Highly toxic Organofluorophosphates as Electrochemical Aging Products during Formation at 4.8 V in NCM622/SG-3 Lithium Ion Batteries

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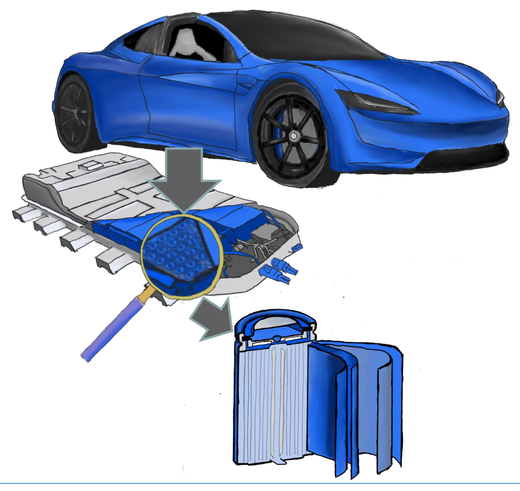
Introduction

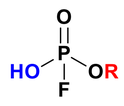
- **State-of-the-art LIB electrolytes:**
  - Linear carbonate (Dimethyl carbonate (DMC), Diethyl carbonate (DEC) or Ethyl methyl carbonate (EMC)) and cyclic carbonate solvents (Ethylene carbonate (EC))[1]
  - Conducting salt like Lithium hexafluorophosphate ($LiPF_6$)
  - A variety of Additives like vinylene carbonate (VC) or fluoroethylene carbonate (FEC)
- **Film-forming additives:**
  - To ensure the formation of the solid electrolyte interphase (SEI) without rapid electrolyte degradation
  - FEC and VC show higher reactivity towards reduction (and oxidation) compared to EC[2]

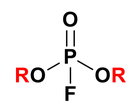
    → FEC and VC are degraded while the base electrolyte composition (e.g. EC/EMC) is mostly unaffected



- **Conducting salt degradation:**
  - $LiPF_6$ is unstable towards moisture reacting to hydrofluoric acid (HF) and POF_3[3]
  - POF_3 is highly reactive and is converted by further reactions with water and electrolyte components to form Organo(fluoro)phosphates[4,5]
  - Organofluorophosphates (OFPs) pose substantial health hazards (structural similarities to pesticides and nerve agents)[6]
  - Two groups of OFPs:

    i) acidic (usually non-toxic) ii) non acidic (mostly toxic)



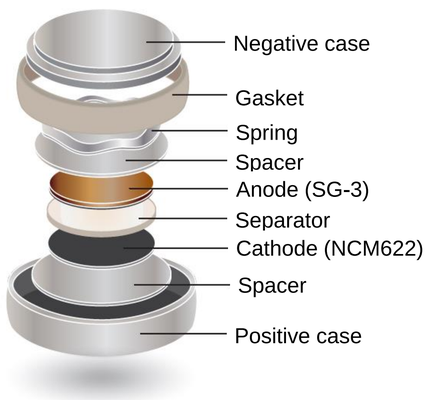


R = organic side chain

Methods

Cell chemistry and aging conditions:

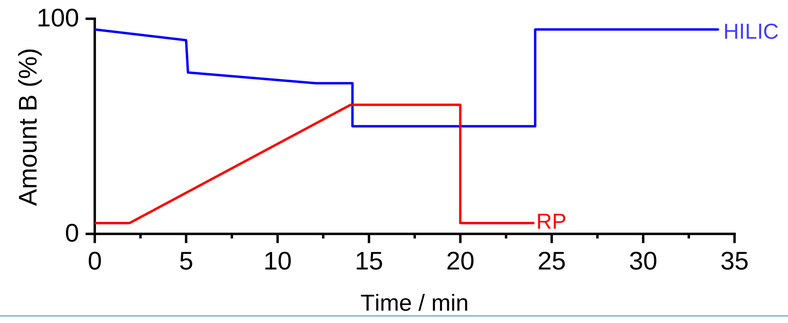
- Cathode: NCM622
- Anode: SG-3
- Separator: Freudenberg FS2190
- Electrolyte: 1 M $LiPF_6$ in EC:EMC (3:7)
  - Additive: x wt.% FEC (x=2, 5, 10)
- Cycling experiments:
  - 3 formation cycles at:
    - 1C; 2.8 V - 4.2 V (CCCV)
    - 1C; 2.8 V - 4.8 V (CCCV)



Analytical devices and methods:

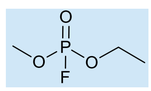
- Identification and structure elucidation was carried out with a LC-IT-TOF-system
- HILIC was used for the separation of acidic OFPs
  - Column: Hypersil GOLD SAX
- RP-chromatography was carried out for the separation of non-acidic OFPs
  - Column: Poroshell 120 SB-C18

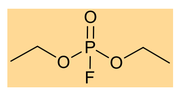
Gradients employed:



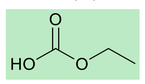
Results

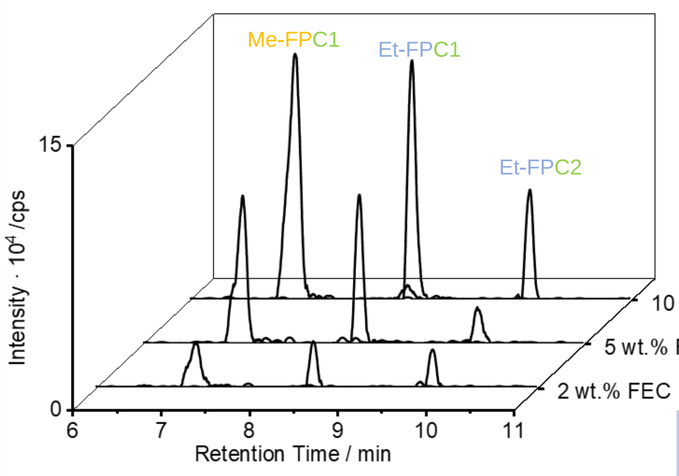
- Analysis of the electrochemically aged FEC-containing electrolyte (4.8 V) revealed the presence of a total of 15 non-acidic OFPs which can be separated into two groups
- Methyl-ethyl-fluorophosphates (Me-FPs) and ethyl-ethyl-fluorophosphates (Et-FPs)

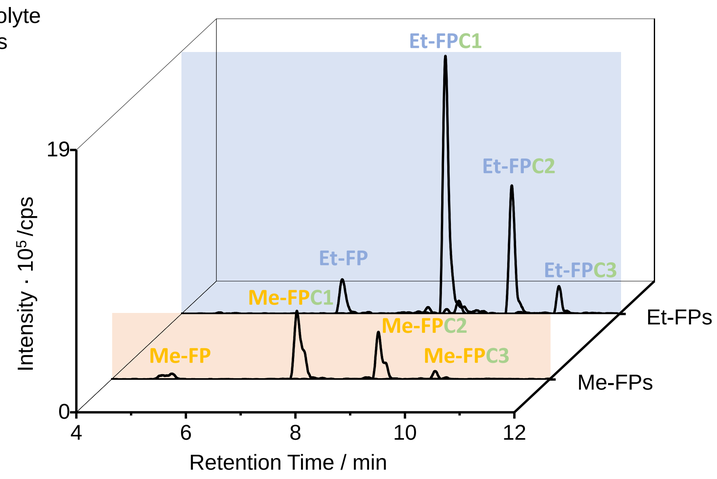




- With ethyl-carbonate (C) sidechains







- Small amounts of OFPs were observable in electrolytes without FEC.
- Higher concentrations of FEC lead to higher signal intensities of the observed OFPs

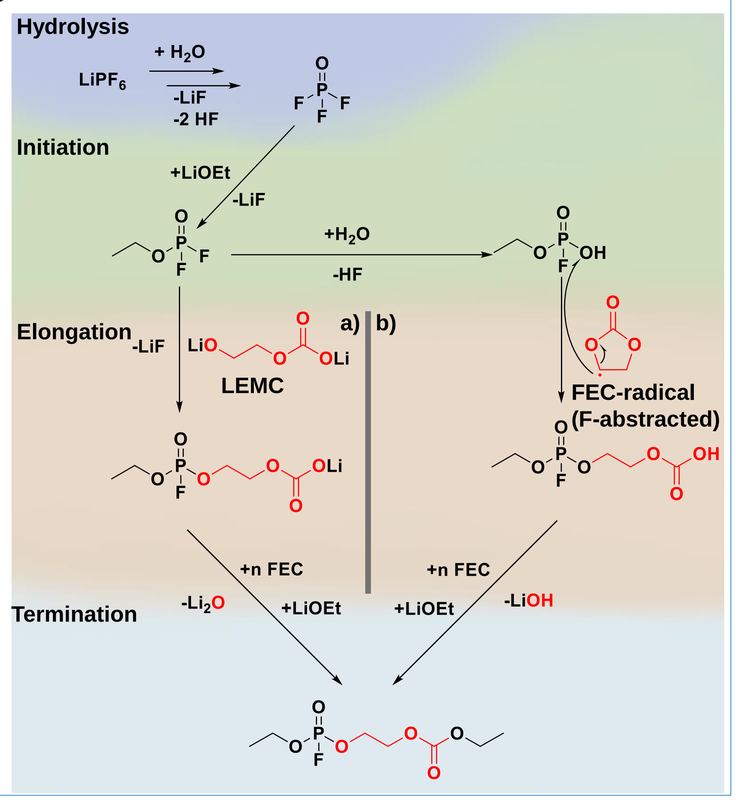
→ FEC plays a substantial role in the formation of OFPs

