Analysis of Electrode Interphases in Lithium Ion Batteries using Laser Desorption/Ionization-Mass Spectrometry

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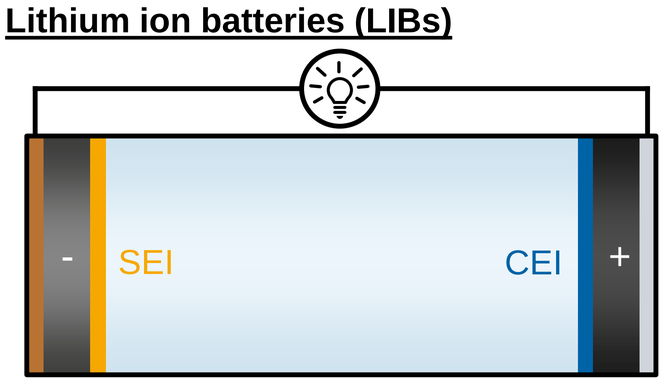
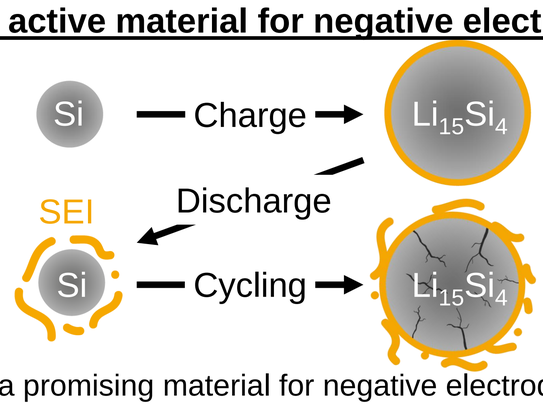
Background

Lithium ion batteries (LIBs)



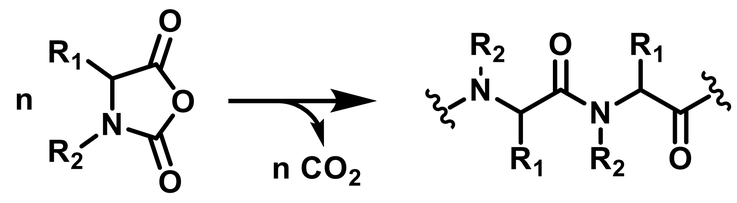
- LIB electrolyte is degraded during charging
- Reduction products form the solid electrolyte interphase (SEI) on the negative electrode
- SEI prevents further electrolyte degradation
- A stable SEI is important for battery lifetime

Silicon as active material for negative electrodes



- Silicon is a promising material for negative electrodes
- Specific capacity is nearly ten times higher than with graphite[1]
- Severe volume change upon (de-)lithiation (up to 300%)[1]
- Continuous (re-)formation of SEI and consumption of active Li[1]
- More flexible SEI is required to withstand mechanic stress

