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Journal of Power Sources 97–98 (2001) 557–560

JOURNAL OF  
POWER  
SOURCES

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# Lithium fluoroalkylphosphates: a new class of conducting salts for electrolytes for high energy lithium-ion batteries

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Received 20 June 2000; accepted 30 December 2000

## Abstract

The effort to develop improved electrolytes that satisfy the requirements of lithium rechargeable batteries has intensified the search for new conducting salts having an improved chemical and electrochemical stability. With lithium fluoroalkylphosphates, we introduce a new class of conducting salts for electrolytes for high energy lithium-ion batteries. The results of electrochemical studies of  $\text{Li}[(\text{C}_2\text{F}_5)_3\text{PF}_3]$  in organic carbonates in comparison to  $\text{LiPF}_6$  including electrochemical stability and charge–discharge efficiency are reported. In addition, the influence of perfluorinated alkyl groups on stability towards hydrolysis is demonstrated. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium battery; Lithium fluoroalkylphosphates; Conducting salts; Non-aqueous electrolytes

## 1. Introduction

With demand increasing for portable electronic devices and even electric vehicles applications, it becomes increasingly important to develop rechargeable battery systems having high energy density and improved cycleability.

Although lithium secondary batteries have been commercially available since the early 90s in Japan, one remaining challenge is to identify a conducting electrolyte that is thermally, chemically and electrochemically stable. The electrolytes under discussion are mixtures of aprotic organic solvents and conducting salts.

Among the conducting salts lithium hexafluorophosphate is the one most commonly used in high energy lithium-ion batteries. Nevertheless, its limited thermal and chemical stability restrict its use, especially if one keeps in mind lithium–polymer systems or larger lithium-ion batteries.

In the last decade, various attempts have been made to overcome the drawbacks of  $\text{LiPF}_6$ . For example, lithium bis(trifluoromethanesulfonyl)imide [1],  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  and lithium tris(trifluoromethanesulfonyl)methide,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$  [2], have been reported to provide electrolytes having a high conductivity and a good thermal and chemical stability [3,4]. Unfortunately, these conducting salts are not

easy to synthesize and purify. In addition, at least  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  shows a strong corrosive behavior towards aluminum, the positive current collector in lithium-ion batteries [5,6].

Recently, conducting salts based on a chelate complex of the borate or phosphate anion with aromatic ligands have been introduced by Barthel [7–11], and Handa [12,13]. These compounds have a good thermal stability. Furthermore, the build-up of a passivating film on aluminum equivalent to that observed for  $\text{LiPF}_6$  is reported [11]. However, due to the limited stability towards oxidation the use is currently limited to primary lithium batteries or 3 V rechargeable systems.

In this paper, we introduce a new class of conducting salts for the use in high energy lithium-ion batteries based on derivatives of the well-known  $\text{LiPF}_6$ .

Our recent work suggests that the substitution of one or more fluorine atoms of  $\text{LiPF}_6$  with electron withdrawing perfluorinated alkyl groups lead to stabilized P–F bonds.

Thereby:

- a very low, respectively, no sensitiveness towards hydrolysis, due to the steric shielding of the phosphorus through the hydrophobic perfluorinated alkyl groups;
- a conductivity comparable to  $\text{LiPF}_6$ , due to the strong electron withdrawing effect of the perfluorinated alkyl groups;

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- as a result of both mentioned effects a stabilization of the P–F bond and, therefore, an improved thermal stability of the corresponding lithium salt are obtained.

## 2. Experimental

### 2.1. Solvents

All solvents used were high purity grade, Selectipur<sup>®</sup> (Merck KGaA) products. The purity was more than 99.9% as determined by gas chromatography. The water content of all solvents was less than 30 ppm as determined by coulombic Karl Fischer titration.

