Solutions of LiAsF$_6$ in 1,3-dioxolane for secondary lithium batteries*

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Abstract

Highly stable solutions of 1,3-dioxolane (DN) with LiClO$_4$ or LiAsF$_6$ may be prepared by the use of tertiary amine additives. Very high Li-cycling efficiency is obtained with stabilized LiAsF$_6$/DN solutions. These electrolytes can be further improved by addition of alkyl carbonates as cosolvents. The correlation between Li-cycling efficiency and Li-surface chemistry in these systems was investigated using surface sensitive Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray microanalysis techniques.

Introduction

1,3-Dioxolane (DN) was listed in the past among the most promising solvents for rechargeable lithium batteries [1]. Quite a high conductivity is obtained with Li salt solutions in DN at high concentration (1 to 2 M), and very good cycling efficiency was obtained in half-cell testing of Li electrodes in LiClO$_4$/DN solutions [2, 3]. Other LiClO$_4$ solutions in most polar aprotic solvents, including ether, alkyl carbonate, lactones and esters, gave very poor performance in Li half-cell testing experiments [4].

However, the interest in DN as a primary solvent for secondary Li batteries declined considerably after a few explosions occurred during laboratory testing of Li cells containing LiClO$_4$/DN solutions [5]. The reason for these cell failures was probably due to a sudden change in the electrolyte solution that increased its internal resistivity; the cells heated and thus exploded.

It seems that this solvent's main problems are its tendency to polymerize. Since DN is a ketal, it is very sensitive to Lewis acids which initiate its polymerization to species such as polyethylene–polymethylene oxide and oligomers that may have the shape of crown ethers [6]. Hence, a sudden polymerization could explain the change in solutions that led to the explosion of Li cells containing DN.

While LiClO$_4$/DN solutions are usually stable, LiAsF$_6$/DN solutions polymerize readily, probably due to an unavoidable presence of Lewis acids such as trace AsF$_5$. This excludes the possibility of using LiAsF$_6$, which is a good electrolyte for secondary Li systems, with DN without a special stabilization. A few attempts to stabilize LiAsF$_6$/DN solutions are reported in the literature. Methylfurane and KOH were used as stabilizing additives for LiAsF$_6$/DN [7].

In this work, DN solutions of LiClO$_4$ and LiAsF$_6$ stabilized by tertiary amines were investigated as electrolyte solutions for secondary Li batteries. Tertiary amines

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are potential stabilizing agents since as bases they can neutralize Lewis acids in solutions and hence avoid DN polymerization.

A variety of tertiary amines were tested. The list includes aliphatic amines such as triethyl, tripropyl and tributylamines, aromatic amines such as tribenzylamine and cyclic amines such as N-methylpiperidine. Possible reaction of the amines with Li, both neat and in DN solution, were investigated using surface sensitive Fourier-transform infrared spectroscopy (FTIR) and X-ray microanalysis. Li-cycling efficiency in half-cell testing using tertiary amine stabilized DN solutions was measured under various conditions. In part of the experiments the situation was very close to that of real commercial cells. The electrochemical window and the degree of stabilization of DN solutions containing tertiary amines was explored using cyclic voltammetry (with noble metal electrodes), as partly-polymerized or pure DN solutions have characteristic voltammetric behavior [6, 8]. Scanning electron microscopy (SEM) was used in order to correlate between the morphology and the cycling efficiency of the Li electrodes under the various experimental conditions.

In addition, several reports describing ethylene carbonate/ether mixtures containing $LiAsF_6$ as very good electrolyte solutions for secondary Li batteries [9] led us to investigate $LiAsF_6$/DN solutions containing ethylene carbonate (EC) or propylene carbonate (PC) as cosolvents.

However, there are two other reasons for testing alkyl carbonates as cosolvents for DN:

(i) Addition of polar cosolvents such as PC or EC should increase the conductivity of DN solutions.

(ii) In case of solvent evaporation due to leakage, the non-volatile PC or EC can protect the Li surface from reaction with air. This is specially important in cases where the surface area of the Li is high due to prolonged charge/discharge cycling. Surface sensitive FTIR, SEM, X-ray microanalysis and standard electrochemical techniques were used in order to correlate cycling efficiency, morphology and surface chemistry of Li electrodes in the above solvent systems.

Experimental

1,3-dioxolane (Aldrich) was triply distilled over sodium and benzophenone under argon (1 atm.). Tertiary amines (Aldrich) were also distilled under argon before use. $LiClO_4$ (Aldrich) was dehydrated in a vacuum oven ($10^{-2}-10^3$ mm/Hg, 150 °C, 3 days). $LiAsF_6$ (Lithco) was used as received. PC (Aldrich) and EC (Aldrich) were vacuum distilled over CaH_2 (in order to obtain the proper pressure, which was about 6 to 8 mm Hg, high-purity argon was used).

All the electrochemical measurements and the preparation for the spectroscopic measurements were performed under high-purity argon in glove box systems and were described previously [4, 10, 11, 12, 13]. The FTIR, the SEM measurements of Li or non-active metal (mostly nickel) surfaces and the transfer techniques from the glove boxes to the spectrometers were described elsewhere [4, 10-13]. X-ray microanalysis of Li surfaces was performed using the Link eXL system, attached to the JEOL JSM 840 scanning electron microscope (using similar transfer procedure as for the SEM measurements). Conductivity measurements were performed using an El Hama TH 2400 conductometer. Lithium-cycling efficiency was measured both in parallel plate cells where the electrodes are separated by a few mm of solution, described elsewhere [4, 8], and in the cell shown in Fig. 1, where the electrodes are pressed together, separated by a 2400 Celgrad polypropylene separator.
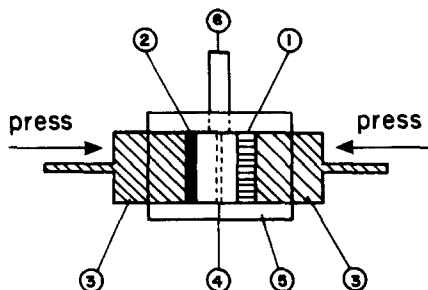
Fig. 1. The small solution volume, compressed cell used for part of the Li-cycling efficiency measurements: (1) working electrode–nickel disk on which Li was deposited (5–20 C/cm²); (2) counter electrode–Li disk; (3) stainless steel current collectors; (4) polypropylene separator and the solution volume; (5) polyethylene cylinder cell body; (6) a glass tube for loading the cell with solution. After loading, the working and counter electrodes are pressed towards each other leaving a very small space between them for solution. The solution excess is removed through tube 6.

In both types of cells the working electrodes were Li deposited on nickel or copper substrates from the electrolyte solution in the cell (5–20 C/cm²). The counter electrodes were Li foils. In a typical experiment, a portion of the deposited Li (DOD ranged from 10 to 80%) was charged/discharged consecutively several times (number of cycles was 5 to 100, depending on the experiment), galvanostatically; (current density ranged from 0.5 to 10 mA/cm²). All of the Li-cycling efficiency tests were performed using a home-made multichannel computerized system whose software was also developed at the author's University. Li-cycling efficiency was calculated from the residual active Li left after the cycling, as previously described [4].

