Advanced Electrolytes for Lithium Ion Batteries

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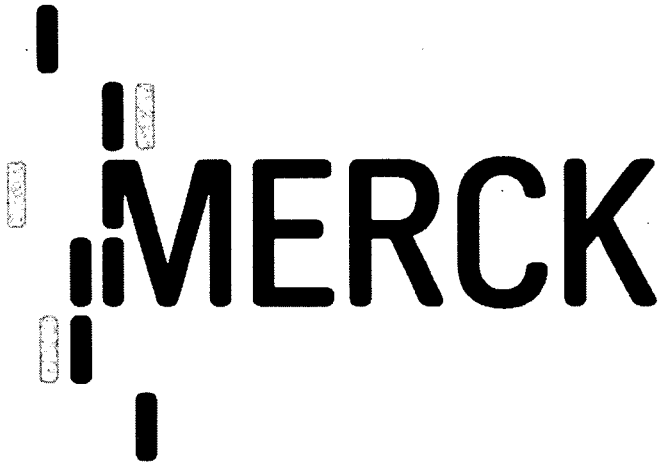

Advanced Electrolytes for Lithium Ion Batteries

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Purpose of the lecture

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- The "tasks" of electrolyte are mainly twofold
  - forming the Solid Electrolyte Interface (interface property)
    - without SEI the carbon anode is not thermodynamically stable
    - solvent and and salt reactions form the SEI
    - the quality of the SEI is very critical for battery performance
  - guarantee fast Li ion diffusion (bulk property)
    - high rate capability
    - thermal and chemical stability (→ problem $LiPF_6$)

⇒ **For both properties improvements will presented**

Contents

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- **SEI improvement**
  - stabilizer-free VC
  - experimental results
- **Stability improvement of the electrolyte**
  - new salt: $Li[PF_3(C_2F_5)_3]$
  - experimental results
- **Concluding remarks**

SEI improvement: VC

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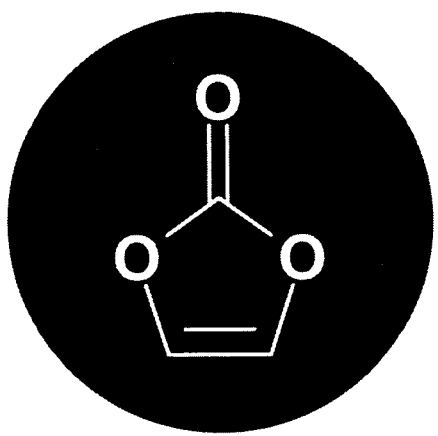
- One of the outstanding additives for cycle life improvement
  - plays an outstanding role in improving the surface chemistry of the anode
  - contains stabilizers, e. g. BHT



- Merck KGaA has developed its own VC which is **stabilizer-free**

Why stabilizer-free VC?

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- The commercial available VC contains stabilizers
- The electrochemical stability of the stabilizers is limited ⇒ side reactions in the battery
- *"Would you accept electrolytes which contain 1000ppm water or HF?"*

Stabilizer	Oxidation potential [V] vs. Li/Li^+
2,5 Bis(tert.-buthyl)-4-hydroxy-toluene (BHT)	**4.0**
Hydroquinone	**3.9**
2,2,6,6 Tetramethyl piperidine-1-oxyl	**3.7**

