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The role of TMSPx additives in stabilizing high-energy Li-ion batteries evidenced by *operando* gas analysis

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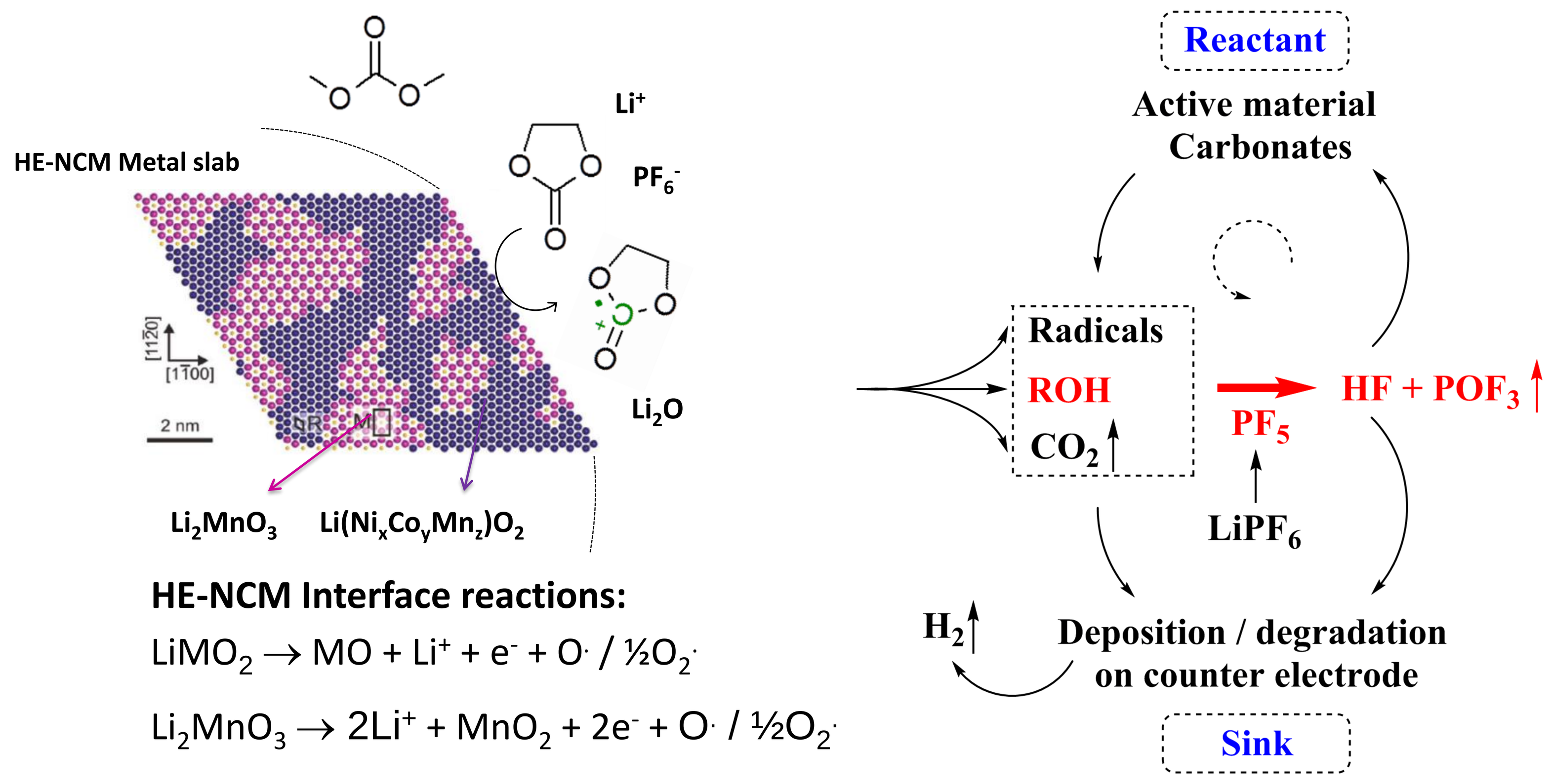
Motivation