Results and discussion

Tertiary amines as stabilizers for DN solutions and their compatibility with lithium
As was previously reported, LiClO₄/DN solutions may partly polymerize due to storage over molecular sieve, activated alumina or contamination with trace Lewis acids, and at potentials above 3–3.2 V (Li/Li⁺) [6].
The voltammetric behaviour of partly-polymerized solutions with noble metal electrodes is characterized by high-cathodic currents below 1.5 V (Li/Li⁺) because of a breakdown of the natural electrode passivation at low potential due to interaction of the electrode passive films with the polymerization products, as already discussed [6].
Figure 2(a) (solid line) presents a typical cyclic voltammogram of partly-polymerized LiClO₄/DN solvent (Au electrode). Polymerization was initiated in this case by applying potentials above 3.2 V to this system. This voltammogram is indeed characterized by high-cathodic currents at potentials below 1.5 V, even in the anodic sweep.
Addition of trace tertiary amines to these solutions seems to prevent this polymerization. Figure 2(a) (dashed line) shows a voltammogram obtained with LiClO₄/DN solution containing tribenzyl amine (TBzA). Although the voltage upper limit in this case was 4 V (Li/Li⁺), which is ≈ 1 V above DN polymerization potentials [6, 8], this voltammogram (Fig. 2(a), dashed line) is typical of unpolymerized solution. The increase in current around 4 V is due to the amine oxidation since amine-free
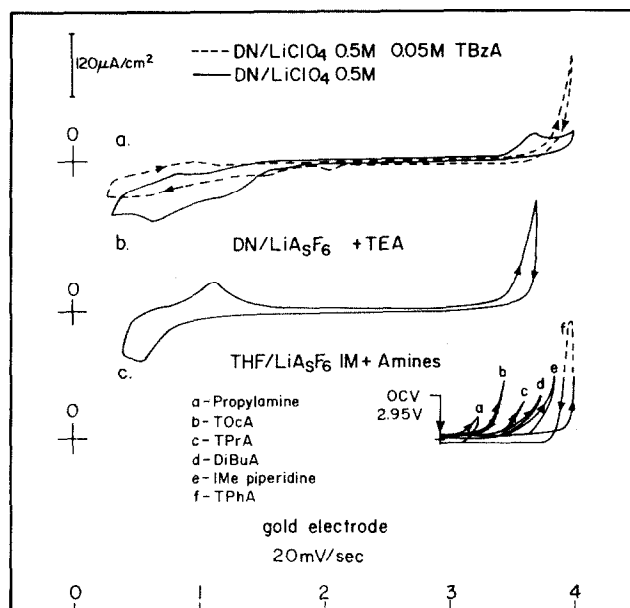
Fig. 2. Typical cyclic voltammograms obtained with stabilized and unstabilized solutions. Gold electrode, 20 mV/sec: (a) solid line — unstabilized LiClO₄/DN 0.5 M solution. Partial polymerization occurs at potentials above 3.2 V; dashed line — same solution, stabilized with TBzA; (b) a typical voltammogram obtained with LiAsF₆/DN 1 M, containing tertiary amine (TEA, 1000 ppm in this case); (c) oxidation potentials of some tertiary amines (dissolved in LiAsF₆/THF 1 M, conc. ≈ 1000 ppm).

solutions have electrochemical windows of 4.2 to 5 V and are oxidized at potentials above 4.2 V (Li/Li⁺ scale).

A similar stabilization effect was observed when other tertiary amines were added, even in trace amounts (> 100 ppm), to LiClO₄/DN solutions. The list include tri-alkylamines (R = ethyl, propylbutyl and octyl) and triarylamines (R = benzyl, phenyl, 1,methylpiperidine and 1,methylmorpholine).

While LiAsF₆/DN solutions readily polymerize, those stabilized by the above-mentioned tertiary amines are very stable. For instance, these solutions were found to be stable after being stored in glass for two years.

Figure 2(b) shows a typical voltammogram obtained from LiAsF₆/DN 1 M solutions stabilized with triethylamine (TEA) (1000 ppm). This voltammogram is typical of those obtained with Li salt solutions in all other polar aprotic solvents such as ethers [13], alkyl carbonates [13] or lactones [12] and therefore, proves that the LiAsF₆/DN solution is stable and unpolymerized in spite of the voltages applied which readily induce polymerization in unstabilized DN solutions. As shown in Fig. 3(c), the electrochemical window of Li salts stabilized by tertiary amines is limited to 3.2 to 3.7 V, depending on the amine used. Indeed, this window is narrower than that of other Li battery electrolyte solutions. However, it is still compatible even with cathodes such as TiS₂, whose open-circuit voltage is around 2.6 V (Li/Li⁺) [14].

The compatibility of tertiary amines as DN stabilizers with Li electrodes was rigorously studied using surface sensitive techniques. Figure 3 compares FTIR spectra obtained from the reaction products of Li amalgam with propylamine and tripropylamine
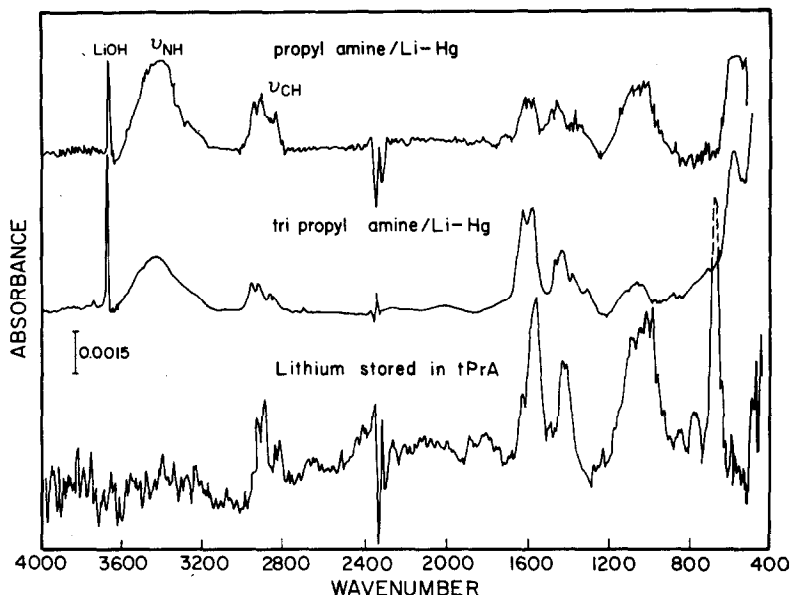
Fig. 3. FTIR spectra obtained from reaction products of propylamine and tripropylamine with Li–Hg amalgam (pelletized with KBr) and an FTIR spectrum obtained from a Li sample stored in tripropylamine for a few days for comparison.

and from Li surface stored for a few days in tripropylamine. The tertiary amine was previously cleaned either by storage over Na–K or Hg–Li amalgams in order to eliminate any protic contaminants. As shown in this Figure, all the spectra are very similar and typical of a mixture of propylamine and dipropylamine [15]. The spectrum obtained from the Li surface (Fig. 3, lower spectrum), also has a Li nitride (Li_3N) peak around 680 cm^{-1}.

