

Thermal Degradation Processes of Fluoroethylene Carbonate-based Electrolytes

Simone L. Holzmann¹, Leon Schmidt¹, David Schäfer², Elisabeth Eiche³, Marcus Rohnke², Ulrike Krewer¹

¹Institute for Applied Materials – Electrochemical Technologies, Karlsruhe Institute of Technology, Germany

²Institute of Physical Chemistry and Center of Material Research, Justus Liebig University Giessen, Germany

³Institute for Applied Geoscience, Karlsruhe Institute of Technology, Germany

Motivation

- Ethylene Carbonate has good SEI forming capabilities. However it is one of the least oxidation-resistant carbonates.
- High-voltage batteries electrolyte approach: Combining a linear carbonate as the main-solvent and adding a different SEI-forming co-solvent (e.g. Fluoroethylene Carbonate (FEC)).

Temperature resilient
(LiF-rich) SEI

How does the cell react
to thermal abuse?

Thermal instability of
FEC causes HF release

Experimental approach

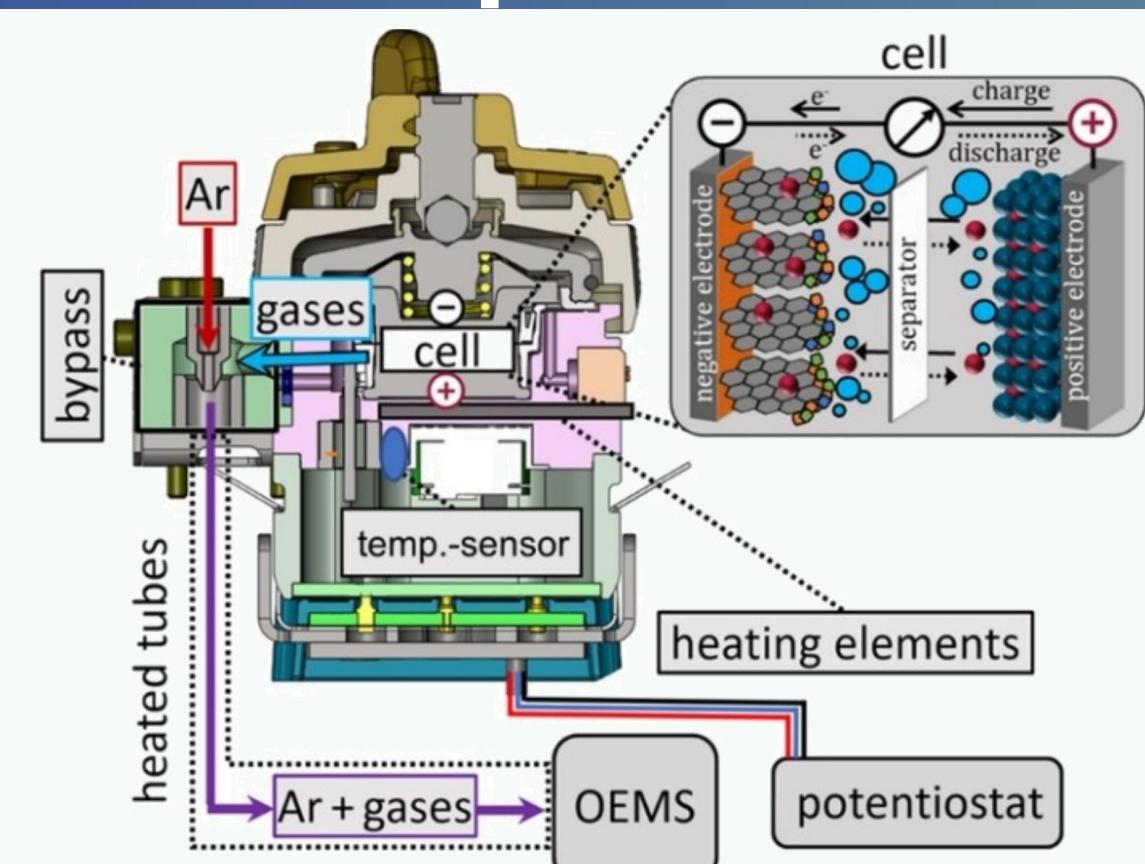
- Comparison of: 1 M LiPF₆ with DMC:FEC or DMC:EC using the mass ratios (90:10).
 - Cell components: Graphite|PTFE|NMC622.
 - Full cell measurements: Experimental cells in coin cell format.

