Battery gas modeling

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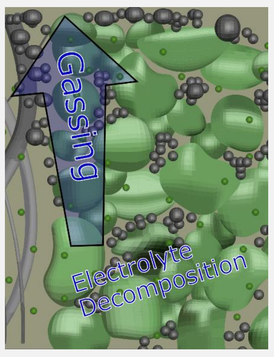
Motivation

- Electrolyte systems in LIBs are a significant ageing and safety factor
  - ➢ Often not fully considered, hardly taken into account in modeling
- Electrolyte reacts with::
  - ➢ Active materials, additives, decomposition products
- Leads to gas generation, initial SEI growth thereof, additional reaction products



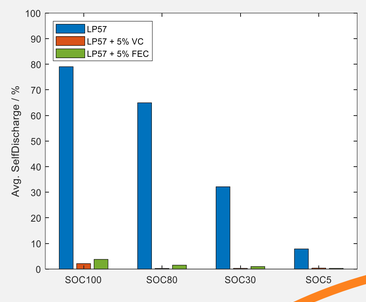
Approach

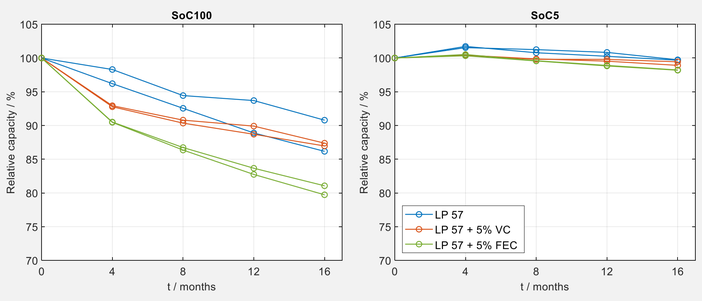
- Consideration of electrolyte aging processes in modeling over relevant service life:
  - ➢ Implementation of SEI formation and gas generation
  - ➢ Thermodynamic modeling of the electrolyte system
- Investigation of formation and aging over the lifetime by:
  - ➢ Electrochemical and thermal cell characterization
  - ➢ Analysis, modeling of SEI formation and gas generation with respect to the used additives
- Consideration of safety-critical scenarios

Results

Aging

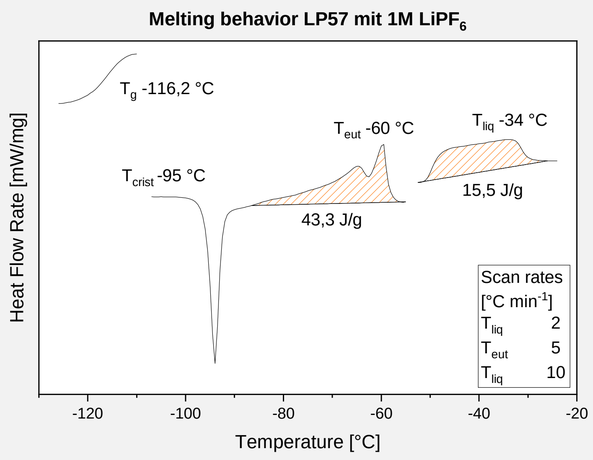
Comparison of calendar aging for different additives under OCV – and open circuit conditions: high self-discharge of MEET cells without additives due to PET tape and corresponding shuttle mechanism, lower self-discharge for LiFun cells [1].





