Lithium fluoroalkylphosphates – a new class of conducting salts for lithium ion batteries

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Lithium fluoroalkylphosphates - a new class of conducting salts for Lithium Ion Batteries

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Contents

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Targets for new salts

- Thermal stability
- At least comparable performance to $LiPF_6$
- Enhanced electrochemical potential window
- High chemical stability
- Compatible with the materials used in Lithium-batteries
- Simple synthesis
- Price comparable to $LiPF_6$ (slightly higher)
- Environmental friendly
- Non-toxic

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Salts under discusssion

Inorganic

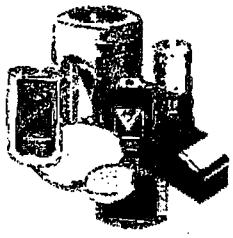
- $LiClO_4$
- $LiBF_4$
- $LiPF_6$
- $LiAsF_6$

Organic

- $LiSO_3CF_3$ (Triflate)
- $LiN(SO_2CF_3)_2$ (Imide)
- $LiN(SO_2C_2F_5)_2$ (Beti)
- $LiC(SO_2CF_3)_3$ (Methide)

Inorganic salts

- $LiBF_4$
  - thermally unstable
  - low conductivity
  - poor cycle efficiency
- $LiClO_4$
  - thermally stable
  - excellent conductivity
  - proclivity to detonate
- $LiAsF_6$
  - thermally more stable
  - good conductivity
  - best cycle efficiency
  - not very stable towards reduction
  - toxic (carcinogenicity of reduced As)



State-of-the-art: $LiPF_6$

- Advantages
  - high conductivity
  - excellent electrochemical performance
  - good electrochemical stability
  - available in huge amounts
- Disadvantages
  - limited thermal stability
  - chemically unstable (moisture sensitive)

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Organic salts I

- $LiN(SO_2CF_3)_2$
  - very good conductivity
  - high thermally stable
  - electrochemical stable
  - chemically stable
  - complex synthesis and purification
  - aluminumcorrosion potential ~ 3.6V
- $LiC(SO_2CF_3)_3$
  - very good conductivity
  - high thermally stable
  - electrochemical stable
  - chemically stable
  - good cycle efficiency in Lithium Ion Batteries
  - very complex synthesis and purification

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Organic salts II

- $LiN(SO_2C_2F_5)_2$
  - very good conductivity
  - high thermal stability (>300°C)
  - chemically very stable
  - aluminum corrosion potential ~ 4.2 - 4.5V
  - difficult to purify

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Li-Imides: the corrosion problem

- **Possible solutions of the corrosion problem**
  - additive in the electrolyte
    - forming a passivation layer prior to the onset of the corrosion potential
  - treatment of the aluminum current collector
    - surface coating, passivation prior to use
  - increase the chain length of the C_xF_y groups of the Imide anion

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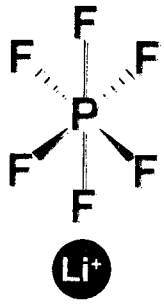
The structural problem of $LiPF_6$

unstable P-F bonds?:
⇒easy to break?
⇒chemically unstable
⇒ thermally unstable



Small size of the lithium cation:
⇒high enthalpy of formation of LiF
LiF has a vey low solubility in the electrolyte

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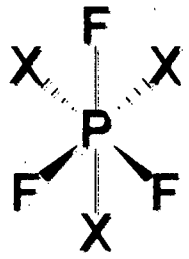
How to improve $LiPF_6$?

X:
- optimized size to avoid F^--abstraction
- hydrophobic character to prevent hydrolysis
- strong electron withdrawing effect for good charge delocalization
  ⇒good dissoziation



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New Salts: LiFAP

Lithium fluoroalkylphosphates

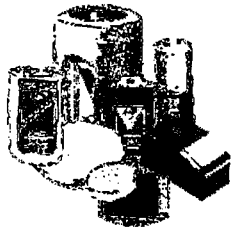
$Li^+[PF_a(CH_bF_c(CF_3)_d)_e]^-$ with a = 1, 2, 3, 4 or 5 and a + e = 6
b = 0 or 1
c = 0, 1, 2 or 3
d = 0, 1, 2 or 3
e = 1, 2, 3 or 4

References:

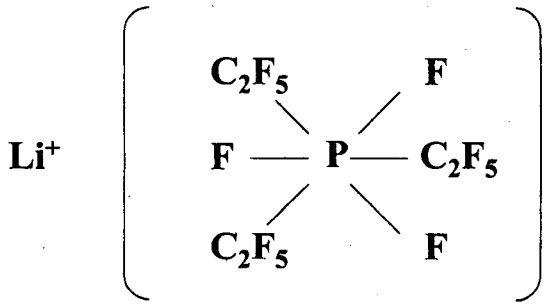
Lithium Fluorophosphates and their use as conducting salts, DE 196 41 138, WO 98/155562
Electrochemical synthesis of Perfluoroalkyl-phorphoranes, DE 198 446 36, WO 00/21969