Cells that only
underwent formation (F)

Comparison

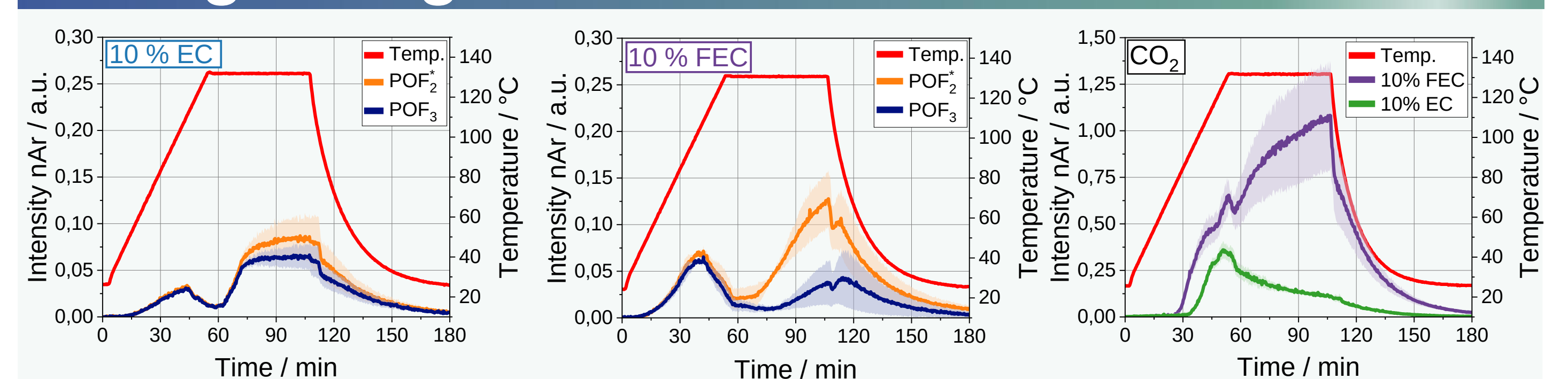
Cells that underwent
formation and subsequent
heating up to 132 °C (ΔT)

High-Temperature Online-Electrochemical Mass Spectrometry (HT-OEMS)

