

Synthesis of New Li-Fluoroalkyl-Phosphates (LiFAP) for the Application in Li-Ion Batteries

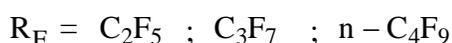
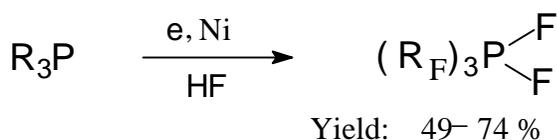
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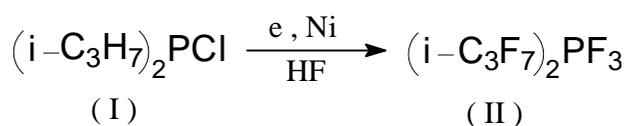
Lithium hexafluorophosphate (LiPF₆) is a common salt for the application in rechargeable lithium-ion batteries. Regardless of the high conductivity of electrolytes with LiPF₆, this salt has distinct disadvantages: first, limited thermal stability and second, by the reaction with water it decomposes with the formation of toxic gaseous products.

Recently we have developed the new convenient method for the preparation of perfluoroalkylfluorophosphoranes via electrochemical fluorination (ECF) in anhydrous hydrogen fluoride (Simons process) [1]:

ECF of trialkylphosphines in HF solution proceeds smoothly and leads to the formation of tris(perfluoroalkyl)-difluorophosphoranes in high yield.

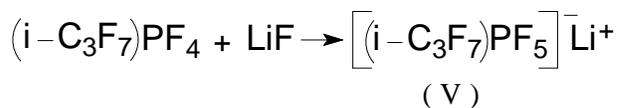
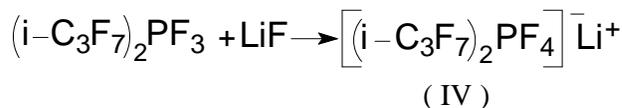


Secondary phosphines, for example di(isopropyl)chlorophospine (I) also can be converted into perfluoroalkylfluorophosphorane (II) via the Simons process.



Perfluoroalkylfluorophosphoranes are very active compounds. They can be easily converted into corresponding Li-

salt (LiFAP) by the action of lithium fluoride in a mixture of organic solvents, typical for battery application [2], for example:



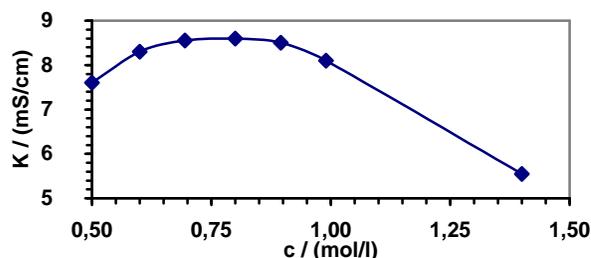
The salts (III – V) have a high solubility in organic solvents and show low association between Li⁺ and the anion. Highly concentrated solutions of the LiFAPs are viscous liquids or, some times, solid materials.

The salts (III – V) are very stable against hydrolysis. The adding of water to the solution of these salts in polar organic solvent does not cause formation of HF.

LiFAPs have the conductivity, comparable to the conductivity of LiPF₆ (see Table), but another profile of the concentration dependence of conductivity (see drawing).

Electrolyte	Table Conductivity (mS · sm ⁻¹)		
	1 mol/l of salt in EC:DMC (1:1)		
	-20° C	+20° C	+60° C
LiPF ₆	3.7	10.7	19.5
Li[(C ₂ F ₅) ₃ PF ₃]	2.0	7.3	14.8

Conductivity as a function of salt concentration
Li[(C₂F₅)₃PF₃] in EC:DMC (1:1)



References.

1. Patent WO 00/21969, Merck KGaA
2. Patent WO 98/15562, Merck KGaA