

# Fluorinated organic solvents in electrolytes for lithium ion cells

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## Abstract

A novel partly fluorinated solvent for lithium ion batteries, *N,N*-dimethyl trifluoroacetamide (DTA), is presented. The physical properties and the electrochemical behaviour of this compound are investigated. With its low viscosity and high boiling point and flash point it could replace low viscosity solvents (thinners) such as dimethyl carbonate or diethyl carbonate currently used in lithium ion battery electrolytes to achieve the demand for safer lithium ion batteries. The outstanding filming properties allow to use the DTA even in mixtures with PC in amounts of 10%. With both solvents having a freezing point below  $-40^{\circ}\text{C}$ , the mixture is promising as low temperature electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium ion batteries; Fluorinated solvents; Electrolyte; Cyclic voltammetry

## 1. Introduction

Currently, commercial graphite-based lithium ion batteries use mixed solvent electrolytes containing highly viscous ethylene carbonate (EC) and low viscosity dilutants such as dimethyl carbonate or diethyl carbonate (DMC, DEC) as main solvents. EC is indispensable, because of its excellent filming properties, DMC and/or DEC are required to get the low temperature performance of the electrolyte at least reasonable [1,2]. Nevertheless, the low temperature performance of these EC based electrolytes still needs some improvement. In addition, DMC and DEC are highly volatile and their flash points are quite low (DMC  $18^{\circ}\text{C}$ , DEC  $31^{\circ}\text{C}$ ), which may have a considerable impact on the battery safety.

In previous work we employed partly fluorinated solvents like glycol ethers [3] of the type  $\text{HC}_2\text{F}_4\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{F}_4\text{H}$ ,  $n = 1, 2, 3, (4, 6)$ , urethanes [4] such as  $(\text{CH}_3)_2\text{NCO}_2\text{CH}_2\text{CF}_3$  or glycol esters [5,6] as dilutants for more viscous solvents such as propylene carbonate (PC), the latter being known for its better low temperature behaviour compared to EC. Exchange of some hydrogen for fluorine causes significant differences in the physical and chemical properties of polar solvents. In particular, viscosities, but also melting

and boiling points of fluorinated solvents are in most cases significantly lower, compared to their hydrogenated counterparts. Moreover, fluorinated solvents are in general much less flammable as less hydrogen is available. As a rule, oxidation stability of partly fluorinated solvents is quite good, due to the stability of the carbon–fluorine bond, and thus promising for lithium battery applications. On the other hand, costs are obvious disadvantages of fluorinated solvents.

It turned out that several of the investigated fluorinated solvents showed very good anode filming properties, as was observed also in other works using fluoroethylene carbonate [7]. Here, we present results where small amounts of 10 vol% of the fluorinated solvent allow to operate graphite anodes in PC based electrolytes; PC being known to lead to strong solvent co-intercalation into graphite, of refs. [6,8].

## 2. Experimental

Commercially available solvents were used without further purification. *N,N*-dimethyl trifluoroacetamide (DTA) was synthesised and purified according as described [8]. Lithium bis-(trifluoromethanesulfonyl) imide (LiTFSI) was dried at  $140^{\circ}\text{C}$  in vacuum with a turbo molecular pump for 5 days. The water content of the prepared electrolytes was determined by Karl Fischer titration to be less than 15 ppm. Graphite based anodes were made from TIMREX<sup>®</sup> synthetic graphites SFG 44 or KS 6 (Timcal Group Ltd.)

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with 5 w/o polyvinylidenefluoride (PVDF) binder (Aldrich). LiCoO<sub>2</sub> based cathodes were made from 90 w/o LiCoO<sub>2</sub> (Merck), 6 w/o carbon black (Printex L6, Degussa), and 4 w/o PVDF.

The electrochemical experiments were carried out in laboratory type glass cells with lithium counter and reference electrodes and excess of electrolyte. Current densities and specific charges are given with respect to the graphite and LiCoO<sub>2</sub> masses, respectively.

### 3. Results and discussion

The physical properties of DTA compared to the unfluorinated homologue *N,N*-dimethyl acetamide (DMAc) and some commercially used solvents are given in Table 1. Compared to low viscosity solvents as DMC or DEC the boiling point and in particular the flash point of DTA is higher, so that a better cell safety can be anticipated. As expected, the melting point and boiling point of DTA are significantly lower than those of DMAc. The melting point of  $-42^{\circ}\text{C}$  is comparable to propylene carbonate (PC) and suggests an application in low temperature electrolytes.

