



18. GDS Anwendertreffen

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Aging mechanisms in Lithium ion batteries revealed by GD-OES depth profiling

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Why Lithium ion batteries?



Lifetime

Price



Safety

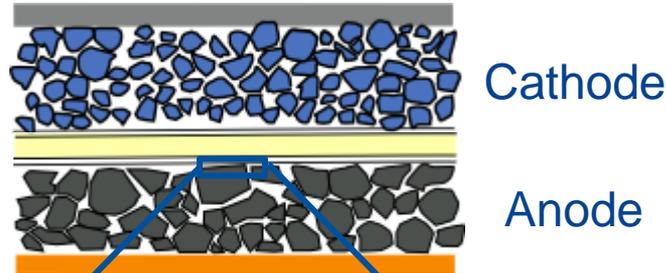
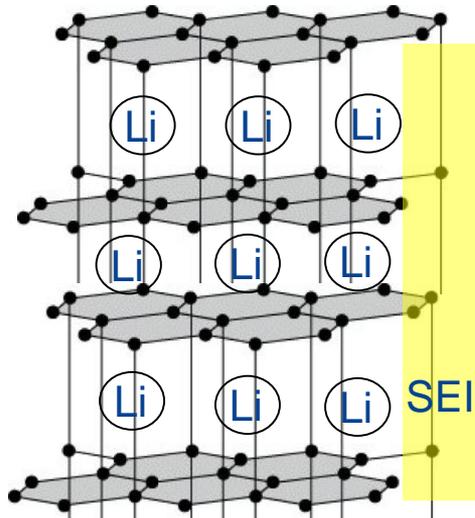
Energy density



Working principal and aging mechanism

Ambient charging conditions

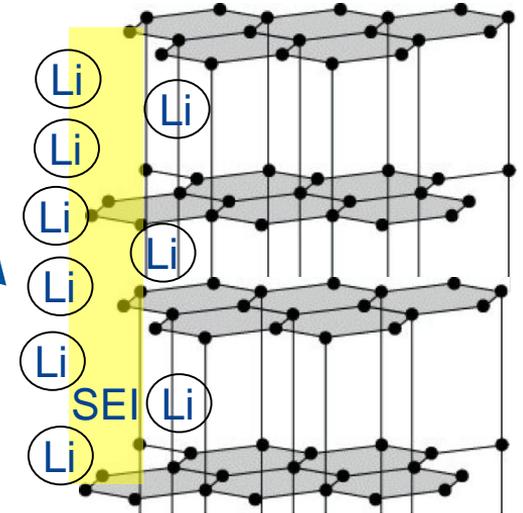
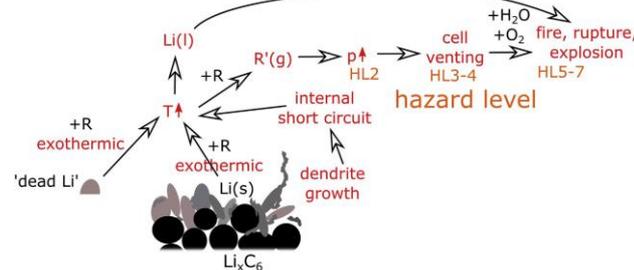
→ Low currents / room temp.



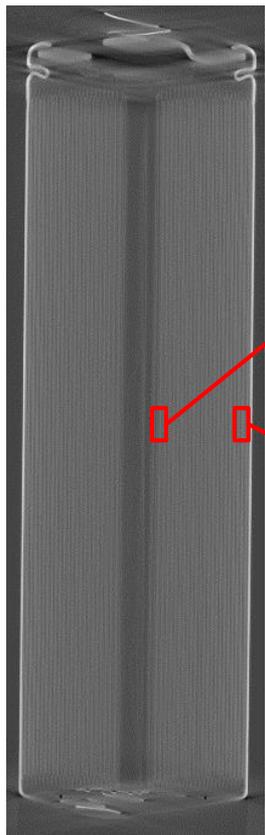
Challenging charging conditions

→ high currents / low temp.