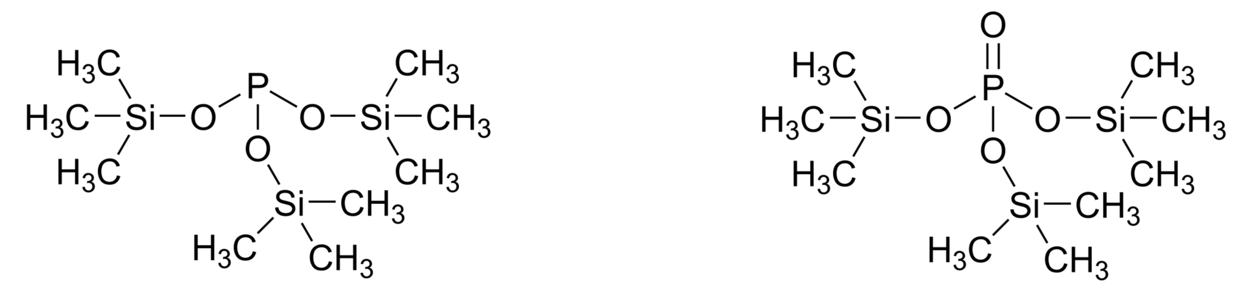
Problem: Electrolyte decomposition → autocatalytic $LiPF_6$ decomposition loop[1]

Goal: Prevent electrolyte decomposition and acidification of the system



Approach: additives

Hypothesis: TMSPx additives suppress gas evolution via layer formation and/or HF scavenging[2,3]



Tris(trimethylsilyl) phosphite (TMSPi)

- SPI layer formation reported
- HF/POF_3 scavenging

Tris(trimethylsilyl) phosphate (TMSPa)

- SPI layer formation reported
- HF scavenging?

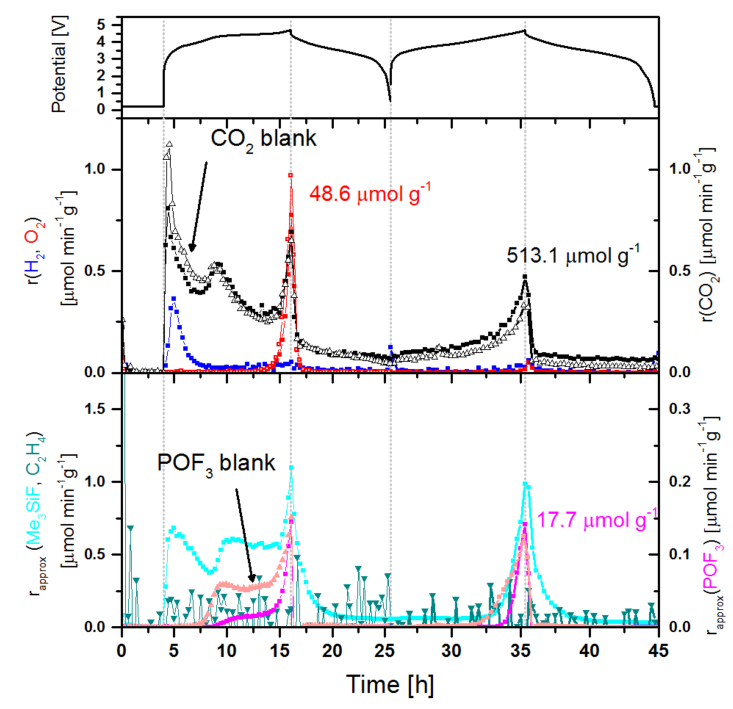
Efficiency of the additives depends on carbonate electrolyte composition:

→ OEMS study on HE-NCM full-cells with carbonate electrolytes:

Investigate influence of TMSPx electrolyte additives on O_2, CO_2, H_2, POF_3 and Me_3SiF evolution.