### 2.2. Salts and electrolytes

The preparation of the conducting salts is fully described in [14–16]. The phosphoranes were more than 99.9% pure as determined by <sup>19</sup>F nuclear magnetic resonance (NMR) spectroscopy. The HF content of all electrolytes was lower than 50 ppm as determined by titration.

### 2.3. HF-determination

The measurement of the HF level was carried out using a specially developed non-aqueous titration technique with Seccosolv<sup>®</sup> methanol (Merck KGaA) as solvent, methanolic bromothymol blue as indicator and tetra-*n*-butylammonium hydroxide (TNBAH) in methanol as titrating reagent. The amount of free acid, calculated as ppm HF:

$$\text{ppm HF} = \frac{\text{conc}_1 \times m_1 \times M(\text{HF}) \times 10^6}{m_2}$$

conc<sub>1</sub> represents the concentration of TNBAH (mol g<sup>-1</sup>), *m*<sub>1</sub> the added mass of TNBAH (g) and *m*<sub>2</sub> the weight of the substance to be tested (g).

## 3. Results and discussion

The typical chemical structure of the fluoroalkylphosphates contains up to three linear or branched perfluorinated alkyl groups, e.g. C<sub>2</sub>F<sub>5</sub> or *iso*-C<sub>3</sub>F<sub>7</sub>.

In order to evaluate their potential for use as conducting salts in lithium-ion batteries, we start by comparing the characteristics of Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] with the currently used standard material LiPF<sub>6</sub>.

### 3.1. Electrochemical stability

Fig. 1 exhibits the anodic stability of the electrolyte as obtained by the cyclic voltammetry of Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] and LiPF<sub>6</sub> in EC:DMC (50:50 wt.%). The sweep range covers the potentials from the open circuit voltage to 6 V versus Li/Li<sup>+</sup>. For the sake of clarity, only the forward scans (scan rate = 20 mV s<sup>-1</sup>) are given.

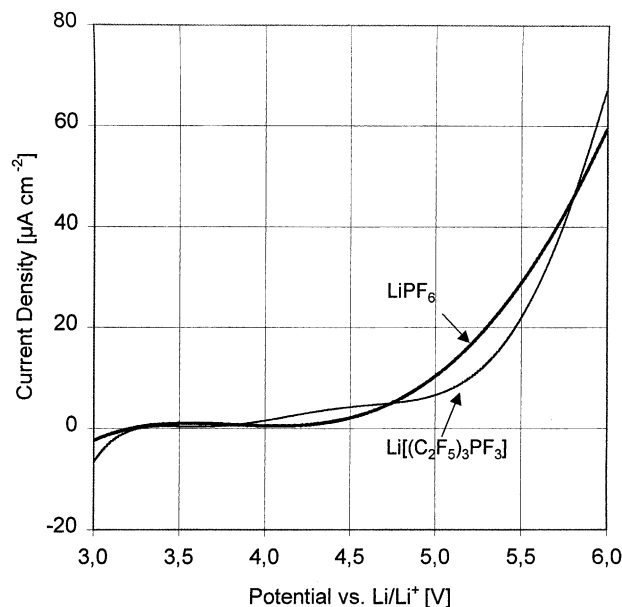


Fig. 1. Stability towards oxidation of LiPF<sub>6</sub> and Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] in EC:DMC (50:50 wt.%) at a platinum electrode upper curve, LiPF<sub>6</sub>; lower curve, Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] (first forward scans are shown).

The cyclic voltammograms of both binary electrolytes are almost identical. The small increase of the anodic stability of the Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] based electrolyte might be explained as a result of a lower HOMO energy level due to the strong electron withdrawing perfluorinated alkyl groups. Current densities lower than 15 µA cm<sup>-2</sup> at 5 V versus Li/Li<sup>+</sup> gives us the first indication that the stability of the lithium fluoroalkylphosphates is at least equal to that of LiPF<sub>6</sub>.