Expected properties

- **improved thermal stability**
  - stable > 150°C ($LiPF_6$: stable < 80 - 100°C)
- **improved stability towards hydrolysis**
  - due to the use of big, hydrophobic groups
  - steric shielding effects (no formation LiF)
- **high oxidation stability**
  - due to the use of strong electron withdrawing groups
- **comparable conductivity to $LiPF_6$**



First example: LiFAP1



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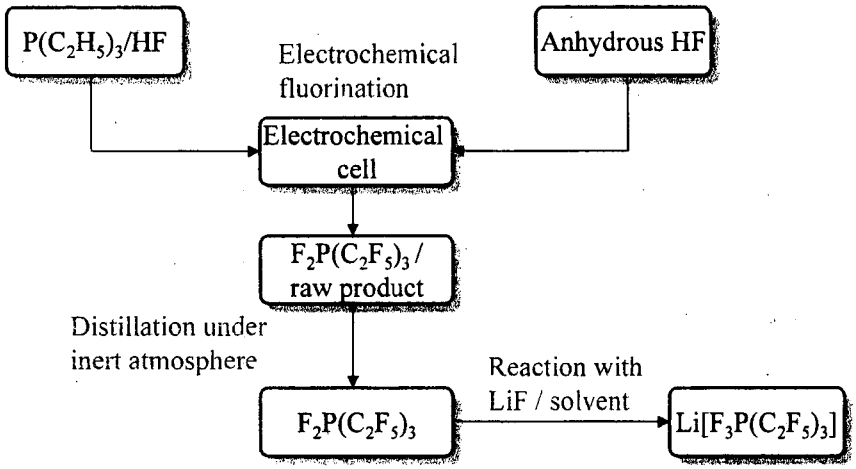
Synthesis scheme of $Li[(C_2F_5)_3PF_3]$



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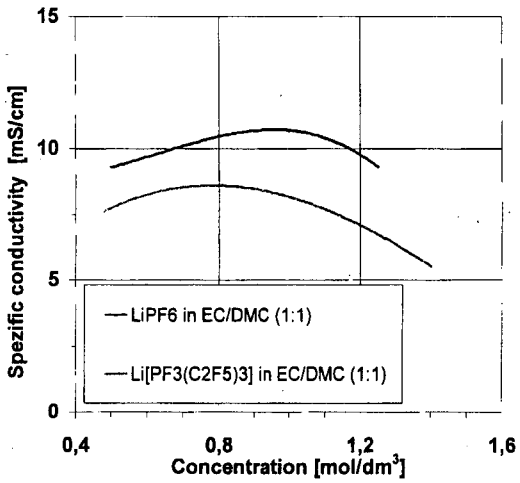
Production process for LiFAP

- **Very flexible** due to the electrochemical fluorination technique
- Three production steps only
- The salt was synthesized **in-situ** in solvents
  - no isolated salt available
  - only available in solvents, ready-to-use electrolytes

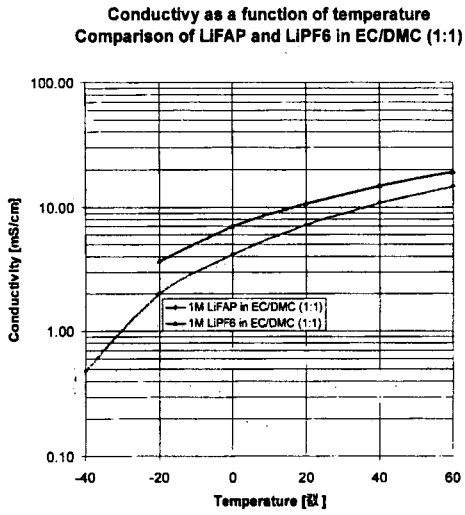
Some analytical remarks

- **LiFAP salts require a complete different analysis procedure compared to $LiPF_6$**
  - the analytical methods applied to $LiPF_6$ are not valid
- The known impurities cannot be quantified so far
  - new analytical methods has to be developed
    - find **appropriate** methods (FT-IR, Raman, etc.)
    - find **appropriate** standards for quantification
    - ...

Conductivity I



Conductivity II



Conductivity III

- Conductivity maximum is about of 0.7 - 0.8mol/l
- in EC:DMC (1:1 wt-%): slightly lower than $LiPF_6$
  - **reason**: larger anion size, higher viscosity
- EC:DMC is an optimized mixture for $LiPF_6$-based electrolytes
- The optimized solvents for LiFAP are not known
  - a lot of optimizing work has still to be done

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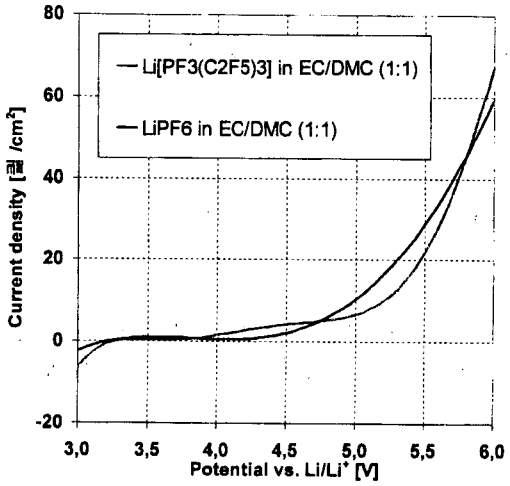
Oxidation stability I



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Oxidation stability II

- At least comparable anodic stability to $LiPF_6$
- EC/DMC maybe not the appropriate solvents
  - decomposition of solvents at higher potentials
  - polarization effects
  - impurity effects
- Only measurements in PC are reliable!