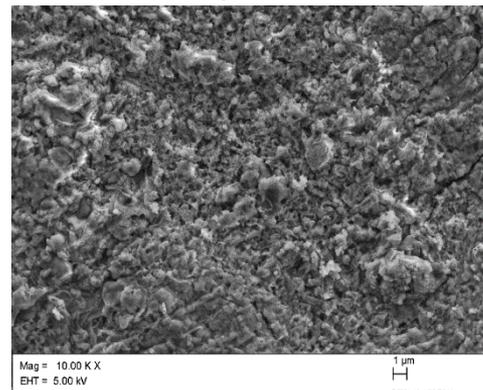
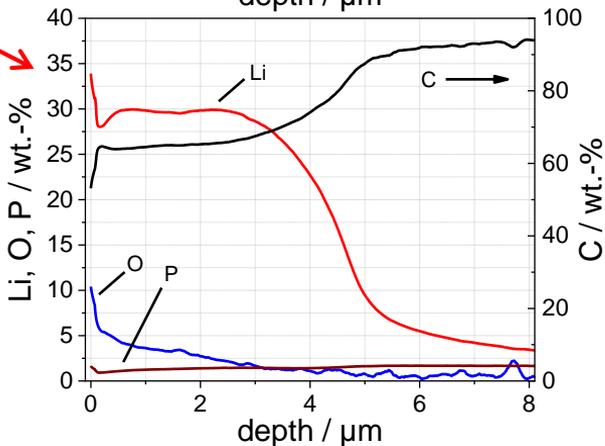
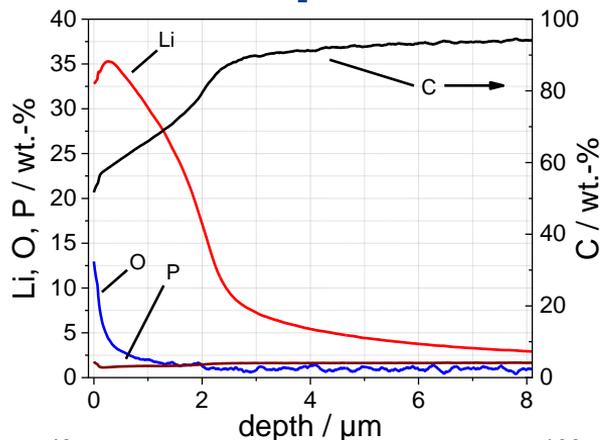
Mechanism related to Li deposition



Li metal deposition – Spatially resolved

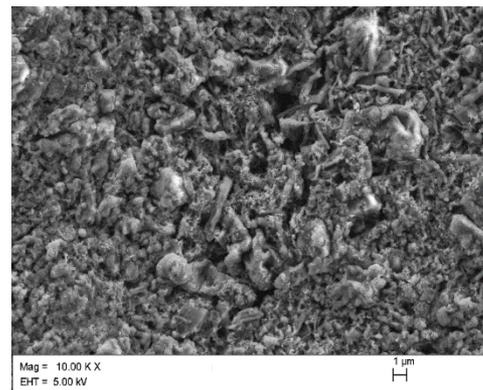


CT



SEM

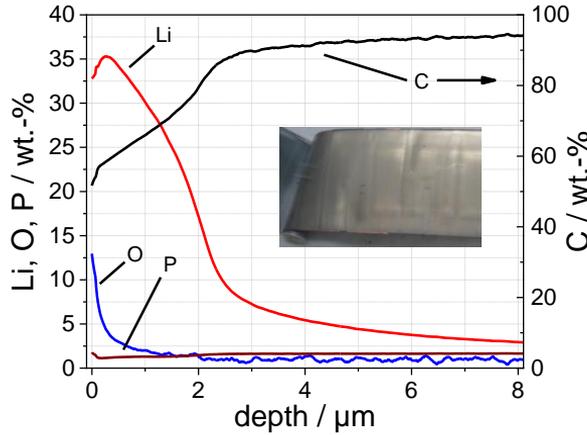
- inhomogeneous and small dendritic structures visible



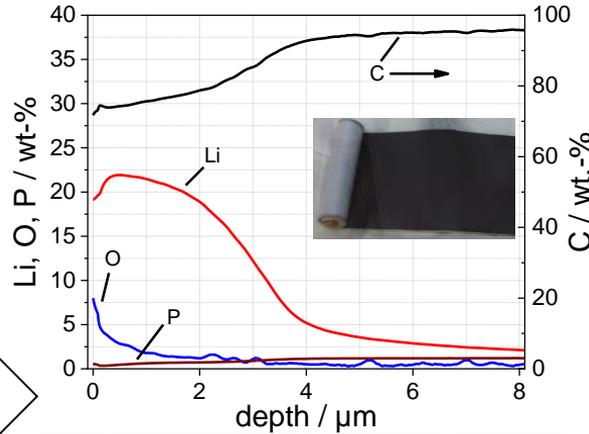
- dominant dendritic structure
→ Li metal deposition