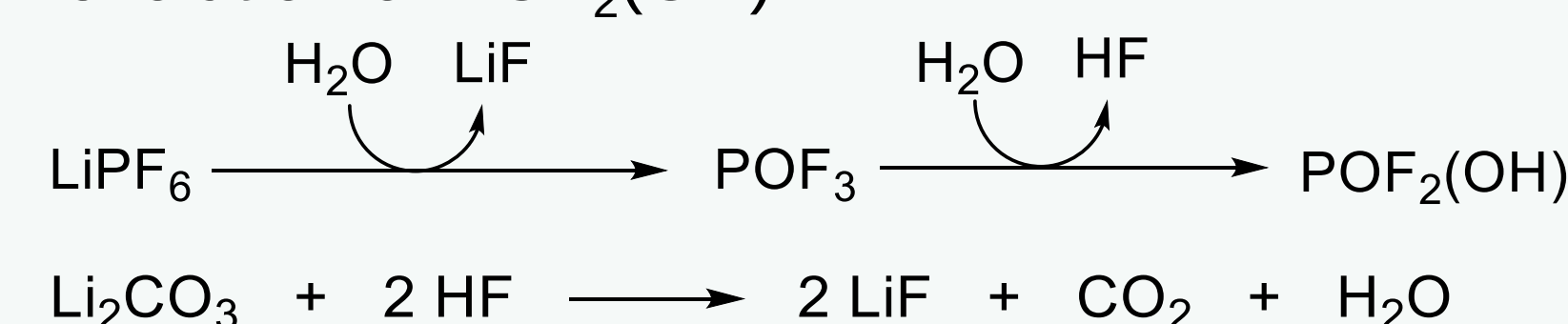


- In-situ tracking of the temperature-dependent gas evolution during thermal abuse up to 132 °C.^[1, 2]
- Deeper understanding of the degradation processes happening at high temperatures.