VC experimental results I

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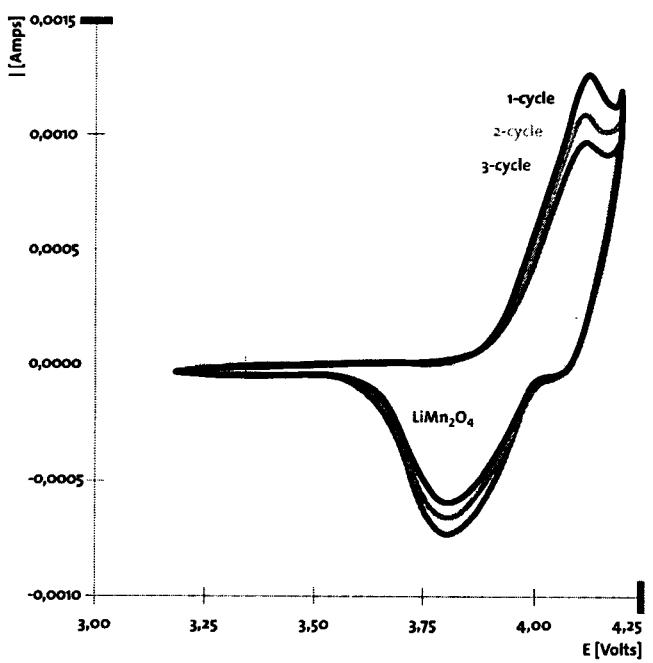
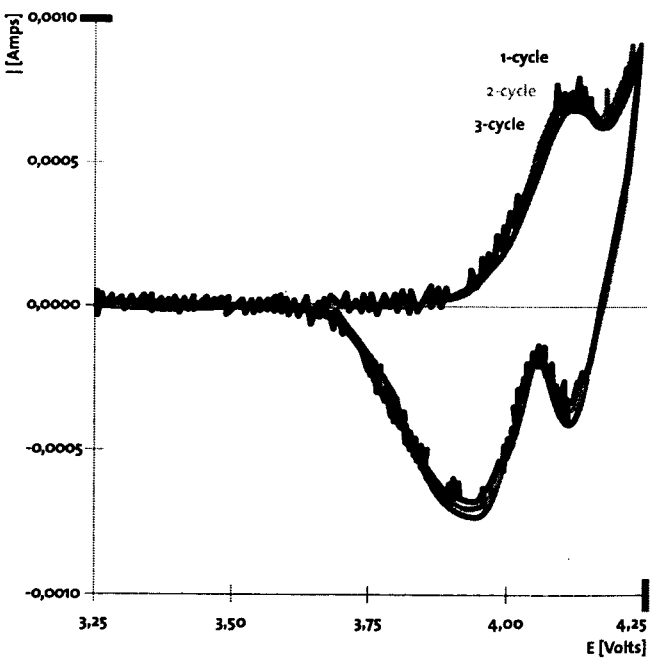
$LiMn_2O_4$, $LiAsF_6$-based electrolyte, 60° C

Electrolyte with stabilized VC



Electrolyte with stabilizer-free VC



VC experimental results II

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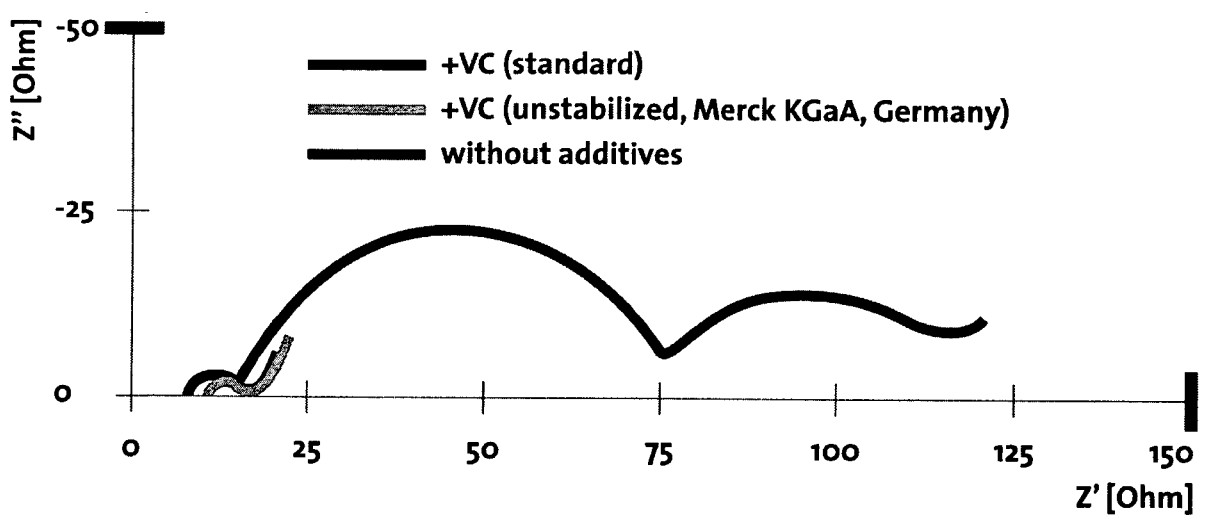
Anode Graphite KS 25
1M $LiPF_6$ based electrolyte
Temperature 25° C