Hence, these studies prove that Li or Li amalgams react with tertiary amines to form three types of amides, R_2NLi, $RNLi_2$ and NLi_3. Other products are R_2 or RH (gas evolution was observed during storage of tertiary amines over Li–Hg amalgam). The fact that the spectra of Fig. 3 are typical of amines should be attributed to an unavoidable reaction of the amides with trace water, as evidenced also by the LiOH peak around 3680 cm^{-1} shown in part of these spectra.

However, in spite of the reactivity of tertiary amines with Li, it would seem that, as trace amounts in DN solutions, they do not react with Li. Figure 4 compares FTIR spectra obtained *ex situ* from Li samples stored for a few weeks in DN–tertiary amine solutions. A spectrum obtained from Li surface stored in pure DN is also shown (Fig. 4(a)). All these spectra are similar and have peaks around 2950–2800, 1100–1000, 850, 800 and 600–500 cm^{-1}, which should be attributed to Li alkoxides (ROLi) [8, 16, 17]. As indicated in Fig. 4, all of these spectra have peaks around 1500–1450 and 870 cm^{-1} which belong to Li_2CO_3, while some of them also have peaks of Li alkyl carbonate ($ROCO_2Li$, 1650–1620 cm^{-1}). Li carbonate is formed by a reaction of the Li with unavoidably present trace O_2 and CO_2 in the glove box (to form Li_2CO_3) during sample preparation. $ROCO_2Li$ is formed due to a reaction of trace CO_2 with Li alkoxides [8, 16]. In fact, these spectra are similar to those obtained during previous
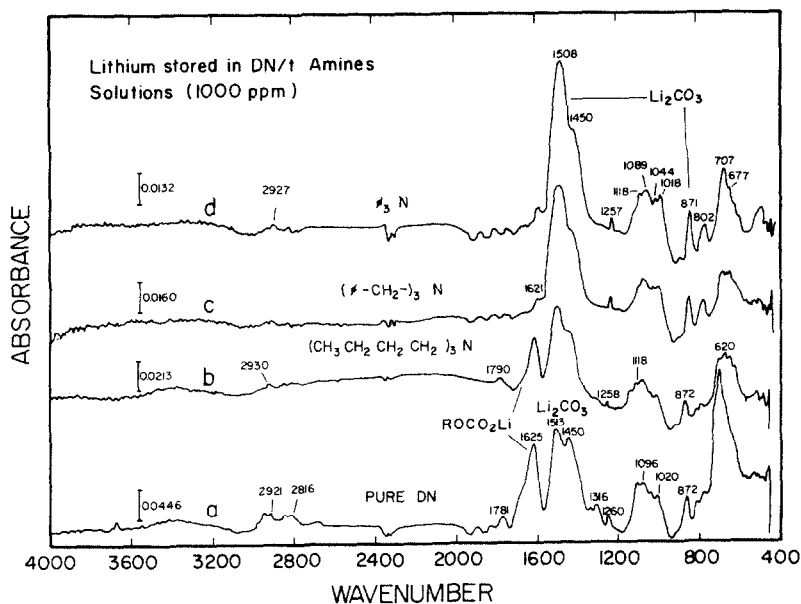
Fig. 4. FTIR spectra obtained from Li surfaces stored in DN containing tertiary amines (1000 ppm) for a few weeks: (a) pure DN for a reference; (b) TBA; (c) TBzA; (d) TPheA.

studies that proved that DN reacts with Li to form Li alkoxides of the type $CH_3CH_2OCH_2OLi$ and others [8].

Hence, these studies prove that the tertiary amines, when present, do not contribute to the build-up of surface films formed on Li in DN solutions. If they would indeed react with Li when dissolved in DN, typical peaks of the aromatic rings would characterize spectra (c) and (d) in Fig. 4 (e.g., C–H stretching peaks above 3000 cm^{-1}). This should be attributed to the fact that the reaction of Li with tertiary amine is slow (as found in this work), while Li–DN reactions are faster. Therefore, this difference in reactivity and the excess of the solvent in these systems lead to the fact that tertiary amines do not participate in the surface chemistry of Li in solutions.

X-ray microanalysis of Li samples stored in DN containing tertiary amines provided further proof that the amines' reaction with Li is not important in these cases as no nitrogen peaks could be observed, while pronounced O and C peaks appear in the spectra. The reactivity and stability of the above-mentioned tertiary amines under the various experimental conditions are summarized in Scheme 1.
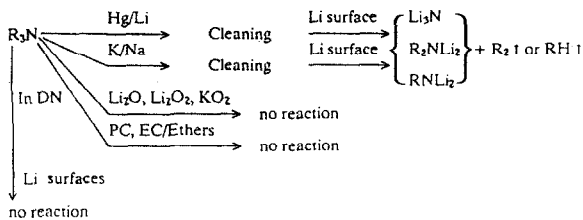
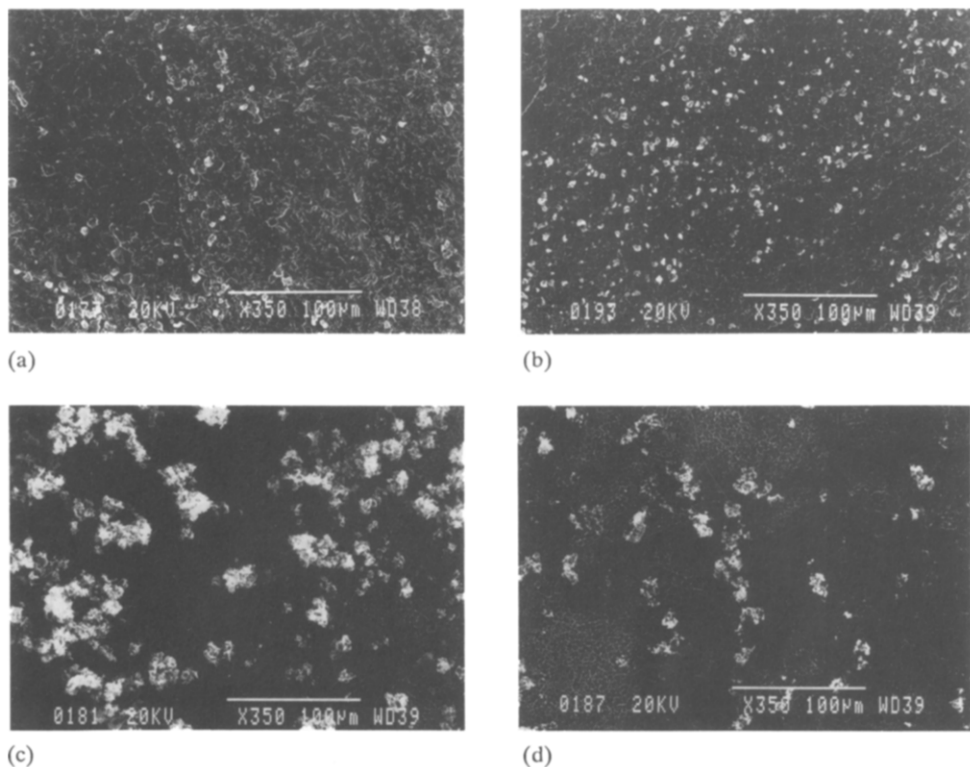Scheme 1. Stability and reactivity of tertiary amines.