### 3.2. Ionic conductivity

The concentration and temperature dependency of the conductivities of LiPF<sub>6</sub> and Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] in EC:DMC (50:50 wt.%) are listed in Tables 1 and 2. The reduced ionic conductivity of the Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] based electrolyte can be explained as a result of reduced ionic mobility due to the larger size of the anion and, therefore, due to an increased

Table 1  
Specific ionic conductivities as a function of concentration (*T* = 25°C)

Concentration (mol dm <sup>-3</sup> )	Conductivity (mS cm <sup>-1</sup> )	
	Li[(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> PF <sub>3</sub> ] in EC:DMC (50:50 wt.%)	LiPF <sub>6</sub> in EC:DMC (50:50 wt.%)
0.5	7.6	9.3
0.6	8.3	
0.7	8.5	
0.8	8.6	10.3
0.9	8.5	
1	8.2	10.7
1.3		9.3
1.4	5.6	

Table 2  
Specific ionic conductivities as a function of temperature ( $c = 1 \text{ mol dm}^{-3}$ )

Temperature ( $^{\circ}\text{C}$ )	Conductivity ( $\text{mS cm}^{-1}$ )	
	Li[(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> PF <sub>3</sub> ] in EC:DMC (50:50 wt.%)	LiPF <sub>6</sub> in EC:DMC (50:50 wt.%)
-20	2.0	3.7
0	4.2	7.0
+25	8.2	10.7
+40	10.8	15.0
+60	14.8	19.5

viscosity of the electrolyte. It is worth mentioning that the solvent mixture EC:DMC (50:50 wt.%) is an optimized binary carbonate mixture for LiPF<sub>6</sub> from the conductivity point of view. With optimized mixtures for Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>], we assume that a conductivity comparable to LiPF<sub>6</sub> should be achievable.

### 3.3. Stability towards hydrolysis

To further prove the assumptions discussed in the introduction and in the last chapter, the behavior of LiPF<sub>6</sub> and Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] towards hydrolysis was studied under controlled conditions.

Therefore, 500 ppm of water were added under an inert glove box atmosphere to 1 M LiPF<sub>6</sub> and 1000 ppm to 1 M Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] in an organic carbonate mixture. Fig. 2

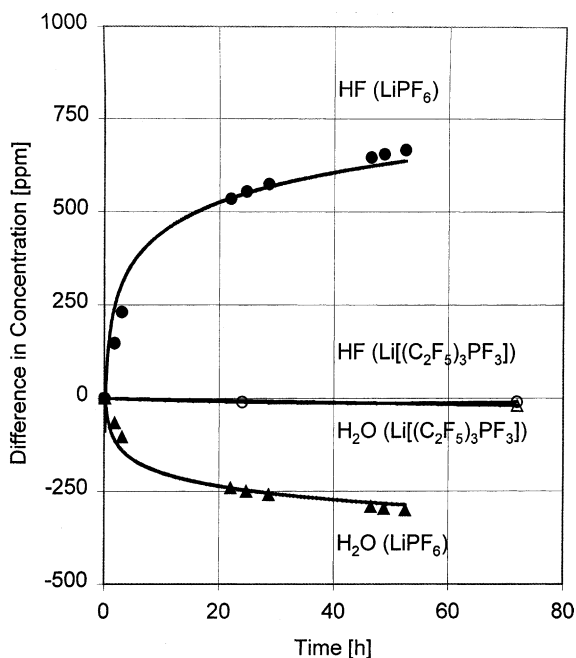


Fig. 2. Hydrolysis studies: 1 M lithium salt in EC:DMC (50:50 wt.%) LiPF<sub>6</sub> + 500 ppm water: (▲) concentration of water; (●) concentration of HF, Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] + 1000 ppm water: (△) concentration of water; (○) concentration of HF.

shows the typical behavior of LiPF<sub>6</sub> based electrolytes with a rapid decrease of the water content and a corresponding increase of the HF level, due to the decomposition of the conducting salt.



A totally different behavior is obtained for the Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] based electrolyte, shown in Fig. 2. Both water content and HF level remain stable over the whole period of evaluation — a clear indication of the superior stability of lithium fluor-alkylphosphates towards hydrolysis.