VC experimental results III

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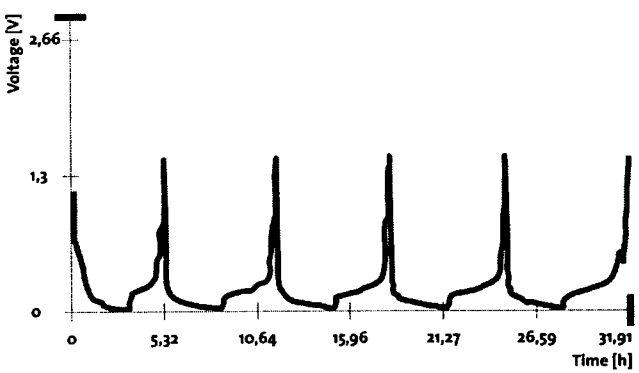
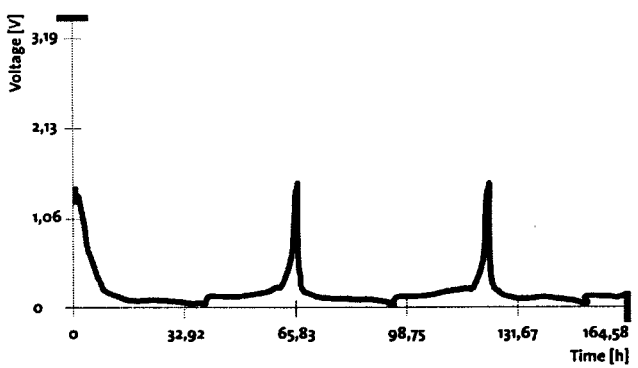
Anode Graphite KS 25
1M $LiPF_6$ based electrolyte
Temperature 60° C



without VC



stabilizer-free VC

VC experimental results IV

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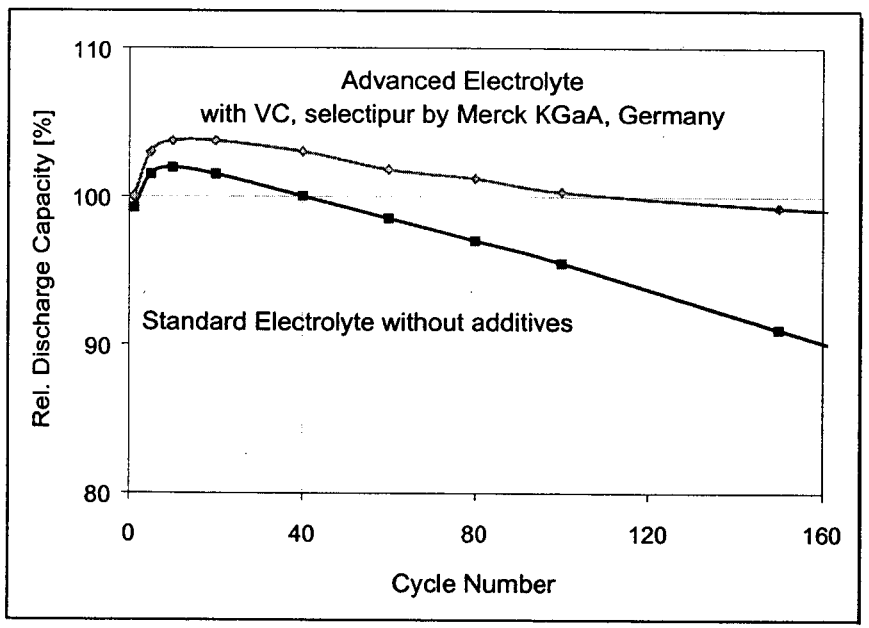
Electrodes $LiCoO_2$ and graphite
1M $LiPF_6$ based electrolyte



VC concluding remarks

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- Significant improvement of the SEI
  - improved cycle life significantly
  - better SEI stability at elevated temperatures
- Stabilizers are oxidized at the cathode
  - irreversible capacities
  - reactions of the stabilizers in the electrolyte are not known

$\Rightarrow$ Solution: stabilizer-free VC!

Improvement of the electrolyte stability

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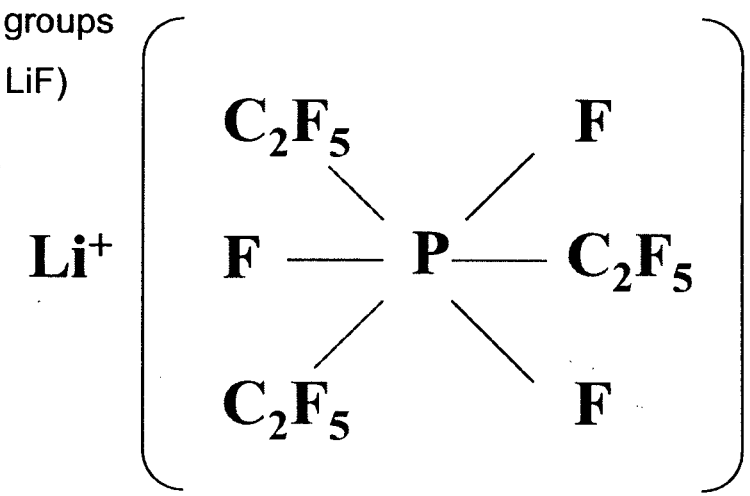
- New salt: $Li[PF_3(C_2F_5)_3]$ (LiFAP)
  - excellent thermal stability (>150° C)
  - excellent electrochemical stability
  - improved stability towards hydrolysis
    - due to the use of large, hydrophobic groups
    - steric shielding effects (no formation LiF)
  - conductivity comparable to $LiPF_6$