(a)

(b)

(c)

(d)

Fig. 5. SEM micrographs obtained from Li electrodes treated in DN solutions (three charge/discharge cycles, 1.5 mA/cm², 0.5 C/cm² per process). A scale appears in each picture: (a) LiAsF$_6$/DN 1 M solution, no additives; (b) LiAsF$_6$/DN 1 M solution containing 1000 ppm TBzA; (c)LiClO$_4$/DN 1 M solution, no additives; (d) LiClO$_4$/DN solution containing 1000 ppm TEA.

The compatibility of the tertiary amines and their stabilizing effect is further proved by SEM of Li electrodes cycled in LiAsF$_6$ and LiClO$_4$/DN solutions. Figure 5 shows 4 micrographs obtained from Li electrodes cycled in DN solutions (3 consecutive charge/discharge cycles, constant current 1.5 mA/cm², 1.0 C/cm² per process). Figures 5(a) and 5(c) are related to LiAsF$_6$/DN and LiClO$_4$/DN solutions, respectively, with no additives, while Figs. 5(b) and 5(d) are related to LiAsF$_6$/DN per 1000 ppm TBzA and LiClO$_4$/DN per 1000 ppm TEA, respectively. These micrographs obviously show that Li morphology during charge/discharge cycling is much smoother when tertiary amines are present in solution. As expected [4], the Li surface in these processes is much smoother, uniform and less dendritic when LiAsF$_6$ is the electrolyte (compared to LiClO$_4$). Hence, all the above spectroscopic studies clearly prove that both aliphatic and aromatic tertiary amines stabilize DN solutions, prevent their sudden polymerization and are not reactive with Li when dissolved in DN, probably due to the competition of solvent reactions that form passive films [6, 8].

Li-cycling efficiency in stabilized DN solution

Li-cycling efficiency in LiAsF$_6$/DN containing tertiary amines was measured (and tested) under a variety of conditions.

Figure 6 shows the variation of Li-cycling efficiency during half-cell testing in LiAsF$_6$/DN 1 M solution stabilized with 100 ppm of tripropylamine (TPrA) as a function of DOD and the number of cycles. The data related to DN–alkyl carbonate mixtures also appearing in this figure are discussed later.

In these experiments, the electrodes were separated by a few mm of solution and the initial charge of the tested Li electrode (prepared by Li electrochemical deposition) was 5 C/cm^2 (current density was 1.5 mA/cm^2). As shown in Fig. 6 average cycling efficiencies around 94–98% could be obtained. In other series of experiments with LiAsF$_6$/DN per 100 ppm (TPrA) solutions in the same type of cells [4, 8], the variation of Li-cycling efficiency was measured as a function of the current density or of the amount of Li in the tested electrodes. Current density ranged from 1 to 10 mA/cm^2 and the charge in the working electrode ranged from 5 to 20 C/cm^2.

In this experimental series the average Li-cycling efficiency ranged between 95 and 98%. The influence on the Li-cycling efficiency of the different tertiary amines used and their solution concentrations in similar half-cell tests was also explored. TEA, TBzA and tributylamine (TBuA) were tested as stabilizers in addition to TPrA. In all these experiments similar Li-cycling efficiency around 95–98% was measured. These results further prove that the tertiary amine does not interfere with the surface chemistry of Li in solutions, as concluded above based on the spectral studies.

In another series of experiments Li-cycling efficiency was measured in LiAsF$_6$/DN 1 M solution containing various amounts of TPrA ranging from 100 ppm to 25% by volume. Even at TPrA content of 25%, Li-cycling efficiency around 95%, was measured. This result is important since high content of tertiary amines in solution increases the safety in the use of DN solutions. In case of accidents, which lead to solvent evaporation and an exposure of Li to the air, the tertiary amines, which are oily and have low vapour pressure, remain on the surface and prevent the dangerous reaction between Li and air.
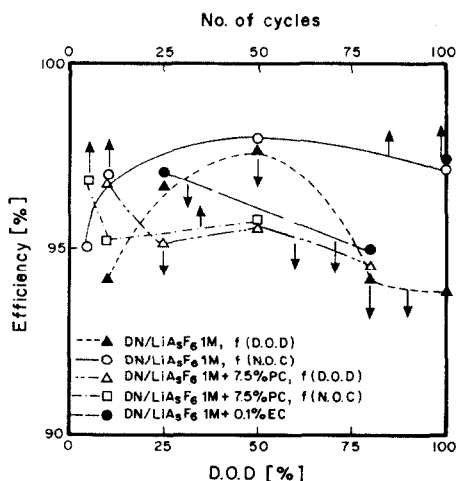

Fig. 6. Variation in Li-cycling efficiency obtained with LiAsF$_6$/DN 1 M, LiAsF$_6$/DN 1 M/PC 7.5% and LiAsF$_6$/DN 1 M/EC 0.1% solution as a function of DOD (10 charge/discharge cycles) and as a function of a number of cycles (DOD = 25%). Working electrode was Li on nickel (5 C/cm^2) and current density was 1.5 mA/cm^2. All the points in this figure are related to average efficiency at accuracy of ±1%.
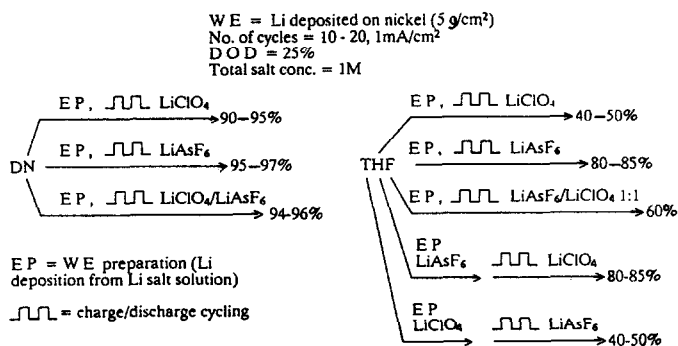
Several series of experiments were performed with the cell shown in Fig. 1, in which the tests are closer to the real situation existing in the batteries as the electrodes are pressed together with a separator in between, allowing a very small volume of electrolyte solution in the cell. In these experiments the salt concentration ranged between 1 and 1.5 M, the amount of charge in the tested electrode ranged between 5 and 10 C/cm^2 and the current densities were 1 to 5 mA/cm^2. The average Li-cycling efficiencies were between 95 and close to 100%.

