and Li/Al alloy (50 at.%) with electrolytes containing PC, AN and PC-AN (50% v/v) at 25 °C

Electrolyte	Observation after 15 min	Observation after one day	Observation after one week	Observation after three weeks
Li in LiClO <sub>4</sub> /PC	No change	No change	No change	Dull Li surface
Li in LiClO <sub>4</sub> /AN	Reddish brown film on Li	Whole solution dark brown	Whole solution gelled	Whole solution gelled
Li in LiClO <sub>4</sub> /PC-AN	Reddish brown film on Li	Dark brown solution	Dark brown solution, Li covered with thick jelly-like material	Dark brown solution, Li covered with thick brown jelly
Li in LiAsF <sub>6</sub> /AN	No change	Dark brown solution	As above	As above
Li in LiAsF <sub>6</sub> /PC-AN	No change	No change	No change	No change <sup>a</sup>
Li/Al in LiClO <sub>4</sub> /PC	No change	No change	No change	No change
Li/Al in LiClO <sub>4</sub> /AN	No change	Reddish brown solution	Reddish brown solution	Reddish brown solution
Li/Al in LiAsF <sub>6</sub> /PC-AN	No change	No change	No change	No change <sup>a</sup>

<sup>a</sup>No change after 3 months.

Lithium shows an unusual degree of stability towards AN in the presence of  $\text{LiAsF}_6$ . For example,  $\text{LiClO}_4/\text{AN}$  reacted with lithium almost immediately whereas the reaction of lithium with  $\text{LiAsF}_6/\text{AN}$  was evident only after one day. Mixing PC with AN in the presence of  $\text{LiAsF}_6$  improved the stability of lithium towards AN still further. Thus, even though  $\text{LiClO}_4/\text{PC-AN}$  reacted immediately with lithium,  $\text{LiAsF}_6/\text{PC-AN}$  showed no reaction over three months.

### 3. Lithium cycling and stripping efficiency

#### (a) Cycling efficiency of lithium on nickel and aluminium substrates

Tests were made over a range of current density with a plating charge of  $0.1 \text{ C cm}^{-2}$ . A stripping potential limit of  $\sim +2 \text{ V vs. Li/Li}^+$  was employed and the cycling efficiency ( $\gamma$ ) was defined as the ratio of the stripping to the fixed plating time at constant current [2]. The cycling behaviour of nickel substrates in  $\text{LiClO}_4/\text{PC}$  and  $\text{LiAsF}_6/\text{PC}$  at  $2 \text{ mA cm}^{-2}$  is shown in Fig. 1.

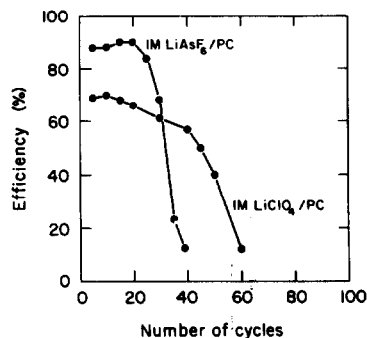


Fig. 1. Lithium cycling efficiency on a nickel substrate in  $1\text{M LiClO}_4/\text{PC}$  and  $1\text{M LiAsF}_6/\text{PC}$  at  $2 \text{ mA cm}^{-2}$  as a function of cycle number.

While the cycling efficiency was somewhat better and more constant over the first  $\sim 25$  cycles in  $\text{LiAsF}_6/\text{PC}$ , failure normally occurred more rapidly than in  $\text{LiClO}_4/\text{PC}$ . As reported in a previous communication [15], marked differences are observed between cycling lithium on nickel (non-alloying) and aluminium (alloying) substrates in  $\text{LiClO}_4/\text{PC}$ . Whereas the cycling efficiency for the nickel substrate fell rapidly from  $\sim 60\%$  to  $\sim 20\%$  in  $\sim 50$  cycles, that for the aluminium remained essentially unchanged at  $\sim 99\%$  for several hundred cycles [15]. The cycling behaviour of aluminium substrates in  $\text{LiAsF}_6/\text{PC}$  was very similar to that observed in  $\text{LiClO}_4/\text{PC}$ , with efficiencies approaching  $100\%$  for up to  $\sim 1000$  cycles ( $0.1 \text{ C cm}^{-2}$ ).