OEMS

FEC:DEC (12:88) 1M $LiPF_6$ + 1wt% TMSPa



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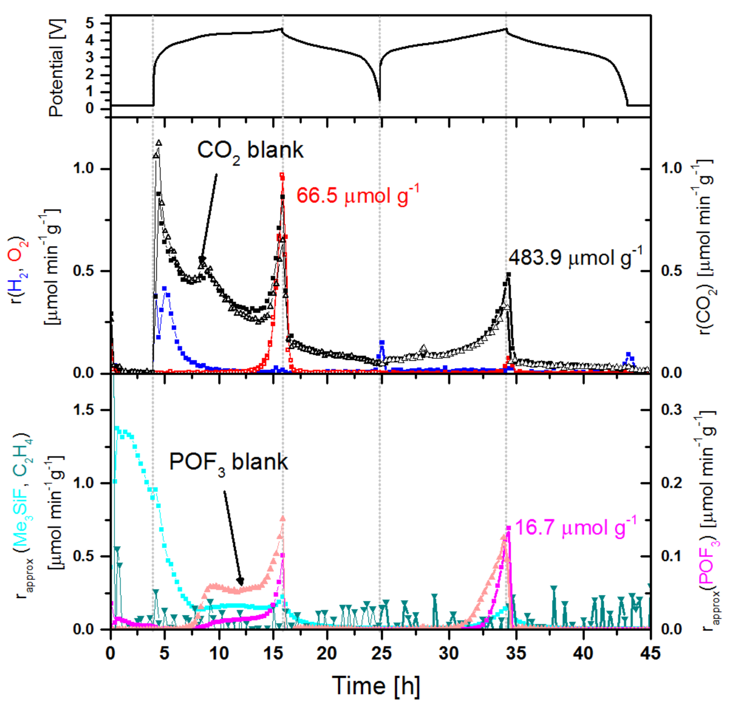

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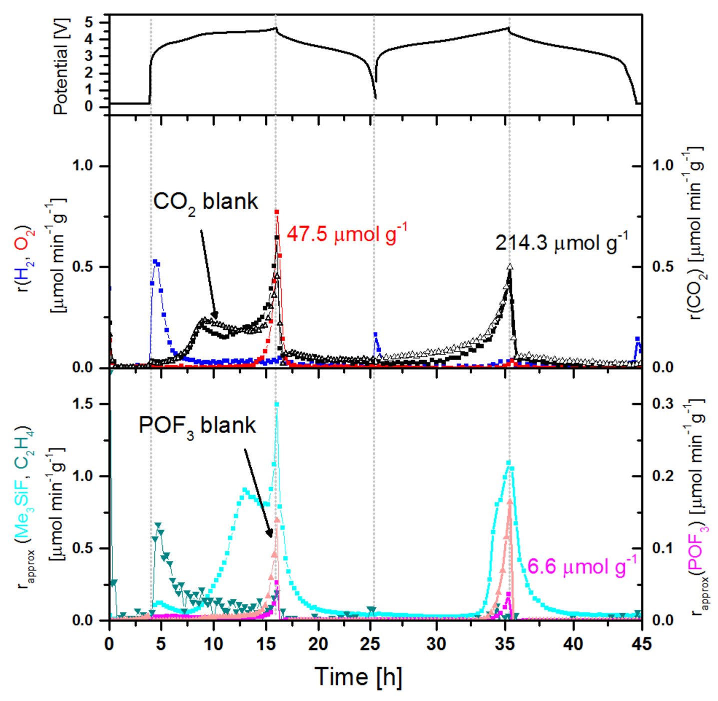
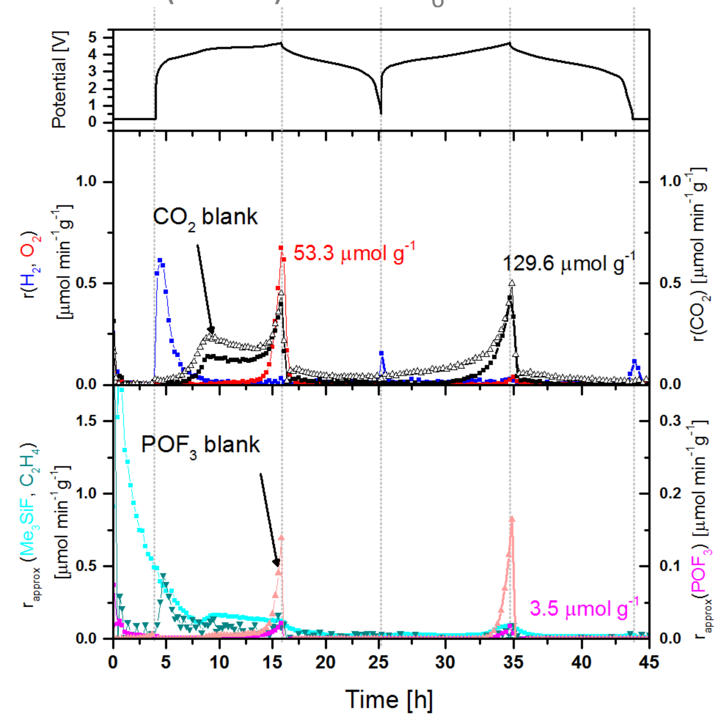