While an average Li-cycling efficiency around 95% in real batteries is not good enough for the prolonged cycle life required for commercial secondary systems, obtaining Li-cycling efficiency of 95% in our laboratory test cells is very significant. Our working electrodes are prepared by Li deposition on nickel or copper substrates in solutions. Hence, the starting point of the test is far worse as compared with Li electrodes in real cells which are bulk Li. Hence, the Li-cycling efficiency values obtained in our experiments are actually the lower limits of the efficiency expected in real systems. Indeed, in experiments where the capacity of the Li electrodes was above 10 C/cm^2 and the testing cells had a compact structure with the electrodes pressed together with separator in between, Li-cycling efficiencies close to 100% were obtained.

The above experiments prove the superiority of stabilized $LiAsF_6$/DN for secondary Li systems compared to $LiClO_4$/DN that was also previously reported as an excellent electrolyte solution for rechargeable Li batteries [1].

The superiority of $LiAsF_6$ over $LiClO_4$ for Li systems was further proved in the following series of experiments using both DN and tetrahydrofurane (THF) as solvents. In these experiments the tested Li electrode was either prepared (by electrochemical Li deposition on nickel or copper substrates) and cycled in the same electrolyte solution, or prepared in one electrolyte and cycled in another electrolyte solution.

THF solutions were also investigated, since the difference in Li-cycling efficiency obtained when $LiAsF_6$ or $LiClO_4$ is used is more pronounced in THF than in DN [4, 6], (80–85% and 40–50% for $LiAsF_6$ and $LiClO_4$ solutions in THF, respectively). Scheme 2 shows the sequence of these experiments. The scheme presents eight types of experiments, three with DN solutions and five with THF. The experiments related to DN included electrode preparation (Li deposition in solution) and cycling (galvanostatic charge/discharge) in $LiClO_4$, $LiAsF_6$ and $LiClO_4$/$LiAsF_6$ 1:1 solutions (total salt concentration was 1 M). The experiments related to THF include three series in which both electrode preparation and cycling were carried out in the same solutions ($LiAsF_6$, $LiClO_4$ and $LiAsF_6$/$LiClO_4$ 1:1, total salt concentration 1 M), and two series

W E = Li deposited on nickel (5 g/cm^2)
No. of cycles = 10 - 20, 1mA/cm^2
D O D = 25%
Total salt conc. = 1M

E P, ⎍⎍ $LiClO_4$
→ 90–95%

E P, ⎍⎍ $LiAsF_6$
→ 95–97%

DN ─────

E P, ⎍⎍ $LiClO_4$/$LiAsF_6$
→ 94-96%

E P, ⎍⎍ $LiClO_4$
→ 40–50%

E P, ⎍⎍ $LiAsF_6$
→ 80–85%

THF ─────

E P, ⎍⎍ $LiAsF_6$/$LiClO_4$ 1:1
→ 60%

E P $LiAsF_6$ ⎍⎍ $LiClO_4$
→ 80-85%

E P $LiClO_4$ ⎍⎍ $LiAsF_6$
→ 40-50%

E P = W E preparation (Li deposition from Li salt solution)

⎍⎍ = charge/discharge cycling

Scheme 2. Lithium cycling efficiency in $LiAsF_6$ and $LiClO_4$ solutions.

in which the electrodes were prepared in one solution ($LiAsF_6$ or $LiClO_4$ 1 M), followed by cycling in another solution ($LiClO_4$ or $LiAsF_6$ 1 M).

As presented in this Scheme, when the electrode was prepared in $THF/LiAsF_6$ followed by cycling in $THF/LiClO_4$, the Li-cycling efficiency obtained is similar to that measured when both electrode preparation and cycling was done in $LiAsF_6/THF$, while electrodes prepared in $LiClO_4/THF$ solutions followed by cycling in $LiAsF_6/THF$ solutions gave the poor cycling efficiency obtained with $THF/LiClO_4$ solutions. As already discussed [4], the relatively high Li-cycling efficiency obtained with $LiAsF_6$ solutions in ethers and other solvents (e.g. PC, butyrolactone) is obviously due to precipitation of LiF and maybe some arsenic compounds [18] resulting from salt reduction on the Li surfaces. The above experiments prove that these inorganic species are stable enough on the Li surface even when the solution is changed, and new active species, such as ClO_4^-, which are also reduced by Li [19], are present.

Figure 7 shows SEM micrographs obtained from Li electrodes treated in $THF/LiClO_4$ and $THF/LiAsF_6$ solutions. These Li electrodes were treated similarly to those presented in Scheme 2. Lithium was deposited (on Li) in one solution, followed
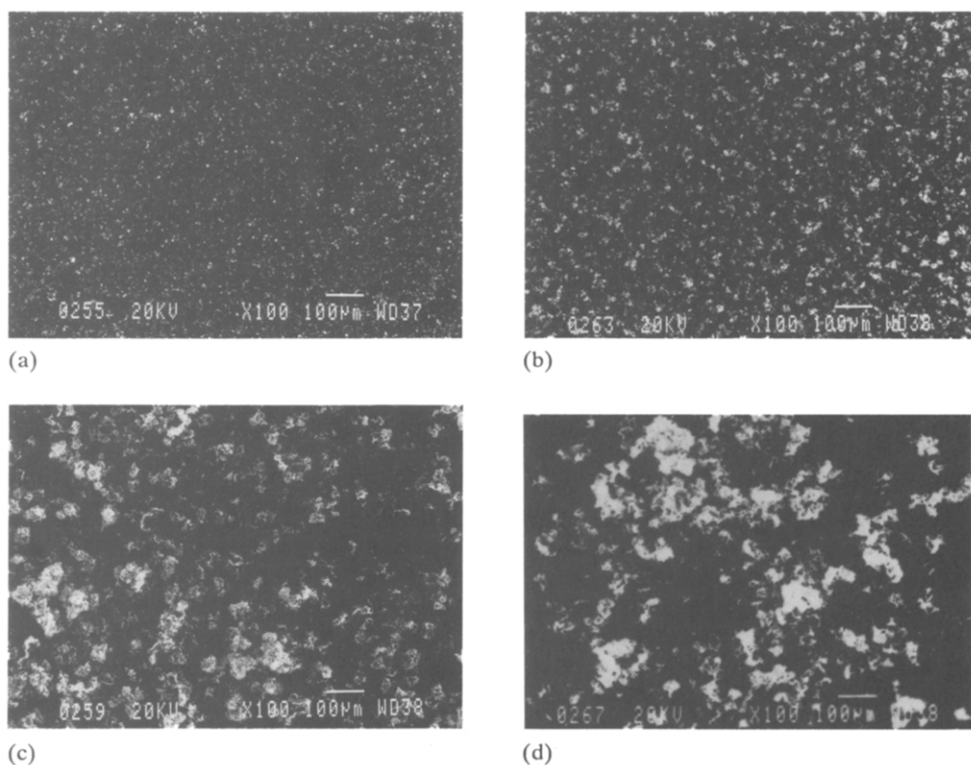