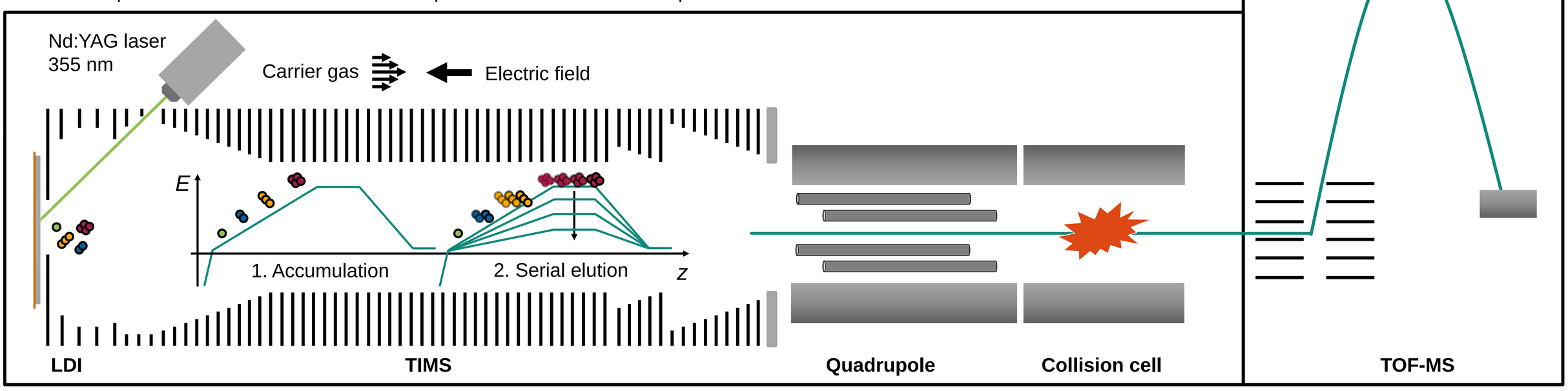
Film-forming electrolyte additives



- Electrolyte additives are used to tailor SEI properties
- *N*-Carboxyanhydrides (*N*-CAs) enhance battery lifetime[2]
- Polymerization after electrochemical reduction proposed[2]
- Polymers incorporated in the SEI may increase flexibility[2]
- No suitable detection method for these polymers available

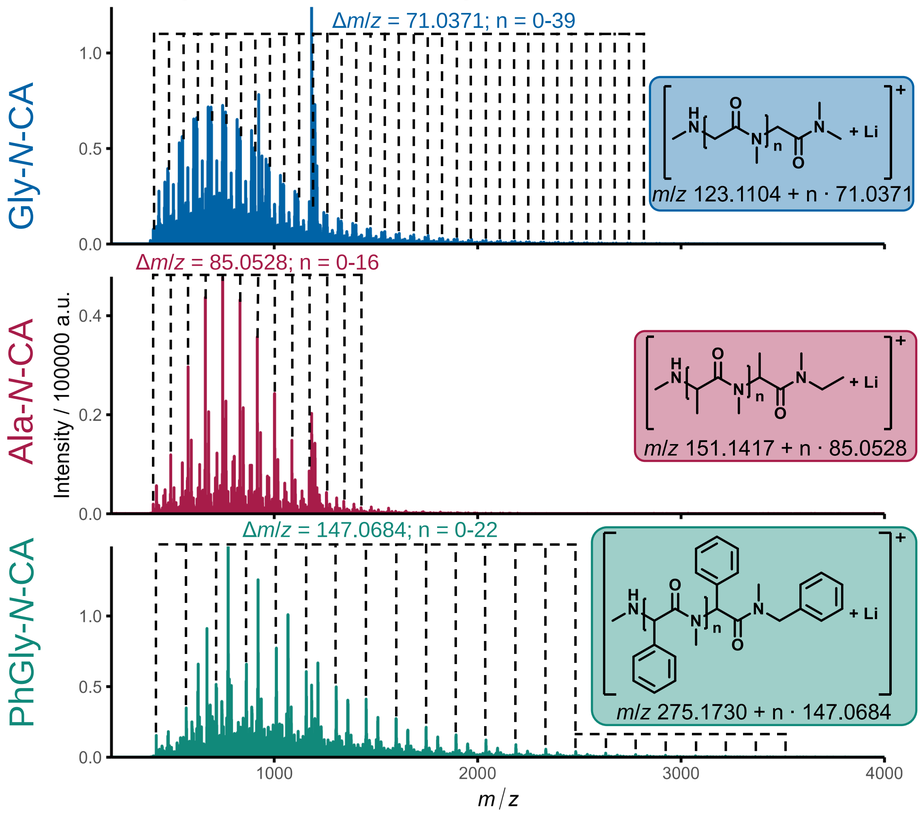
Instrumentation

- A timsTOF fleX mass spectrometer from Bruker Daltonics (Bremen, Germany) was used for all analyses
- Laser desorption/ionization was used in combination with trapped ion mobility spectrometry and time-of-flight mass spectrometry in positive ion mode (LDI(+)-TIMS-TOF-MS)
- The samples were introduced into the mass spectrometer under Ar-atmosphere to avoid contact to ambient air