EC:DEC (12:88) 1M $LiPF_6$ + 1wt% TMSPi



FEC-based electrolyte vs. EC-based electrolyte:

- More CO_2 (FEC reduction) and POF_3 released in FEC-based electrolyte
- C_2H_4 evolution at beginning of charge for EC-based electrolyte (EC reduction)

Addition of TMSPx additives to FEC-based electrolytes:

- No impact on O_2, H_2 and CO_2 evolution rate
- Strong decrease of POF_3 evolution rate

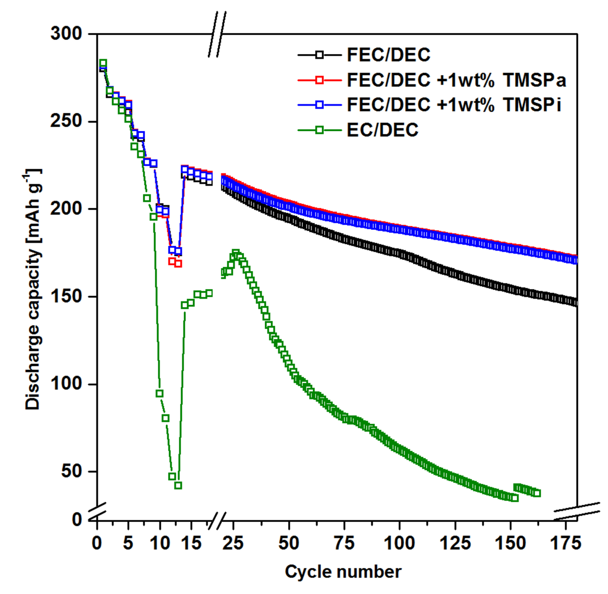
Addition of TMSPx additives to EC-based electrolytes:

- Decrease of CO_2 evolution rate during Li_2MnO_3 activation plateau with TMSPi
- Decrease of the maximum POF_3 evolution rate at end of charge with TMSPx

Me_3SiF: chemical reaction between TMSPx and F- moieties

- TMSPi: Me_3SiF evolution during OCP → strong reactivity TMSPi
- TMSPa: earlier Me_3SiF evolution during 1st charge with FEC electrolyte