(a)

(b)

(c)

(d)

Fig. 7. SEM micrographs obtained from Li electrodes treated in various THF solutions. The treatment included Li deposition on Li (5 C/cm^2) followed by five consecutive charge/discharge cycles either in the same or in different solution. (1.5 mA/cm^2, 1 C/cm^2 per process). A scale appears in each picture: (a) Li was deposited and charged/discharged in $LiAsF_6/THF$ 1 M; (b) Li was deposited first in $LiAsF_6/THF$ 1 M and charged/discharged in $LiClO_4/THF$ 1 M; (c) Li was deposited in $LiClO_4/THF$ 1 M; (d) Li was deposited in $LiClO_4/THF$ 1 M followed by charge/discharge cycling in $LiAsF_6/THF$ 1 M.

by charge/discharge cycling in another one. The results shown in Fig. 7 are in line with the Li-cycling efficiency results summarized in Scheme 2, as the morphology of Li electrodes treated only in $LiAsF_6$/THF or in $LiAsF_6$/THF and then in $LiClO_4$/THF is similar (Fig. 7(a) and 7(b), respectively) and much smoother as compared to electrodes treated first in $LiClO_4$/THF (Figs. 7(c) and 7(d)).

Figure 8 presents X-ray microanalysis data related to Li electrodes treated in various DN solutions. The treatment included galvanostatic charge/discharge cycling (3–5 cycles, 1 mA/cm^2, 0.5–1 C/cm^2 per process). As demonstrated in this Figure, spectra obtained from Li electrodes treated in $LiAsF_6$/DN have pronounced fluorine and small arsenic peaks in addition to the expected C and O peaks. Spectra related to Li treated in $LiClO_4$/DN have chlorine peaks and the ratio of the O/C peaks is much higher than that obtained from samples treated in $LiAsF_6$ solutions. Hence, these results prove that $LiAsF_6$ in DN is reduced by Li to LiF and possibly to insoluble arsenic compounds. $LiClO_4$ is reduced to LiCl and Li_2O as already suggested [4, 17, 19], (Li_2O formation, in addition to the chloride, explains the high O/C ratio).

It can be concluded that the halides precipitating on Li play an important role in determining cycling efficiency and morphology. This may be attributed either to their properties as Li^+ ionic conductors and/or their degree of interference with precipitation of homogeneous, ordered organic films, as already suggested [4, 17].

Mixtures of DN and alkyl carbonates

It was already reported that mixture of ethers (e.g., 2,MeTHF) and EC are very good electrolyte solutions for secondary Li batteries [9]. Addition of PC or EC to ethers also increase their conductivity [20]. Hence, it was interesting to study the effect of PC or EC addition to stabilized DN/$LiAsF_6$ solutions on Li-cycling efficiency.
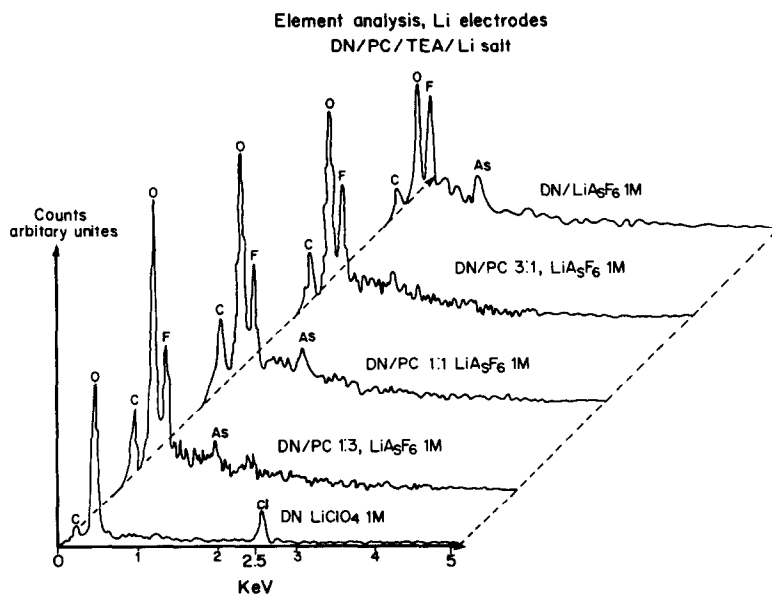

Fig. 8. X-ray microanalysis data obtained from Li electrodes treated in various DN solutions; the treatment included three charge/discharge cycles, 1.5 mA/cm^2, 0.5 C/cm^2 per process.

As mentioned in Scheme 1, PC or EC does not react with the tertiary amines in DN solutions.

Figure 9 shows variation of Li-cycling efficiency and conductivity obtained with DN/PC/LiAsF$_6$ solution as a function of % PC (by volume).

For a comparison, Li-cycling efficiency obtained with THF/PC/LiAsF$_6$ solutions is also presented. Cycling efficiency was measured in these cases with Li deposited on nickel (5 C/cm^2) working electrode which was charged/discharged 10 times (1.5 mA/cm^2, 25% DOD). As expected, addition of the polar PC to DN solution increases its conductivity. The effect of PC addition on Li-cycling efficiency is more complicated. However a maximum in average Li-cycling efficiency was measured with mixtures containing 5–10% PC. In contrast, Li-cycling efficiency deteriorates with addition of PC to THF, as also shown in Fig. 9. As shown in Fig. 10, somewhat similar behaviour was observed with EC/DN/LiAsF$_6$ solutions (stabilized with tertiary amine). An increase in Li-cycling efficiency (compared to DN/LiAsF$_6$) could be measured with solutions containing 0.1–3% EC. Some other data related to Li-cycling efficiency measured with EC/DN or PC/DN LiAsF$_6$ solutions close to the optimal ratios are presented graphically in Fig. 6.

Morphology studies of Li electrodes treated in these solutions are in line with the variations in Li-cycling efficiency shown in Figs. 9 and 10 as demonstrated in Fig. 11, which presents SEM micrographs obtained from Li electrodes treated in DN, DN/PC and DN/EC solutions. All the Li electrodes related to Fig. 11 were similarly treated: 3 charge/discharge cycles, at 1.5 mA/cm^2 and 0.5 C/cm^2 per process.