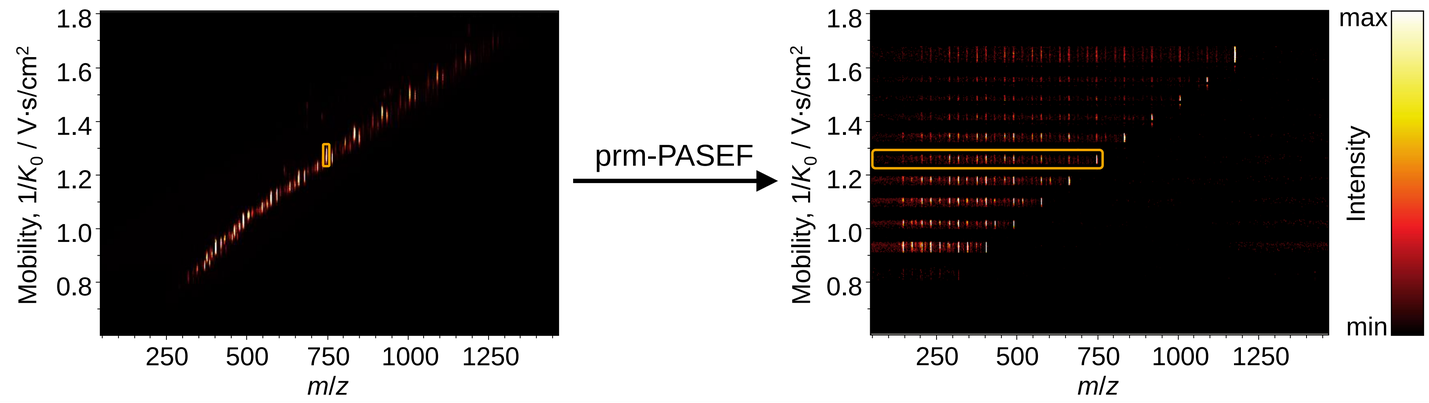
Results

LDI-MS analysis of electrodes cycled with different *N*-CAs:

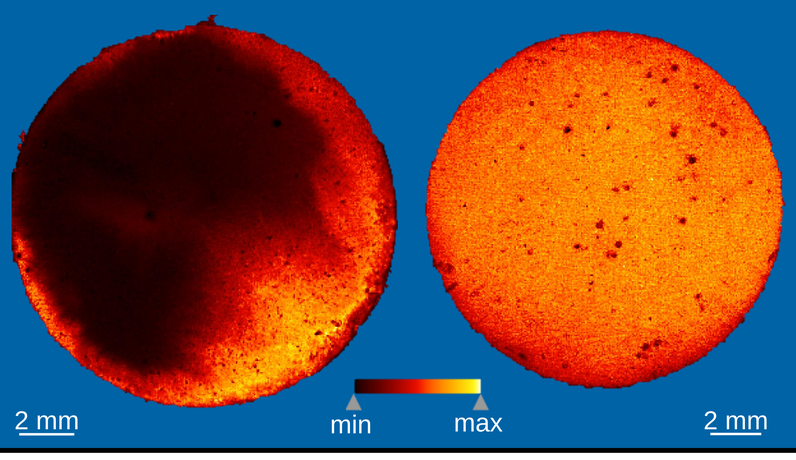


- Detection of oligomers derived from *N*-CAs after cycling
- Substituents influence the size of the formed oligomers
- LDI-MS can support a more targeted additive design

Fast structural elucidation by simultaneous fragmentation of oligomers using prm-PASEF:



Mass spectrometry imaging (MSI) visualizes lateral distribution on the electrode surface:



- Spot size: 50 µm
- LDI-MSI visualizes the distribution of SEI components on electrode surfaces
- Substituents of *N*-CA additives influence the lateral distribution patterns of the resulting oligomers on electrodes
- PhGly-*N*-CA leads to more homogenous SEI formation than Ala-*N*-CA
- Homogeneity of the SEI layer influences battery performance and lifetime

Conclusion

- LDI-MS is suitable for the detection and characterization of SEI components in LIBs derived from electrolyte additives
- Obtained information is complementary to established methods like XPS, SIMS, FTIR and Raman Spectroscopy
- Upon reduction, *N*-CA-based electrolyte additives form oligomers which increase the flexibility of the SEI
- TIMS separation and prm-PASEF fragmentation enhance structural elucidation and speed up the data acquisition
- LDI-MSI analysis reveals the lateral distribution of SEI components on electrode surfaces
- The acquired data supports a more targeted approach on the design of electrolyte additives

References: [1]A. Franco Gonzalez, N. H. Yang, R. S. Liu, *J. Phys. Chem. C*, **2017**, *121*, 27775–27787. [2]J.-P. Schmiegel, R. Nölle, J. Henschel, L. Quach, S. Nowak, M. Winter, F. Glorius, T. Placke, *Cell Reports Phys. Sci.* **2021**, *2*, 100327.

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