Li metal deposition – Effect of resting time

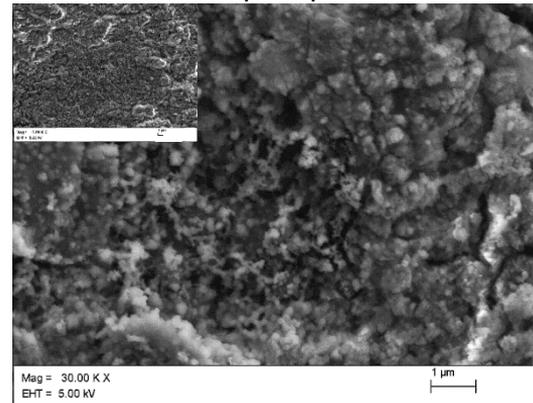
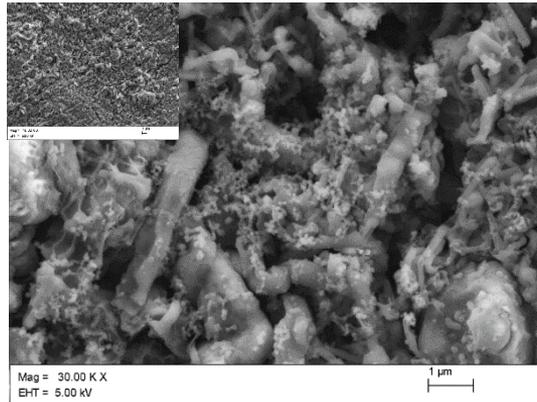
GD-OES



8 h
rest



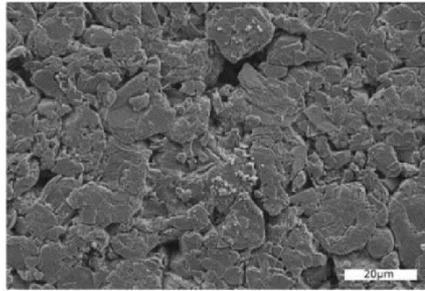
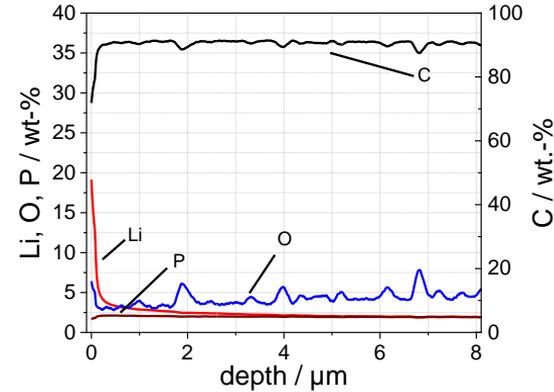
SEM



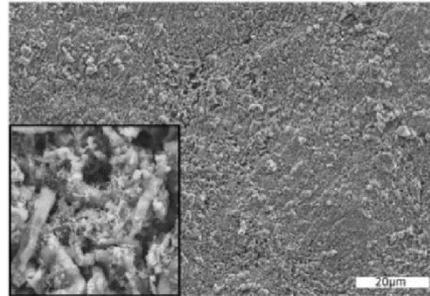
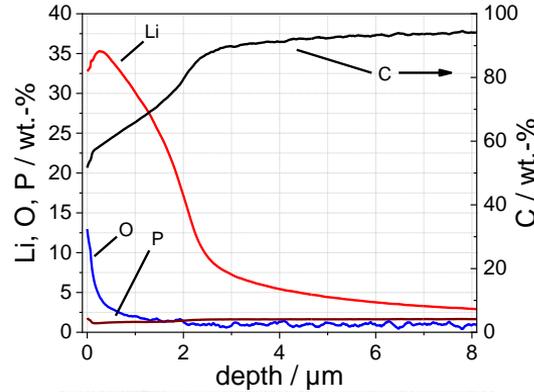
- after cell operation:
→ dominant Li metal deposition and high surface concentration of Li

- after resting broad and flat Li distribution
→ GD-OES reveals reintercalation of Li
→ No dendritic structure visible

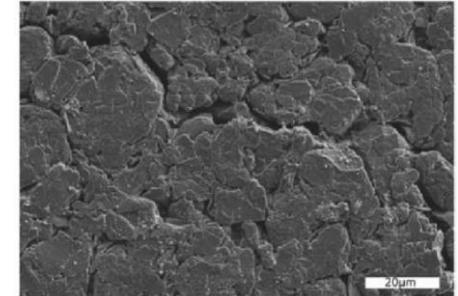
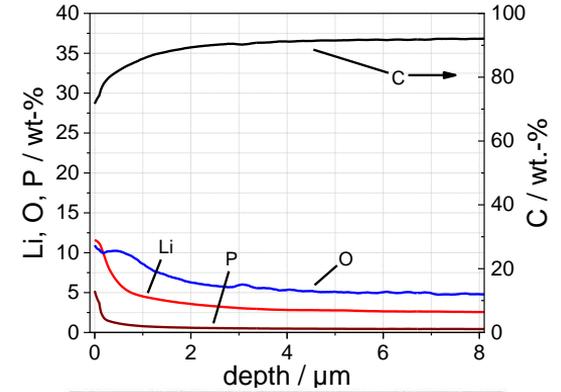
Aging mechanism – Effect of operating temperature