The effect of addition of AN to the PC-containing electrolytes can readily be seen in Table 3 which shows the *maximum* lithium cycling efficiencies on nickel and aluminium substrates under various conditions. The maximum cycling efficiency on nickel was normally reached in less than 20 cycles, while on aluminium it sometimes took up to 100 cycles to develop, whereupon it remained almost constant. The nickel substrate behaved very

TABLE 3

Maximum lithium cycling efficiencies ( $\gamma$ ) observed on nickel and aluminium substrates in electrolytes containing PC, AN, and PC-AN (50% v/v)

Substrate	Solute	$\gamma$ in PC (%)		$\gamma$ in PC-AN (%)		$\gamma$ in AN (%)	
		1 mA cm <sup>-2</sup>	5 mA cm <sup>-2</sup>	1 mA cm <sup>-2</sup>	5 mA cm <sup>-2</sup>	1 mA cm <sup>-2</sup>	5 mA cm <sup>-2</sup>
Nickel	LiClO <sub>4</sub>	60	70	< 5	< 5	~ 0	~ 0
Nickel	LiAsF <sub>6</sub>	85	90	< 15	< 15	—	—
Aluminium	LiClO <sub>4</sub>	~100	~100	88	88	70	75
Aluminium	LiAsF <sub>6</sub>	~100	~100	95	90	—	—

poorly in AN and PC-AN mixtures, apparently because of the chemical reactivity of lithium with AN-containing electrolytes (see Table 2). The cycling efficiency on the aluminium substrate decreased as the proportion of AN in the electrolyte was increased.

As observed previously [15], the plating/stripping curves in LiClO<sub>4</sub>/PC showed distinct differences between nickel and aluminium substrates. Those for lithium cycling on nickel substrates were sharp and well defined, while those on aluminium were more rounded and possessed less distinct stripping end-points. On aluminium substrates, two stripping plateaus could often be detected during the first ~20 cycles, depending in particular on the current density [15]. The first and second stripping plateaus corresponded to a lithium-rich (*e.g.*, Li<sub>3</sub>Al<sub>2</sub> + Li<sub>9</sub>Al<sub>4</sub>) and an aluminium-rich composition (( $\alpha$  +  $\beta$ )-LiAl), respectively [13, 15]. While the shapes of the plating/stripping curves did not vary markedly from the above description in electrolytes containing AN, it was not possible to detect more than one stripping plateau on aluminium substrates. Figure 2 shows a comparison between the plating/stripping curves in LiClO<sub>4</sub>/PC and LiClO<sub>4</sub>/AN electrolytes at 5 mA cm<sup>-2</sup>. The presence of only one stripping plateau in LiClO<sub>4</sub>/AN indicates that the lithium-rich composition normally detected under these conditions is reacting with the AN electrolyte before stripping.

The performance of aluminium substrates in LiAsF<sub>6</sub>/PC-AN also indicates the generally higher reactivity of these electrolytes compared with electrolytes containing only PC. Figure 3 shows the variation in lithium cycling efficiency with cycle number for several current densities. The poorer performance in PC-AN compared with PC for the first ~10 cycles could be explained in terms of the lithium-rich phases discussed above. However, the lower efficiencies observed overall indicate that even the ( $\alpha$  +  $\beta$ )-LiAl composition (the major plateau) is somewhat reactive with PC-AN mixtures. There was a relatively rapid approach to the maximum cycling efficiency at low current densities ( $\leq 5$  mA cm<sup>-2</sup>), but at higher current densities, where more free lithium would have been available, much lower efficiencies were observed. On extended cycling (~500 cycles) in electrolytes containing PC-AN, aluminium substrates often exhibited extensive shedding which was sometimes observed as a powdery material suspended throughout