As shown in Figs. 11 (a–h), Li electrodes treated in LiAsF$_6$/DN containing low percentages of PC or EC (Figs. 11(b), 11(c) and 11(g)) are very smooth. As the amount of the alkyl carbonate in solution increases, the Li surface becomes rougher
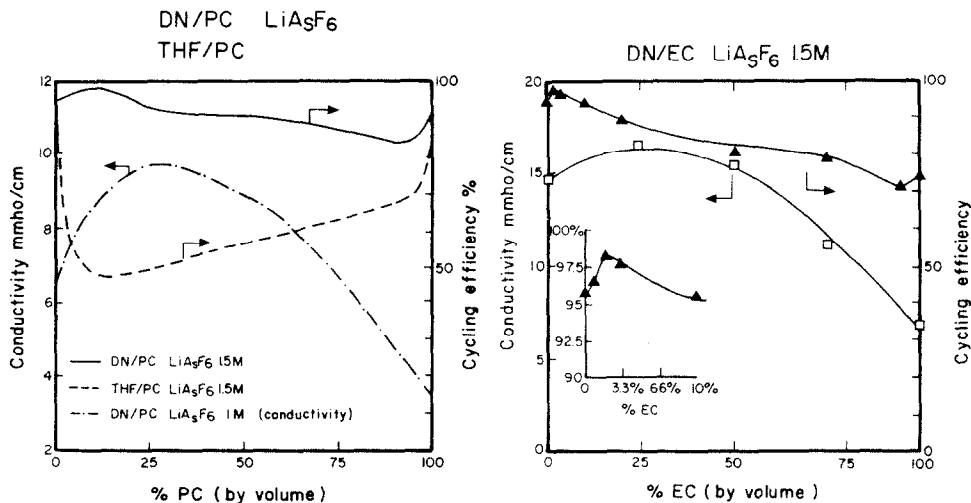

Fig. 9. Variation in Li-cycling efficiency and conductivity measured with DN/PC/LiAsF$_6$ solutions as a function of % PC. Li-cycling efficiency obtained with THF/PC/LiAsF$_6$ solutions is also presented for a comparison. The standard experiment included ten charge/discharge cycles; Li deposited on nickel or copper working electrode, 5 C/cm^2, DOD = 25%, 1.5 mA/cm^2.

Fig. 10. Variation in Li-cycling efficiency and conductivity measured with DN/EC/LiAsF$_6$ solutions as a function of %EC. The standard experiments are similar to those related to Fig. 9.

(Figs. 11(d), 11(e), 11(f) and 11(h)), which correlates well with the decrease in cycling efficiency as the percentage of PC or EC increases, as shown in Figs. 9 and 10.

One would assume that addition of reactive cosolvents such as PC or EC to $LiAsF_6/DN$ affects Li-cycling efficiency so pronouncedly, due to the impact on $LiAsF_6$ reduction because of the competition of alkyl carbonate reduction on Li to form stable passive films. However, X-ray microanalysis of Li samples treated in PC, EC/DN mixture shows that $LiAsF_6$ reduction is not strongly affected by the presence of PC or EC in DN. As demonstrated in Fig. 8, the spectra obtained from Li surfaces treated in $LiAsF_6/DN/PC$ mixture are very similar to those treated in $LiAsF_6/DN$.

Hence, the presence of PC or EC probably affects mostly the Li surface chemistry related to solvent reactions. Figure 12 shows FTIR spectra obtained from nickel electrodes treated at Li deposition potential (0.V Li/Li^+) in $LiAsF_6/DN/EC$ and $LiAsF_6/DN/PC$. For a comparison, a spectrum obtained from nickel treated in $LiAsF_6/THF/PC$ is also present. All the three spectra of Fig. 12 are typical of Li alkyl carbonates which are the PC and EC reaction product with Li (peaks around 1650, 1500, 1450, 1400, 1350–1320, 1090, 820 cm^{-1}) [21]. However, these spectra are different from each other in several wavenumber domains where DN or THF reduction products (Li alkoxides) have IR peaks. There are pronounced differences in these spectra around 2900–2800 (ν C–H), 1500–1350 (δ CH_2, CH_3) and around 1100–1000 cm^{-1} (ν CO). Hence, these spectral results prove that in spite of the reactivity of the alkyl carbonate, both solvents contribute to the build-up of surface films on Li. As already discussed
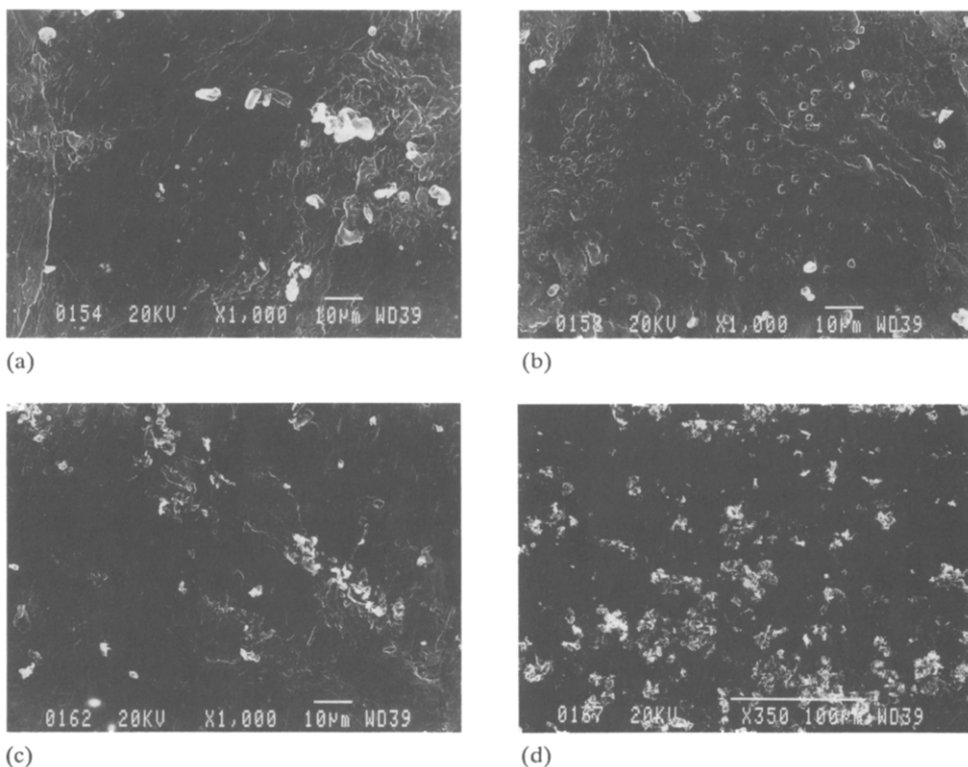