### 3.4. Discharge efficiency

Fig. 3 shows the results of the cycling experiments accomplished in a two electrode coin cell with a LiMn<sub>2</sub>O<sub>4</sub> positive electrode (active mass = 10 mg) and a lithium metal negative electrode. All studies were carried out in the voltage window between 3.5 and 4.3 V versus Li/Li<sup>+</sup> with a charge and discharge rate of C/5. The results indicate the improved performance of the Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] compared to the LiPF<sub>6</sub> based electrolyte. This effect becomes more pronounced with increasing cycle number.

How could one explain these differences? As various assumptions of the capacity loss of LiMn<sub>2</sub>O<sub>4</sub>-electrodes are given in the literature and as currently no data are available for the surface chemistry of Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] based electrolytes, we are not in the position to give a final explanation. However, if we take into account the difference

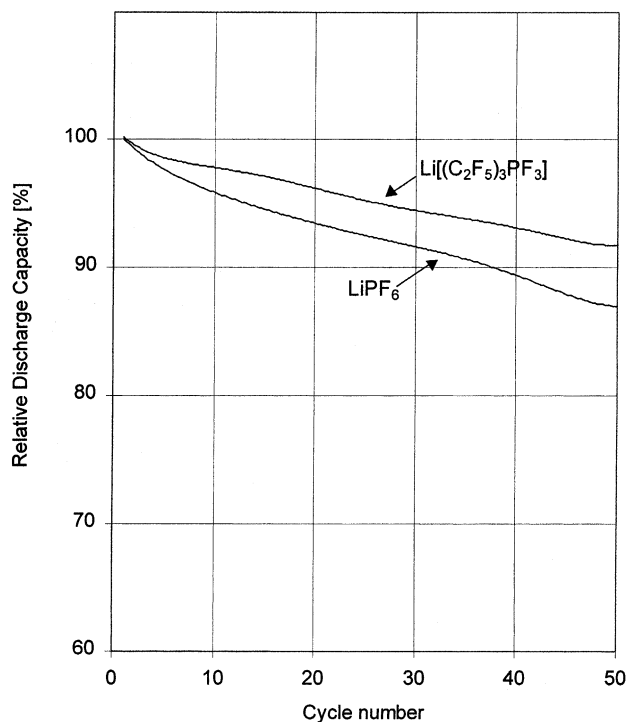


Fig. 3. Cycle number dependency of the relative discharge capacity of LiPF<sub>6</sub> and Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] in EC:DMC (50:50 wt.%) : lower curve, LiPF<sub>6</sub>; upper curve, Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>].

stability of  $\text{Li}[(\text{C}_2\text{F}_5)_3\text{PF}_3]$  and  $\text{LiPF}_6$  towards protic impurities like water, ethylene glycol or methanol and the sensitivity  $\text{LiMn}_2\text{O}_4$  toward HF, we would assume that the better chemical stability of  $\text{Li}[(\text{C}_2\text{F}_5)_3\text{PF}_3]$  maybe influences the cycling behavior in a desired way. Nevertheless, further evaluations have to be done.

#### 4. Conclusion

A new class of lithium salts, lithium fluoroalkylphosphates, was studied for application as lithium battery electrolytes. The electrochemical measurements prove the superior characteristics of the lithium fluoroalkylphosphates. These results could be attributed to an improved steric shielding of the phosphorous through the hydrophobic perfluorinated alkyl groups and a good delocalization of the negative charge, due to the strong electron withdrawing effect of the perfluorinated alkyl groups.

In addition, the sterical shielding together with the hydrophobic character of the perfluorinated alkyl groups result in a superior stability to hydrolysis, not reacting even in the present of 1000 ppm water. In battery application, therefore, we expect that lithium fluoroalkylphosphates will provide significant advantages over  $\text{LiPF}_6$ .

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