In contrast to EC, pure PC is not able to form an effective solid electrolyte interphase (SEI) film on the graphite anode, which prevents the graphite from solvated intercalation and exfoliation.

The situation changes completely when DTA is added to the PC electrolyte (Fig. 1). Even only 10% of DTA allow for reversible intercalation of unsolvated lithium. PC cointercalation is effectively suppressed. Apparently, a film, permeable for lithium, but impermeable for the solvating PC molecules, is formed between 2.6–1.5 V versus Li/Li<sup>+</sup>, i.e. at potentials high above the potentials of solvated intercalation (the latter are typically below  $\approx 0.9$ – $0.7$  V versus Li/Li<sup>+</sup>). In the second sweep, no further filming is visible in the voltammogram, emphasising the effectiveness of the film formed on graphite in the presence of DTA in the first cycle.

A comparison of DTA with the unfluorinated DMAc (Fig. 2) displays that the DMAc does not form an effective film on graphite, even when 50 vol.% of DMAc in combina-

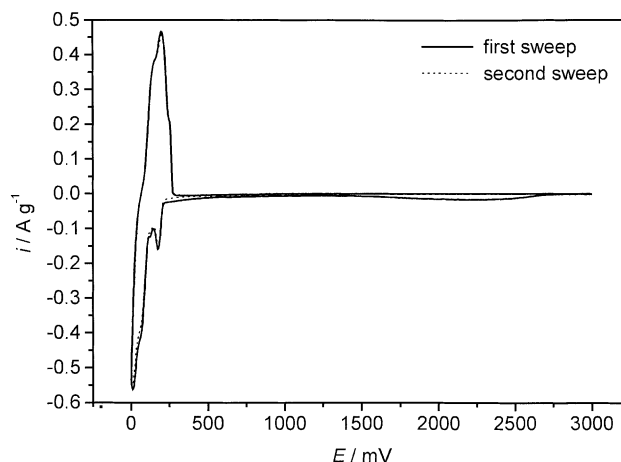


Fig. 1. Cyclic voltammograms of a graphite KS 6 composite electrode in 1 M lithium bis-(trifluoromethansulfonyl) imide (LiTFSI) + PC/DTA (90:10, by volume); scan rate: 50  $\mu\text{V/s}$ ; V vs. Li/Li<sup>+</sup>; counter/reference electrode: lithium.

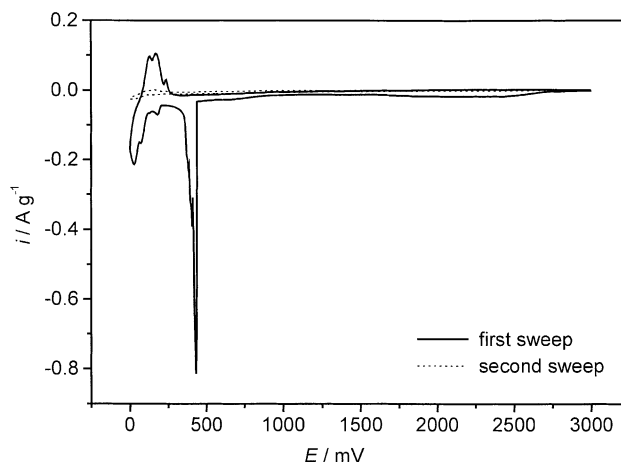


Fig. 2. Cyclic voltammograms of a graphite KS 6 composite electrode, in 1 M LiTFSI + PC/DMAc (50:50, by volume); scan rate: 50  $\mu\text{V/s}$ ; V vs. Li/Li<sup>+</sup>; counter/reference electrode: lithium.

tion with PC are used. After the first sweep the electrode is apparently more or less inactive to lithium intercalation.