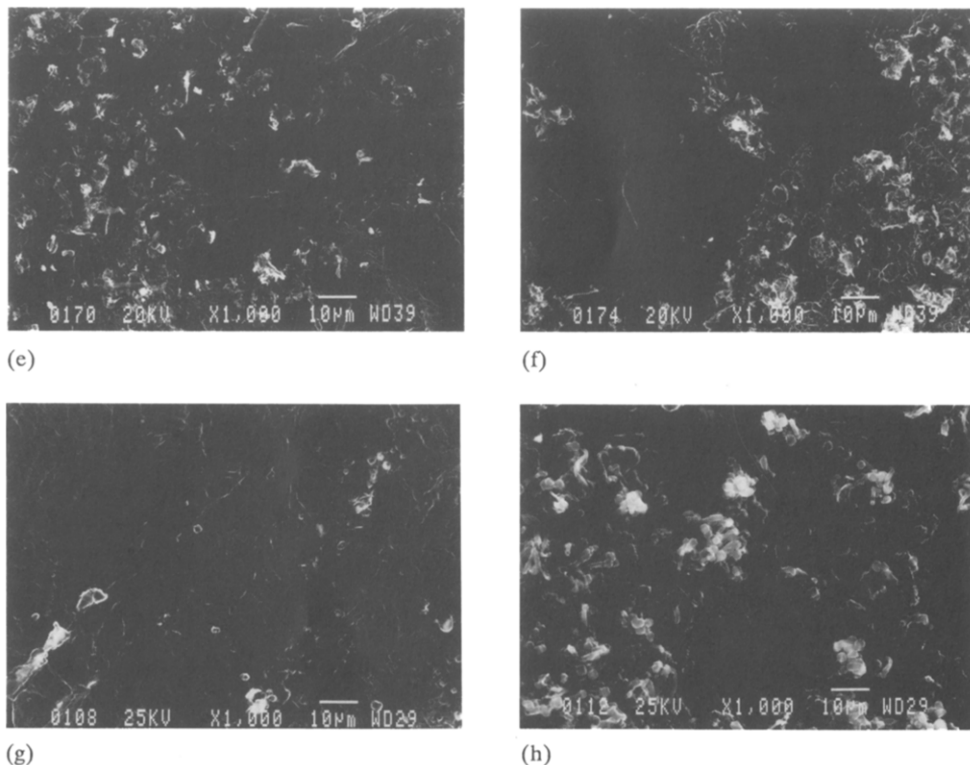
(a)

(b)

(c)

(d)

Fig. 11.

Fig. 11. SEM micrographs obtained from Li electrodes treated in tertiary amine stabilized LiAsF$_6$/DN 1 M solutions containing different amounts of PC or EC (three charge/discharge cycles, 0.5 C/cm^2 per process, 1.5 mA/cm^2). A scale appears in each picture: (a) 100% DN/100 ppm TEA; (b) 1% PC/100 ppm TEA; (c) 25% PC/100 ppm TEA; (d) 50% PC/100 ppm TEA; (e) 75% PC/100 ppm TEA; (f) 100% PC; (g) 1% EC/3000 ppm TBuA; (h) 10% EC/3000 ppm TBuA.

[17, 22], this further proves that Li-cycling efficiency depends mostly on a complicated surface chemistry which is determined by a delicate balance of several simultaneous film forming processes related to solvents and salt (and other active contaminants/additives, if present). Hence, at certain PC/DN or EC/DN ratios the surface film formed which contains both ROCO$_2$Li and ROLi compounds (resulting from DN reduction) allows improved, homogeneous Li deposition and dissolution (as proved by the SEM studies) and, therefore, improved cycling efficiency. In contrast, the presence of alkoxides formed by THF reduction (mostly Li butoxides) [16] together with ROCO$_2$Li species on the Li surfaces when PC/THF solutions are used, adversely affects Li-cycling efficiency and morphology.

One would ask how, in spite of the superior reactivity of the alkyl carbonates toward Li compared to ethers, the latter also strongly influences Li surface chemistry when ether/PC or EC mixtures are used. This may be explained as follows: Li does react predominantly with PC or EC to form a porous Li alkyl carbonate film. It is possible that since PC or EC molecules are polar, their mobility to the Li surface through the pores is limited while the less polar ether molecules can better diffuse
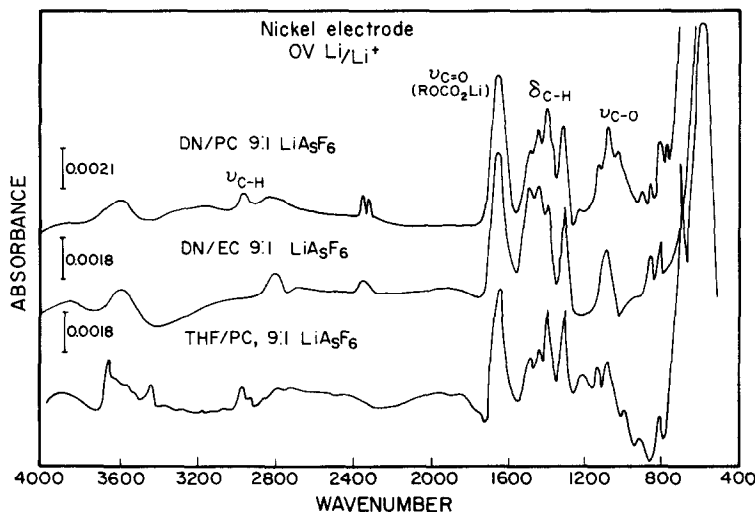
Fig. 12. FTIR spectra (measured *ex situ*) obtained from nickel electrodes treated in DN/PC, DN/EC and THF/PC for a comparison. All solutions contained 10% (by volume) alkyl carbonate and LiAsF₆ 1 M. The treatment included a potentiostatic step from open-circuit voltage ($\approx$2.5–3 V) to 0.V (Li/Li⁺). The electrodes were held at this potential for 15 min before washing (pure ether) and drying.

through the films and reach the Li surface and be reduced in the pores to form Li alkoxides.

Conclusion

Tertiary amines stabilize Li/DN salt solutions even when present in trace amounts (100 ppm). The stabilized solutions have a shelf life of years. The tertiary amines dissolved in DN do not interfere with Li surface chemistry in solutions. Stabilized LiAsF₆/DN solutions are superior electrolyte solutions for secondary Li batteries.

Li-cycling efficiency of 96–98% was measured in a variety of tests at different conditions, part of which were very similar to those of real battery situations. Further improvement could be obtained by the use of PC or EC as cosolvents in LiAsF₆/DN/ tertiary amine solutions. In part of the tests, Li-cycling efficiencies of more than 98% could be measured at DN/PC and DN/EC ratios around 12 and 30–50, respectively. The use of alkyl carbonates as cosolvent in DN solutions has several advantages (in addition to the increase in cycling efficiency):

(i) Conductivity increases as EC or PC is added to LiAsF₆/DN.

(ii) Should leakage causing DN evaporation occur, dangerous contact between the unvolatile PC or EC and Li and air is avoided. A thin layer of alkyl carbonate, remained on the Li, protects it from vigorous reactions with water and oxygen, since a protective Li₂CO₃ layer is formed due to reaction of Li, trace water and PC or EC.

The electrochemical windows of the stabilized LiAsF₆/DN is 3.2–3.7 V (depending on the oxidation potential of the tertiary amine), making them compatible with a variety of cathodes such as TiS₂, MoS₂, V₂O₅ and others. Since Li-cycling efficiency depends mostly on a delicate balance of film forming reactions related to solvent salt

and additives, it is believed that further optimization of these systems related to the amount of salt, cosolvent and stabilizer can lead to even better performances than those reported in this work.

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