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Other LiFAP salt

- **Kita et al.*** : $LiPF_{6-x}(CF_3)_x$, x = 1, 2 or 3
  - almost comparable conductivity to $LiPF_6$
  - very high anodic stability in pure PC (≥ 6V)
  - from a theoretical point of view: thermally stable

*F. Kita et al., 10. IMLB, 28. May – 2. June 2000, Como/Italy, Abs. No. 283
H. Kamizori et al., The 40th Battery Symposium in Japan, November 14 – 16, 1999, Kyoto, Japan, Abs. No. 3D09

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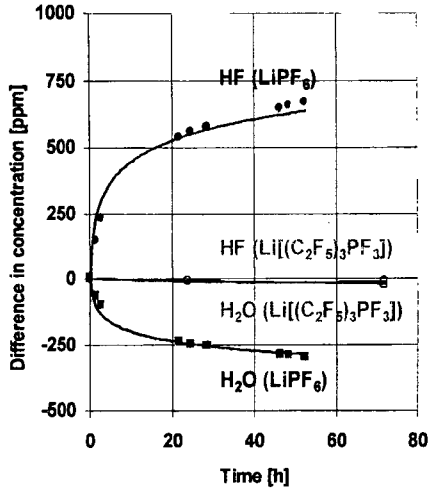
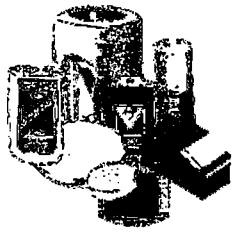
Hydrolytic behavior of LiFAP

Doping the electrolyte with H_2O:
500ppm $LiPF_6$-electrolyte
1000ppm LiFAP-electrolyte





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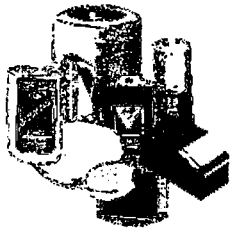
Hydrolysis: results

- LiFAP
  - no reaction with water observable
  - **stable against water!**
- $LiPF_6$
  - fast reaction with water forming HF
    - the HF reacts with the SEI
    - the HF attacks the $LiMn_2O_4$ cathode
  - not stable against water



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Reaction of $LiPF_6$ with H_2O

Proposed reaction mechanism:

$$LiPF_6 \xrightarrow{+H_2O} 2\,HF + LiF + POF_3 \xrightarrow{+H_2O} H_xPO_yF_z + HF \xrightarrow{+H_2O} H_3PO_4$$

[Barlow, ESSL, 2(8) 1999]

Reaction of HF with the SEI:

$$Li_2CO_3 + 2\,HF \longrightarrow 2\,LiF + H_2CO_3$$

$$(CH_2OCO_2Li)_2 + 2\,HF \longrightarrow (CH_2OH)_2 + 2\,LiF + 2\,CO_2$$

[Aurbach et. al., JES 143 (1996)]

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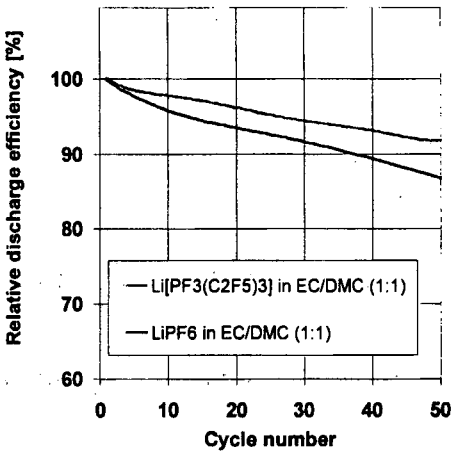
Cycle behavior I

Three electrode configuration:
cathode $LiMn_2O_4$
anode Li metal
reference Li metal
discharge rate C/5



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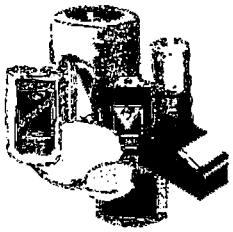
Cyclic behavior II

- Cycle life of spinel seems to be improved with a LiFAP-based electrolyte
  - the acid problem (HF) is less pronounced
- Simple coin cell tests with $LiCoO_2$ as cathode and Li-metal as anode shows no difference

$\Rightarrow$ the performance has to be proven in full cell tests



Conclusions

- **LiFAP is a very promising group of salts**
  - thermally very stable
  - chemically stable (not moisture sensitive)
  - electrochemical very stable
  - relatively flexible synthesis
- **The full potential of LiFAP is unknown so far**
  - a lot of experimental work has still to be done