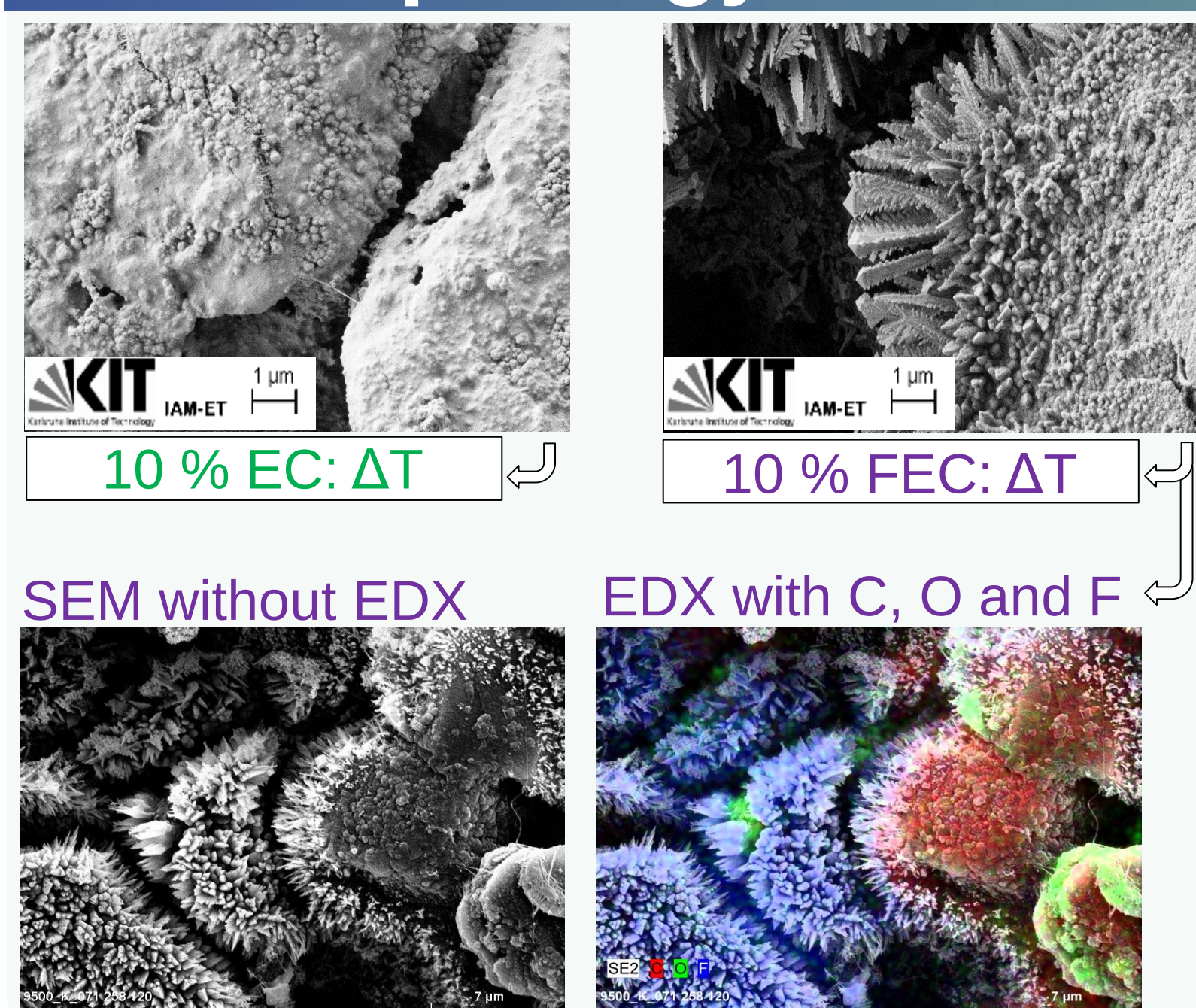
Cell gassing – HT-OEMS



- 10 % FEC shows continuously increasing CO₂ evolution during thermal abuse indicating a self-accelerating reactions, likely originating from SEI degradation.
- 10 % FEC shows evolution of a POF₂* species during the holding time due to evolution of POF₂(OH).

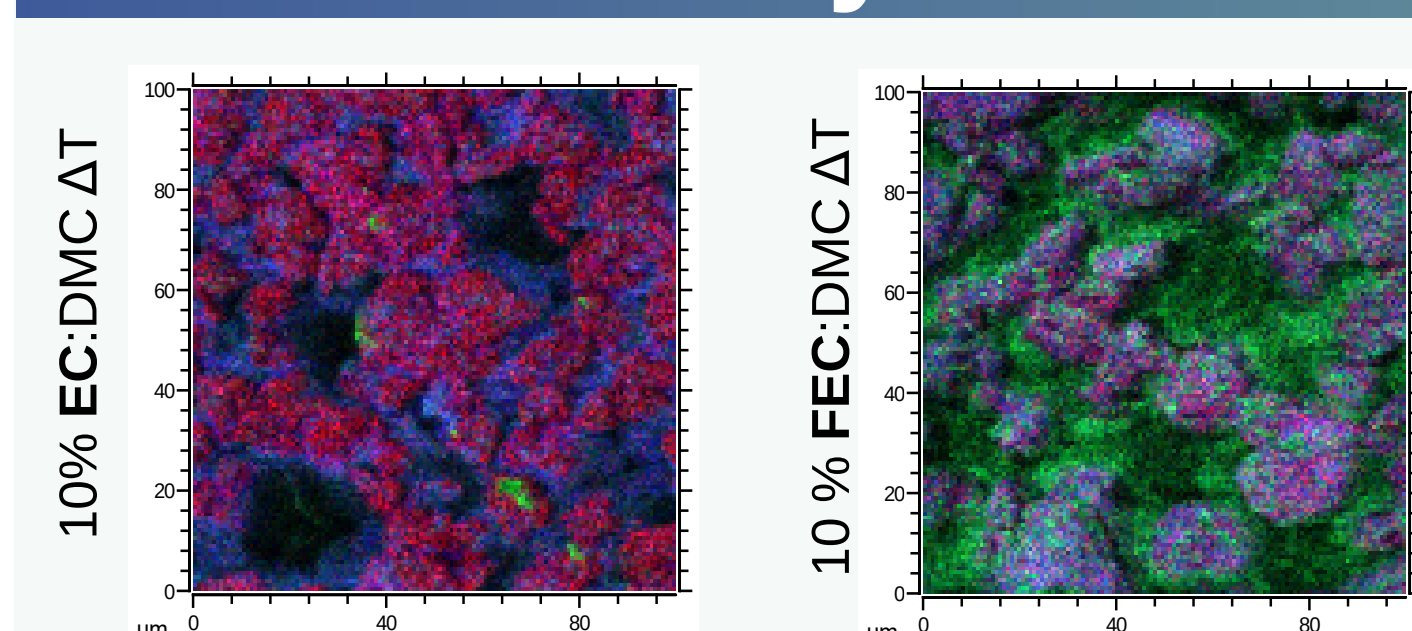


SEI morphology – SEM and EDX



- After thermal abuse: FEC containing cells show dendrite growth and 10 % EC shows polymerization.
- Dendrites appear only within distinct interparticle voids. → Significant heterogeneity
- EDX indicates that the dendrites are a fluoride-rich species.
- Emerging of dendrites due to conducting salt degradation e.g. LiF or Li_xPF_yO_z.