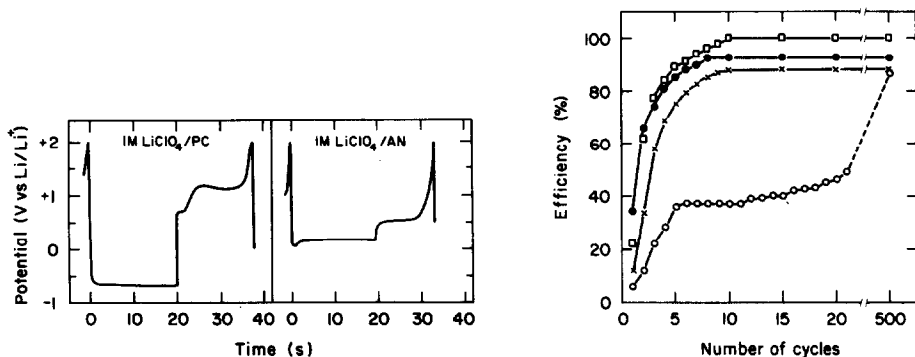


Fig. 2. Lithium plating and stripping chronopotentiograms on aluminium substrates at  $5 \text{ mA cm}^{-2}$  in  $1 \text{ M LiClO}_4/\text{PC}$  and  $1 \text{ M LiClO}_4/\text{AN}$  (cycle 10).

Fig. 3. Lithium cycling efficiency on aluminium substrates in  $1 \text{ M LiAsF}_6$  electrolytes at various current densities as a function of cycle number.  $\square$ ,  $1 \text{ M LiAsF}_6/\text{PC}$ ,  $1 \text{ mA cm}^{-2}$ ;  $\bullet$ ,  $1 \text{ M LiAsF}_6/\text{PC-AN}$ ,  $1 \text{ mA cm}^{-2}$ ;  $\times$ ,  $1 \text{ M LiAsF}_6/\text{PC-AN}$ ,  $5 \text{ mA cm}^{-2}$ ;  $\circ$ ,  $1 \text{ M LiAsF}_6/\text{PC-AN}$ ,  $10 \text{ mA cm}^{-2}$ .

the electrolyte. This phenomenon has also been observed by Besenhard [14] in  $\text{LiI}/\text{PC}$  electrolytes and is probably due, in part, to higher electrolyte reactivity in this case. Alternatively, the rate of lithium incorporation into the aluminium may be faster in the PC-AN system than in PC. This would result in faster roughening and disintegration of the aluminium lattice. Aluminium substrates cycled in  $\text{LiAsF}_6/\text{PC-AN}$  tended to fail in 500 - 800 cycles compared with  $>1000$  in  $\text{LiAsF}_6/\text{PC}$ .

#### (b) Plating-stripping potential difference

One of the most prominent features observed in the AN-containing electrolytes was the relatively small difference between plating and stripping potentials (as measured between the mid-points of the respective plateaus, see, for example, Fig. 2). The difference was much smaller than observed in the less highly conducting PC-containing electrolytes. The observed potential differences were corrected for the  $iR$  component using an estimate based on the slope of the potential difference *vs.* current plots in each case. Although the data could not be estimated precisely because of the large corrections involved, the  $iR$ -corrected plating-stripping potential differences were always less for electrolytes containing PC-AN than for electrolytes containing only PC. Lithium plating and stripping apparently has a lower activation polarization in PC-AN than in PC. Despite the minor advantage in activation polarization, the smaller potential differences observed in AN-containing electrolytes compared with PC-containing electrolytes are due mainly to the greater conductivity of lithium salts in PC-AN (Table 1).

#### (c) Comparison of Li/Al electrode cycling behaviour in $\text{LiAsF}_6/\text{PC-AN}$ and $\text{LiAsF}_6/\text{PC}$

Experiments were conducted using previously prepared Li/Al electrodes to determine the stripping efficiency where plating was followed by standing



TABLE 4

Lithium stripping efficiencies on Li/Al electrodes allowed to stand for various times after plating in electrolytes containing 1M LiAsF<sub>6</sub>