Constant current charge/discharge cycling reveals excellent performance both with regard to discharge capacities

Table 1

Melting points (mp), boiling points (bp), flash points (fp) and viscosities (visc) of the fluorinated organic solvent *N,N*-dimethyl trifluoroacetamide (DTA) in comparison to its unfluorinated homologue *N,N*-dimethyl acetamide (DMAc) and several lithium battery solvents

Solvent	mp/ $^{\circ}\text{C}$	bp/ $^{\circ}\text{C}$	fp/ $^{\circ}\text{C}$	visc/ $\text{mm}^2/\text{s}^{\text{a}}$
Ethylene carbonate (EC)	39	248	160	1.86 <sup>b</sup>
Propylene carbonate (PC)	-49	240	132	2.09
Dimethyl carbonate (DMC)	5	91	18	0.59
Diethyl carbonate (DEC)	-43	126	31	0.75
<i>N,N</i> -dimethyl trifluoroacetamide (DTA)	-42	135	72	1.09
<i>N,N</i> -dimethyl acetamide (DMAc)	-20	165	70	1.01

<sup>a</sup> At 25 $^{\circ}\text{C}$ .

<sup>b</sup> At 40 $^{\circ}\text{C}$ .

Table 2  
Charge/discharge of a graphite SFG 44 composite electrode in 1M LiTFSI + PC/DTA (90:10, by volume)<sup>a</sup>

Cycle	Charge (mAh/g)	Discharge (mAh/g)	Efficiency (%)
1	406.0	353.7	87.1
2	354.1	349.0	98.6
3	350.2	346.8	99.0
4	343.9	341.6	99.3
5	343.9	341.8	99.4
6	343.4	341.8	99.5
7	338.7	337.2	99.5
8	342.9	341.5	99.6
9	334.5	333.3	99.6
10	340.7	339.6	99.7
⋮	⋮	⋮	⋮
28	349.6	349.3	99.9
29	349.5	349.0	99.9
30	349.5	349.3	100.0

<sup>a</sup> Current/cut-off conditions:  $-100 \mu\text{A}/\text{mg}/52 \text{ mV} \parallel -20 \mu\text{A}/\text{mg}/24 \text{ mV} \parallel 100 \mu\text{A}/\text{mg}/255 \text{ mV} \parallel 20 \mu\text{A}/\text{mg}/1500 \text{ mV}$ ; counter/reference electrode: lithium.

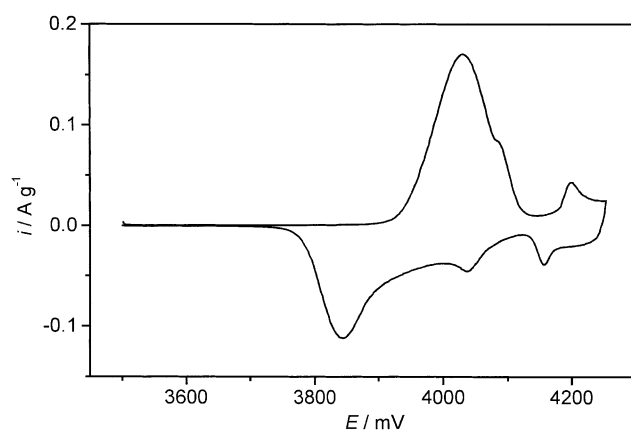


Fig. 3. Cyclic voltammogram of a LiCoO<sub>2</sub> composite electrode in 1M LiTFSI in PC/DTA (50:50, by volume); scan rate: 50  $\mu\text{V}/\text{s}$ ; V vs. Li/Li<sup>+</sup>; counter/reference electrode: lithium.

and charge/discharge efficiencies (Table 2). Beginning with about 87% efficiency in the first cycle, the efficiency is rapidly reaching values close to 100% in the later cycles.

Finally, also the oxidation stability of the DTA/PC electrolyte mixture is satisfactory as has been verified versus a LiCoO<sub>2</sub> composite electrode (Fig. 3).

#### 4. Conclusions

*N,N*-dimethyl trifluoroacetamide (DTA) is a promising solvent for use as electrolyte component in lithium ion batteries. The advantageous properties of DTA presented in this study are: (i) beneficial filming behaviour on graphite, even in combination with propylene carbonate resulting in excellent anode cycling stability; (ii) satisfactory oxidation stability at a typical lithium ion battery cathode; and (iii) moderate viscosity, low melting point and comparatively high boiling point and flash point, suggesting the use of DTA for lithium ion batteries with improved low temperature performance and higher safety.

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