Proposed Mechanism of FEC-based OFP-formation:

1. **Hydrolysis** of $LiPF_6$
2. **Initiation** of the chain reaction with lithium ethoxide (LiOEt)
3. **Elongation**
   - Two possible influences of FEC during formation of OFPs

   a) origin of carbonyl carbon
   - Lithium ethyl monocarbonate (LEMC) as the reactive species
   - FEC as the origin of the carbonyl carbon in the elongation mechanism

   b) FEC as the reactive species
   - Due to the presence of fluorine or its abstraction FEC radicals at the ethyl-backbone of the carbonate are stabilized
4. **Termination** with LiOEt



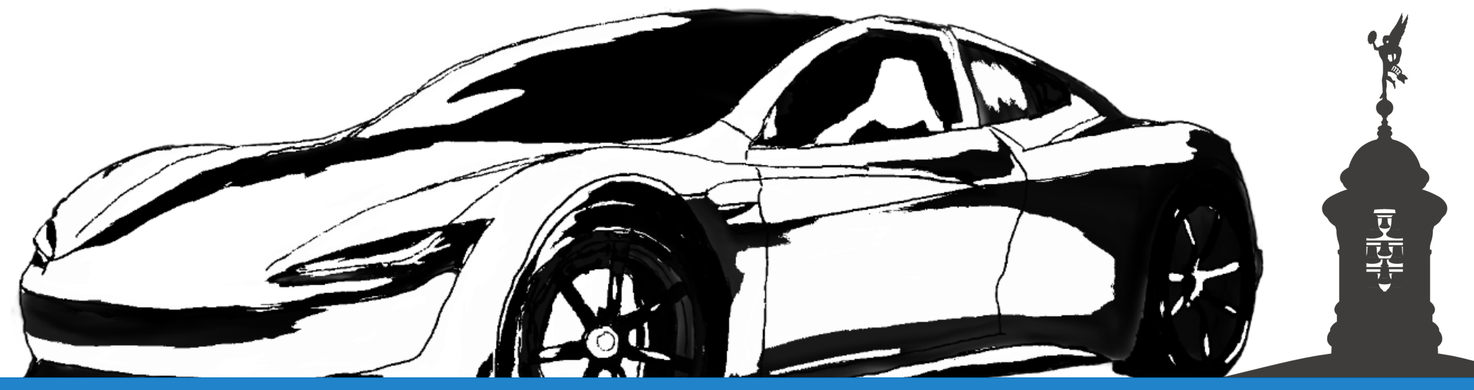
Conclusions and Outlook

- The formation of toxic non-acidic OFPs was observed during high voltage formation in NCM622/SG-3 coin cells
- While OFPs were observable in electrochemically aged LP57 the amount is negligible compared to that of OFPs in LP57 + FEC
- Greater concentrations of FEC played a substantial role in the amount of OFPs formed
- The presence of OFPs illustrates the need for particular caution when working with high voltages in NCM622/SG-3 LIBs
- An investigation of the impact of the cathode material is of need due to the high reactivity of NCM622 at high voltages.

Acknowledgments

The authors would like to thank the German Federal Ministry of Education and Research for funding the project BatGasMod (03XP0311C)

Bundesministerium für Bildung und Forschung



References

[1] Xu, K. *Chemical reviews* **2004**, *104* (10) 4303–4417.

[2] Markevich, E.; *et al*. *the ACS journal of surfaces and colloids* **2014**, *30* (25) 7414–7424.

[3] Gachot, G.; *et al*. *Analytical chemistry* **2011**, *83* (2) 478–485.

[4] Campion, C. L.; *et al. Journal of Fluorine Chemistry* **2005**, *152* (12) A2327.

[5] Campion, C. L.; *et al. Journal of Power Sources* **2004**, *7* (7) A194.

[6] Henschel, J.; *et al. Journal of Power Sources* **2020**, *447*227370.

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