Solvent	Total charge <sup>a</sup> (mC cm <sup>-2</sup> )	Time following Li-deposition (h)	Stripping efficiency (%)
PC-AN (50% v/v)	120	28.0	50
	3600	18.0	57
	120	0.0	98
	120	0.083	98
	120	0.167	98
	120	0.50	90
	600 <sup>b</sup>	0.0	90
	600 <sup>b</sup>	0.083	90
	600 <sup>b</sup>	0.167	90
	PC	7200	18.0
3600		18.0	60
120		0.0	98
120		0.083	98
120		0.167	98
120		0.50	96
120		1.0	96
600 <sup>b</sup>		0.0	90
600 <sup>b</sup>		0.083	90
600 <sup>b</sup>		0.167	90

<sup>a</sup>At 1 mA cm<sup>-2</sup> unless stated otherwise.

<sup>b</sup>At 5 mA cm<sup>-2</sup>.

for various times before stripping. The results of these experiments are shown in Table 4. It is evident from the data that the cycling behaviour of Li/Al electrodes in LiAsF<sub>6</sub>/PC-AN was very similar to that in LiAsF<sub>6</sub>/PC. For example, both of these electrolytes produced 98% and 90% stripping efficiencies at 1 and 5 mA cm<sup>-2</sup> respectively, if stripping immediately followed deposition over 2 min. If a freshly deposited electrode was left at open circuit for different periods of time, the stripping efficiency decreased in both electrolytes. A greater loss in efficiency was observed for the PC-AN mixture than for PC when the open circuit time was short; however, for long periods the loss in efficiency was similar. For example, after 30 min at open circuit there was an 8% loss in efficiency in PC-AN compared with a 2% drop in PC. After 18 h of standing the loss was 40% in both electrolytes. These drops in efficiency were measured relative to their efficiencies when stripping immediately followed plating. These results suggest that the rate of corrosion of Li/Al is slightly faster in electrolytes containing PC-AN than in electrolytes containing only PC, but it is still low.

## Conclusions

The addition of AN to concentrated solutions of  $\text{LiClO}_4$  and  $\text{LiAsF}_6$  in PC increased the conductivity substantially. This means that it is possible to reduce the internal resistance in a conventional PC-containing cell and allow larger currents to be drawn for the same voltage loss. While the  $\text{LiClO}_4/\text{PC-AN}$  mixture reacted readily with lithium, and was thus unsuitable, the  $\text{LiAsF}_6/\text{PC-AN}$  mixture was visually stable in contact with lithium for more than 3 months. This unexpected behaviour was apparently due to a strong inhibiting effect of the hexafluoroarsenate anion. Since lithium-aluminium alloys are even less reactive than pure lithium with the  $\text{LiAsF}_6/\text{PC-AN}$  electrolyte, primary battery applications involving long term storage may be feasible with such alloys or with lithium.

Galvanostatic lithium cycling efficiencies on nickel substrates in  $\text{LiAsF}_6/\text{PC}$  were markedly better in the short term ( $\sim 25$  cycles) than in  $\text{LiClO}_4/\text{PC}$ . However, there was a more sudden decrease in efficiency in  $\text{LiAsF}_6/\text{PC}$  than in  $\text{LiClO}_4/\text{PC}$  as cycling was continued. Efficiencies on nickel substrates in AN-containing electrolytes were very low, emphasising the inherent reactivity between AN and lithium. It was possible to cycle aluminium substrates in  $\text{LiAsF}_6/\text{PC-AN}$  at efficiencies approaching those in  $\text{LiClO}_4/\text{PC}$  and  $\text{LiAsF}_6/\text{PC}$ . There was, however, a loss of efficiency, indicating reactivity for the various Li/Al alloys formed. The efficiency loss became more evident at higher current densities. Stripping efficiencies on Li/Al electrodes after a period of standing ( $\sim 18$  h) were similar ( $\sim 60\%$ ) in  $\text{LiClO}_4/\text{PC}$  and  $\text{LiAsF}_6/\text{PC-AN}$ . Extended cycling of the lithium-aluminium electrode in electrolytes containing PC-AN at practical efficiencies does not seem feasible. The 1M  $\text{LiAsF}_6/\text{PC-AN}$  electrolyte had the most favourable overall characteristics of those studied and it may prove useful in primary battery applications.

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