The "structural" problem of $LiPF_6$

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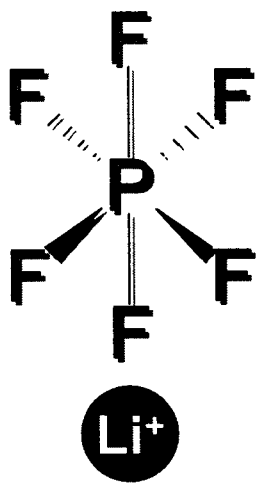
Unstable P-F bonds?:

⇒ easy to break?

⇒ chemically unstable

⇒ thermally unstable



Small size of the lithium cation:

⇒high enthalpy of formation of LiF

LiF has a very low solubility in the electrolyte

How to solve the problem?

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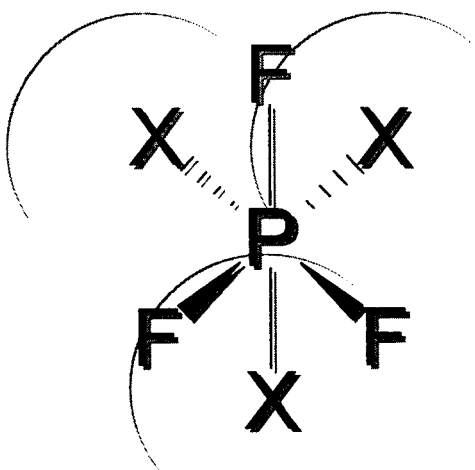
X:

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

  $\Rightarrow$ good dissoziation



Conductivity

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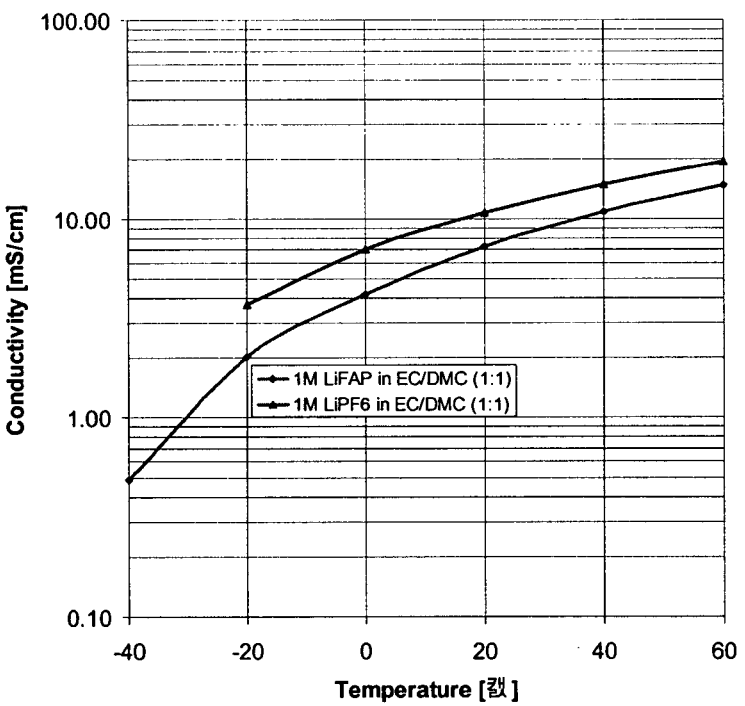
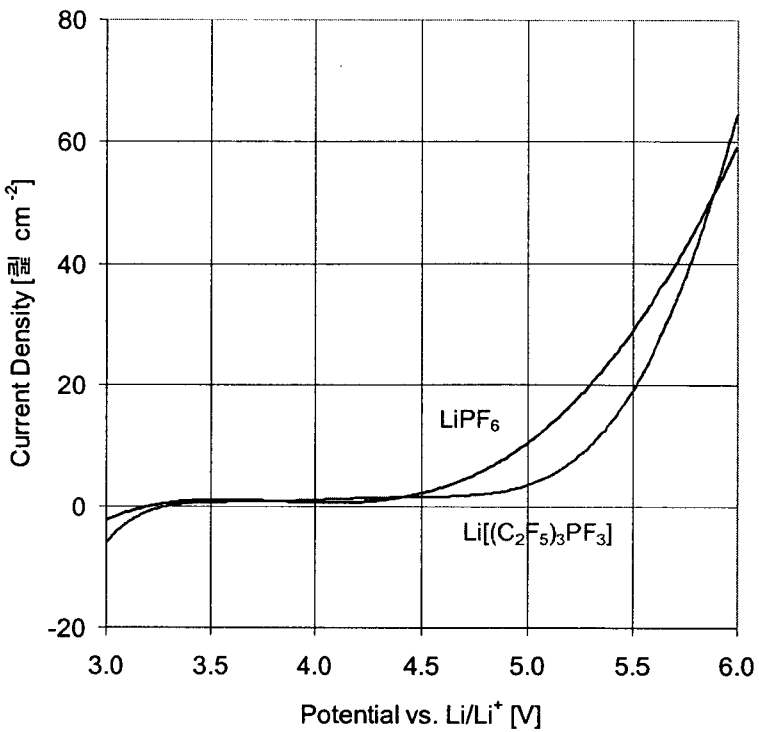
Conductivy as a function of temperature
Comparison of LiFAP and LiPF6 in EC/DMC (1:1)