SEI chemistry - ToF-SIMS



- 10 % EC shows strong C₂H⁺ signals indicating a thinner SEI.
- 10 % FEC show strong PO₂F₂⁻ signal localized in the interparticle voids.

- Both electrolytes show homogeneously distributed LiF₂⁻ signals and for 10 % FEC the LiF₂⁻ signal intensity does not increase significantly after thermal abuse.
 - Dendrites consist of POF₂(OLi) and originate therefore from conducting salt degradation.

References: [1] L. Bläubaum, U. Krewer et al., *Batter. Supercaps*, **2024**, 7, e202300534.
[2] L. Schmidt, U. Krewer et al., *Chem. Sci.*, **2025**, 16, 5118 – 5128.
[3] K. Kim, *Electrochimica Acta*, **2017**, 225, 358 – 368.

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Acknowledgements:

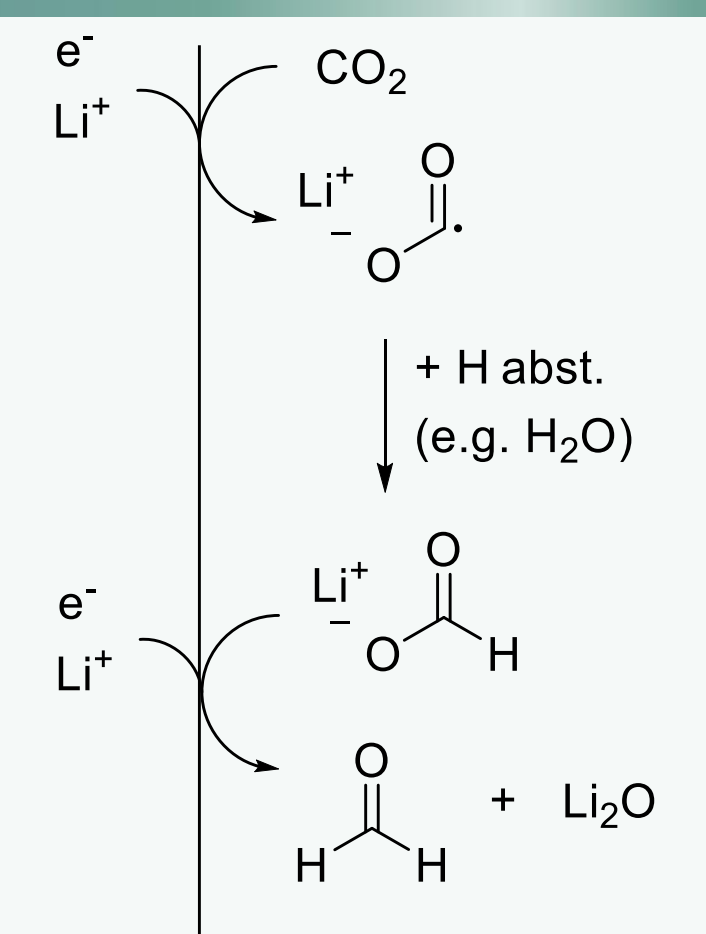
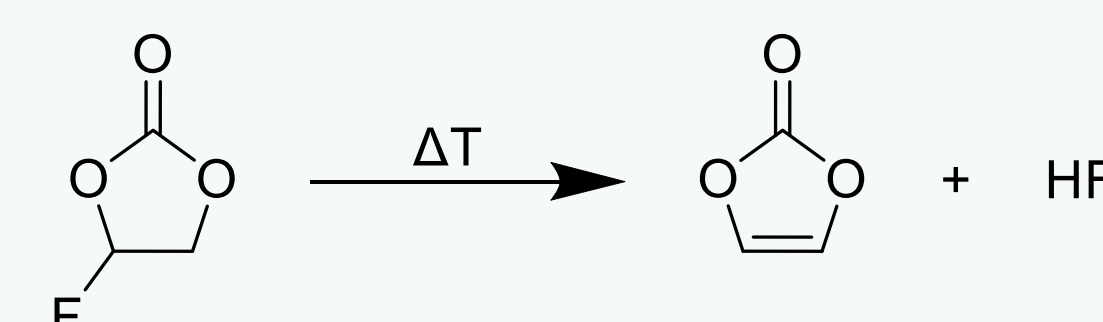
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Contact:

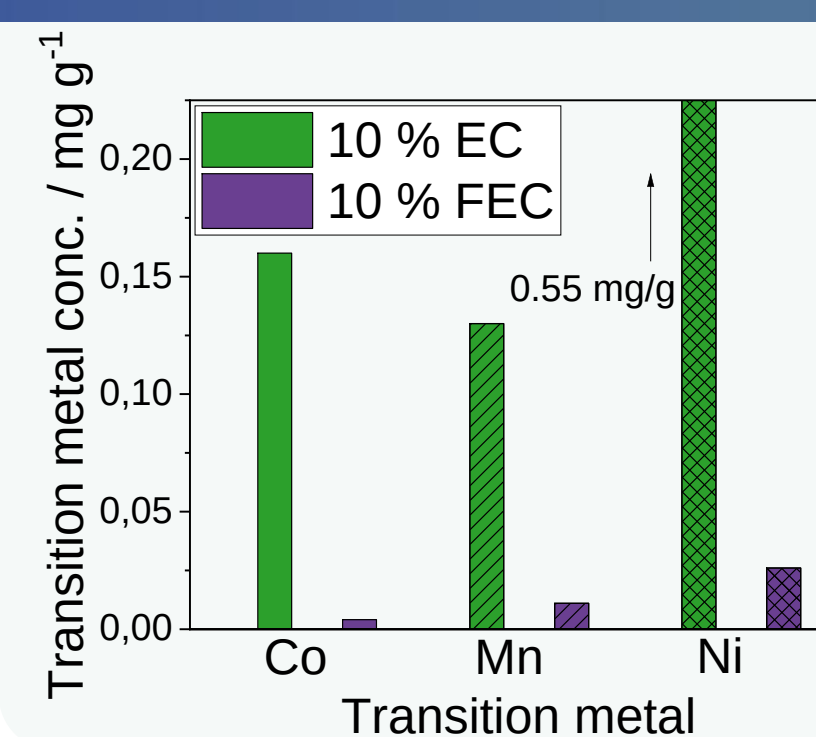


Soluble degradation products – NMR

- FEC-based electrolyte shows formation of formaldehyde.
- ¹⁹F-NMR of the FEC-based electrolytes exhibits signals corresponding to POF₂(OH) / - (OLi) and unreacted HF.
- Detection of Vinyl Carbonate (VC) using ¹H NMR indicating the formation of HF.



Transition metal dissolution – ICP-OES



- Acids like HF may cause transition metal dissolution.^[3]
- 10 % EC cells show significantly greater transition metal precipitation on the graphite electrode than the 10 % FEC cells.
 - 10 % EC cannot protect the cathode against HF attack.

Conclusion

- Decomposing of the FEC-based electrolyte at elevated temperatures generates toxic HF and POF₂(OH).
 - Strong CO₂ evolution indicates severe SEI breakdown.
 - Strong cell gassing may lead to cell rupture.
- FEC seems to form more protective interfaces after thermal abuse compared to EC.
 - Oxidation reactions on the cathode are often generate heat and may therefore increase cell self-heating.
- Thermal degradation behavior of cells differs significantly when substituting EC with FEC as the main SEI-forming co-solvent.
 - New challenges for mitigating thermal runaway.