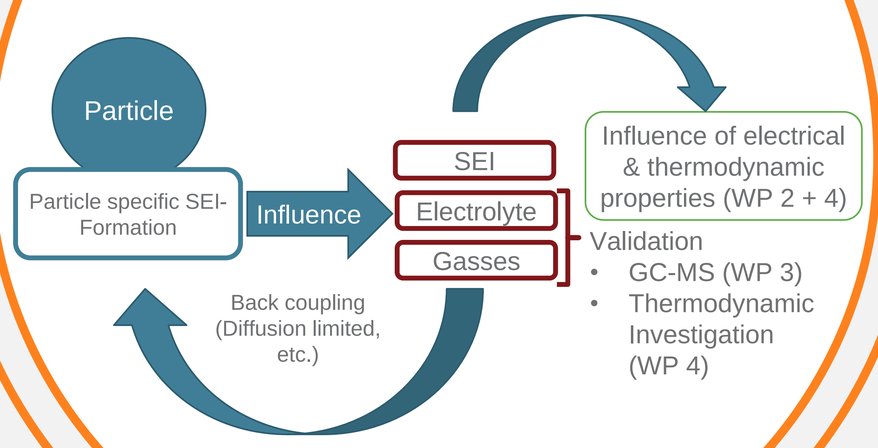
Thermodynamic Modeling

Investigation of the melting behavior of LP57 with 1M $LiPF_6$
Determination of the heat capacity of EC and EMC and consideration in thermodynamic modeling [4].

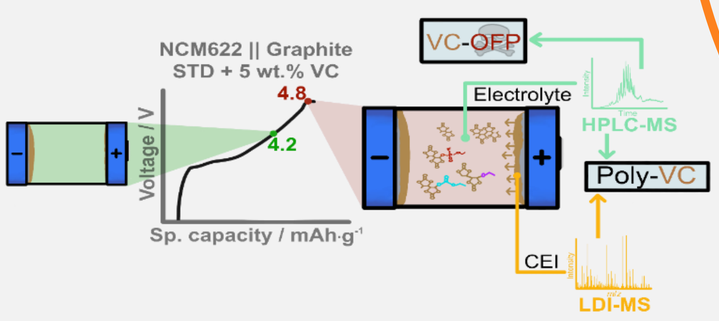


Entire model

Integration of gas generation and electrolyte aging into physico-chemical battery model



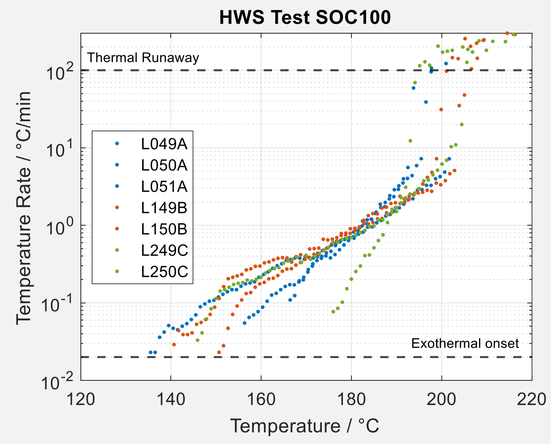
Electrolyte analysis



Oxidative decomposition of VC leads to toxic decomposition products and initiates further error cascades such as crosstalk phenomena
➔ not suitable for Li/Mn-rich cathodes at voltages beyond 4,7 V [2,3]

Safety

Investigation of the influence of electrolytes on safety in various abuse scenarios, using accelerating rate calorimetry (ARC).



Comparison of unaged LiFun cells with different additives in the HWS test in the ARC. Comparable onset and maximum temperatures of the cells.

References

[1] K. Geuder, P. Finster, S. Klick, K.M. Graff, S. Nowak, H. J. Seifert, C. Ziebert, Influence of Vinylene Carbonate and Fluoroethylene Carbonate on Open Circuit and Floating SoC Calendar Aging of Lithium-ion Batteries, TBS to Batteries 2024
[2] Kubot, M, et al., Lithium Difluorophosphate: Boon for High Voltage Li Ion Batteries and a Bane for high Thermal Stability/low Toxicity: Towards Synergistic Dual-Additives to Circumvent this Dilemma, ChemSusChem. DOI: 10.1002/cssc.202202189.
[3] M. Kubot, et int., S. Nowak, Organofluorophosphates as Oxidative Degradation Products in High-Voltage Lithium Ion Batteries with NMC or LNMO Cathodes, J. Electrochem. Soc. 169 (2022) 110534
[4] P. Finster, J. Jung, H. J. Seifert, C. Ziebert, Heat capacity of ethylene carbonate and ethyl methyl carbonate for the liquid phase at elevated temperatures measured by differential scanning calorimetry, TBS 2024

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