

Online Electrochemical Mass Spectrometry for Rechargeable Batteries (IBAp-0225)

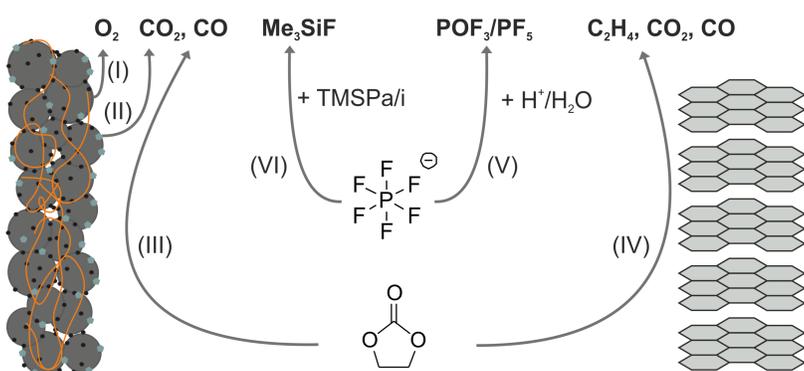
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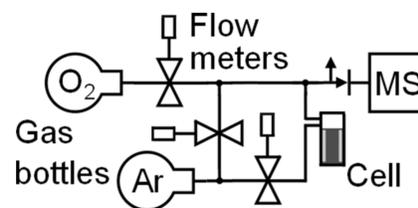
Sources for gas release in LIBs



| | |
|---|--|
| I. Surface reconstruction: | O ₂ |
| II. Surface impurities (e.g. Li ₂ CO ₃): | CO ₂ |
| III. Electrolyte oxidation: | CO ₂ , CO |
| IV. Electrolyte reduction/SEI formation: | CO ₂ , C ₂ H ₄ , CO, H ₂ |
| V. Electrolyte hydrolysis: | POF ₃ /PF ₅ , CO ₂ |
| VI. HF scavenging: | Me ₃ SiF |

Studying Gas Release in LIBs

- *In situ* mass spectrometry (MS) was established in the 1980s^[1]
- Previous setup at PSI was a constant flow setup^[2,3]

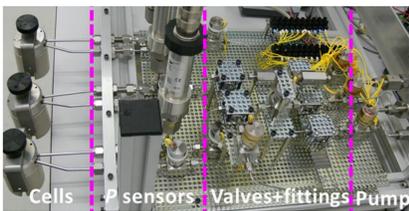


Working principle:

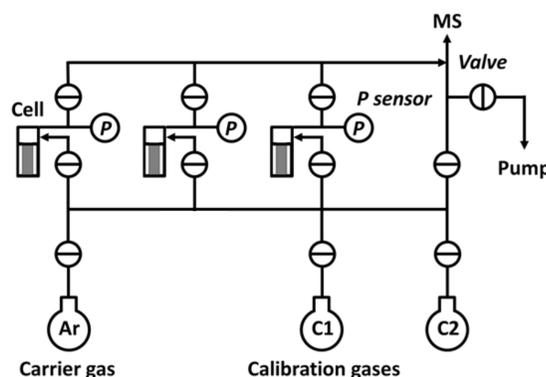
- Continuous Ar flow transports gases to the MS
- Gases reach the MS after ~30s
- Calibration by dilution of calibration gases

Disadvantages:

- Only one cell per measurement
- Constant electrolyte evaporation
 - high electrolyte volume
 - risk of capillary clogging
- Relatively low sensitivity (100 ppm background)



Current OEMS setup at PSI^[3]



Advantages:

- + Several cells in parallel possible
- + Higher sensitivity (1 ppm O₂ background)
- + Setup can be placed in climate chamber
- + Direct sampling of calibration gases for fast calibration

Disadvantages:

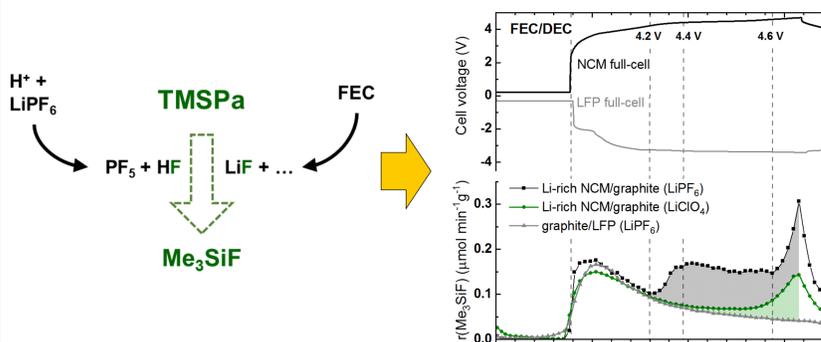
- Decreased time resolution (one measurement / 15 min)
- Electrolyte evaporation still significant for t > 48h

Working principle:

- Valves for carrier gas and cell open for about 10s to transport gas from cell to MS
- Step is repeated for the other attached cells
- Computer controlled system with automatic data processing

Method Development: Additives as Chemical Probe^[4]

Scope of study: Application of TMSPa as chemical probe for F⁻ formation in LIBs

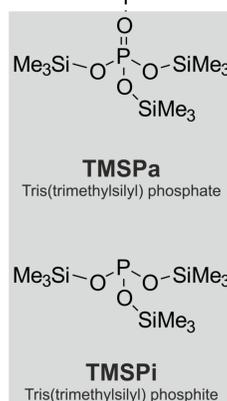


Observations:

- TMSPa reacts with *in situ* formed inorganic fluorides such as HF, LiF
- Different contributions can be identified:
 - LiF during SEI formation (FEC reduction)
 - HF from LiPF₆ (due to proton formation)
 - Further contributions from PVDF binder

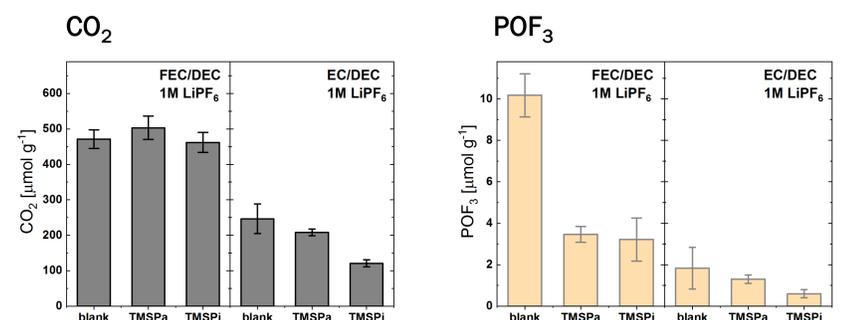
Conclusions:

- Formation of reactive species can be monitored *in situ* by OEMS using suitable additives as chemical probes



Screening: Additives and Electrolytes for Li-rich NCM^[5]

Scope of study: Investigation of gas suppression and action mechanisms for TMSPa/i additives in Li-rich/graphite cells



Observations:

- Suppression of POF₃ by TMSPi/a due to HF scavenging
- Suppression of CO₂ formation only by TMPSi in EC based electrolyte

Conclusions:

- TMSPi/a lead to decreased electrolyte acidification (especially with FEC)
- TMSPi has a further action mechanism in EC (analysis of CO₂ gas evolution profile indicates rather chemical scavenging than SPI formation).

Summary

- The new setup allows parallel measurement of several cells with improved sensitivity
- The improved sensitivity allows to apply the electrolyte additive TMSPa as chemical probe to study *in situ* the formation of HF/LiF in LIBs
- The multi-cell setup allows to study additive operation mechanisms and to show that TMSPi/a act mainly as chemical scavengers

References

[1] G. Eggert, J. Heitbaum, *Electrochim. Acta*, 31 (1986) 1443-14487 [2] M. Holzapfel, A. Würsig, W. Scheifele, J. Vetter, P. Novák, *J. Power Sources*, 174 (2007) 1156-1160. [3] M. He, *Elucidating Interface Reactions in Li-Ion Batteries and Supercapacitors by In Situ Gas Analysis*. ETH Zürich, 2016. [4] C. Bolli, A. Guéguen, M. A. Mendez, E. J. Berg, *Chem. Mater.* DOI: 10.1021/acs.chemmater.8b03810 [5] C. Bolli, A. Guéguen, M. A. Mendez, E. J. Berg, *in preparation*.

Acknowledgement

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