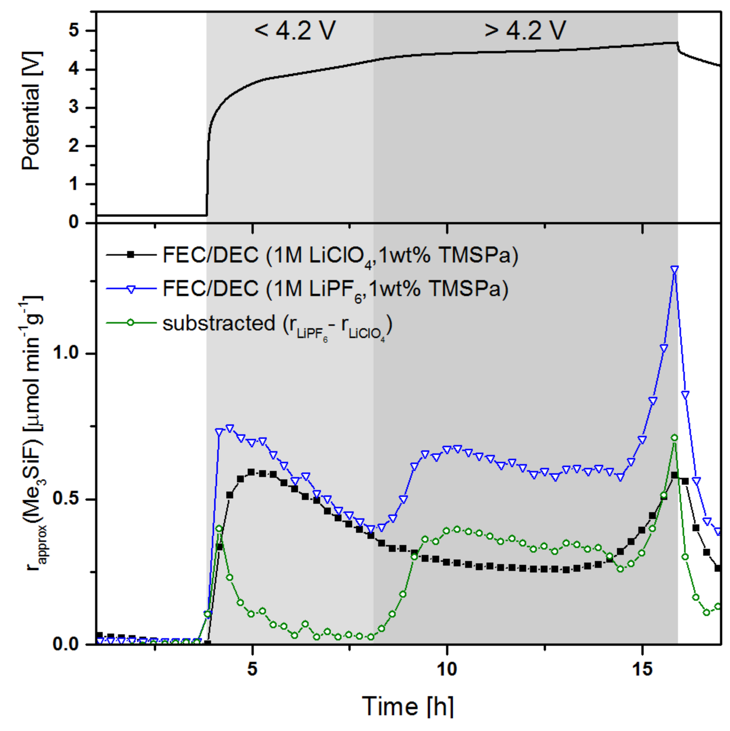
Cycling stability

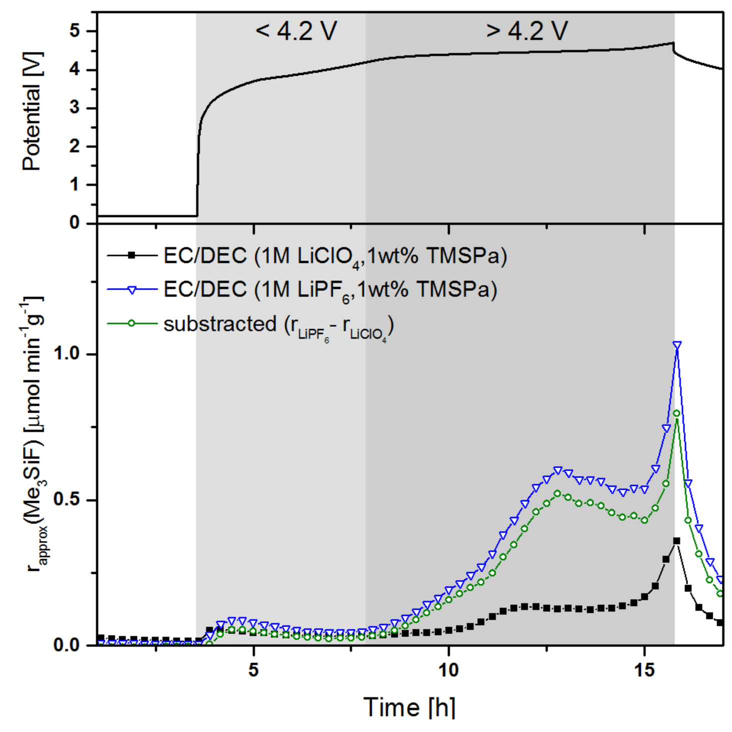


Blank electrolytes: EC:DEC (2:8) 1M $LiPF_6$ and FEC:DEC (12:88) 1M $LiPF_6$

- Better cycling performance with FEC-based electrolytes
- EC-based electrolytes: no improvement with addition of TMSPx (not shown)
- FEC-based electrolytes: better cycling with addition of TMSPx

Sources of F^- species reacting with TMSPa





TMSPa reacts at least with 2 different F^- sources in FEC-based electrolyte:

1. reaction with LiF produced from FEC reduction at beginning of charge
2. reaction with F^- species formed during side reactions involving electrolyte degradation products and reactive oxygenated species released during Li_2MnO_3 activation

Summary / conclusions

- TMSPa and TMSPi are chemically active and scavenge F^- sources such as HF and LiF.
- Decrease in POF_3 amount with addition of TMSPx, more particularly in FEC-based electrolyte where more POF_3 is formed.
- TMSPi is more reactive than TMSPa toward $LiPF_6$ → need to work with fresh electrolytes.
- Li_2MnO_3 activation plateau: no strong impact on O_2 or CO_2 evolution with addition of TMSPx.

Acknowledgement

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References

[1]. Guéguen et al., J. Electrochem Soc., 163, A1095 (2016)

[2]. Han et al., ACS Appl. Mater. Interfaces, 7, 8319 (2015)

[3]. Hong and Choi et al., J. Power Sources, 302, 23 (2016)