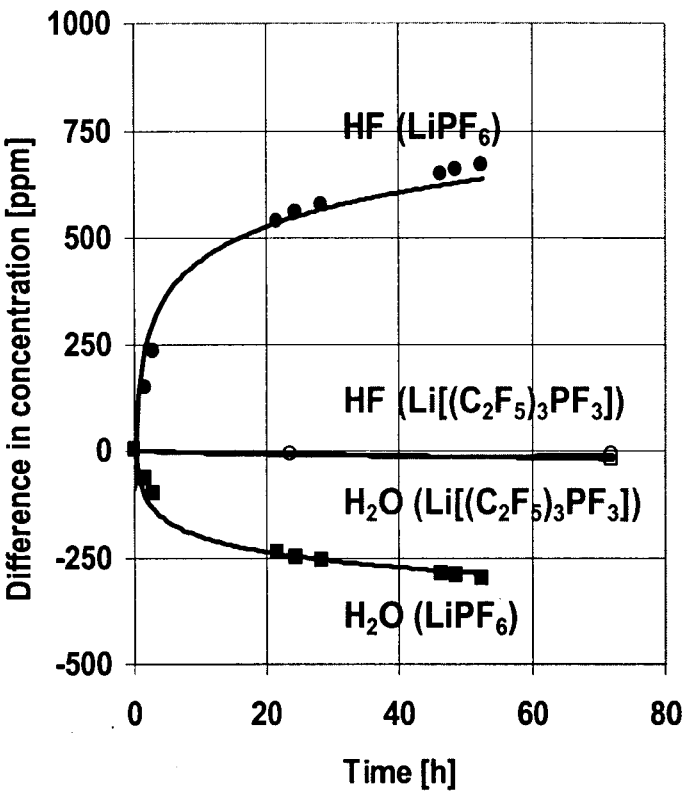


Electrochemical stability



Solvent mixture
EC:DMC 1:1 w/w

Hydrolysis behavior



Doping the electrolyte with H_2O:

500ppm $LiPF_6$-electrolyte

1000ppm LiFAP-electrolyte

Safety improvements?

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Does the substitution of three fluorine by perfluorinated alkyl chains affects the flammability of the electrolyte?

- Non-flammable electrolytes: fluorinated carbonates and/or phosphoric acid esters
- LiFAP can be regarded as "combination" of a fluorinated solvent and a phosphoric compound

Solvents	Flashpoints of	
	LiFAP based electrolyte	$LiPF_6$ based electrolyte
EC/DEC/DMC (2/1/2 w/w)	37.8° C	24° C
EC/DEC (3/7 v/v)	42.8° C	
GBL	96.4° C	

LiFAP concluding remarks

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- LiFAP is stable towards hydrolysis
  - the HF problem does not exist (!)
- The electrochemical stability is better compared to $LiPF_6$
- The conductivity is similar compared to $LiPF_6$
  - similar performance expectable
- Flash point of the electrolyte is increased

Acknowledgement

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