Fresh cell: initial SEI

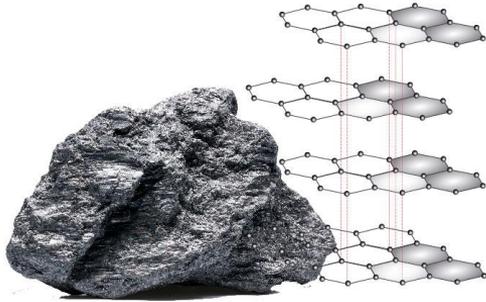


Cycling at 0 °C: Li metal covers anode Surface

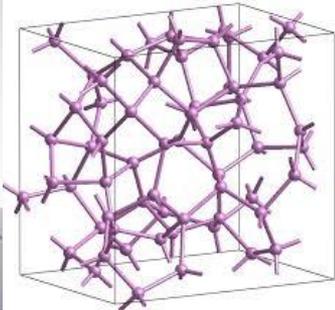


Cycling at 45 °C: Unceasing film formation (e.g. Li_2O , Li_2CO_3)

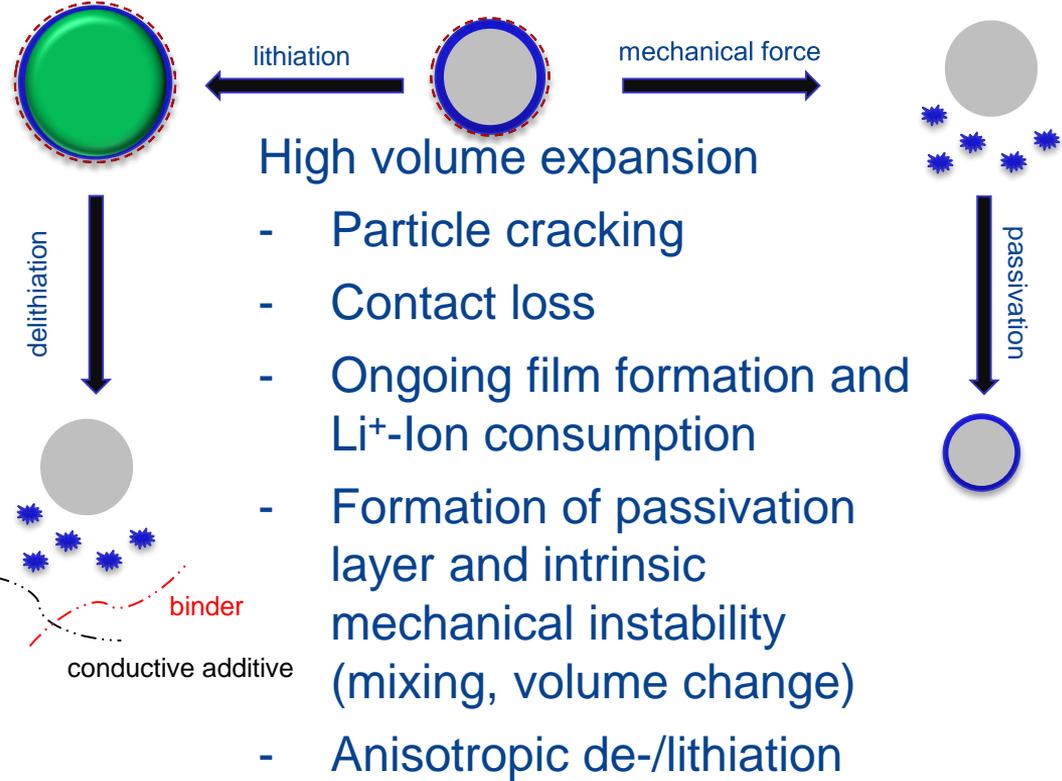
Increasing demand for energy



Graphite, LiC_6 : 372 mAh g^{-1}



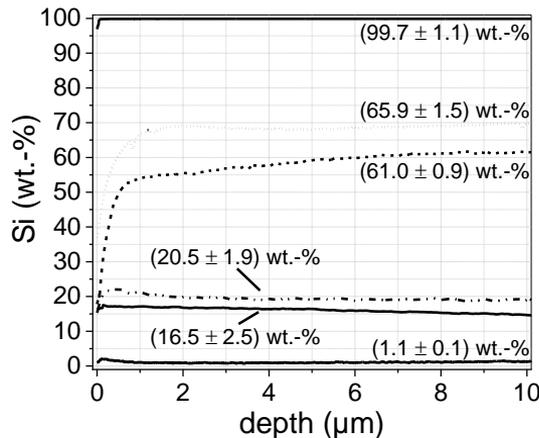
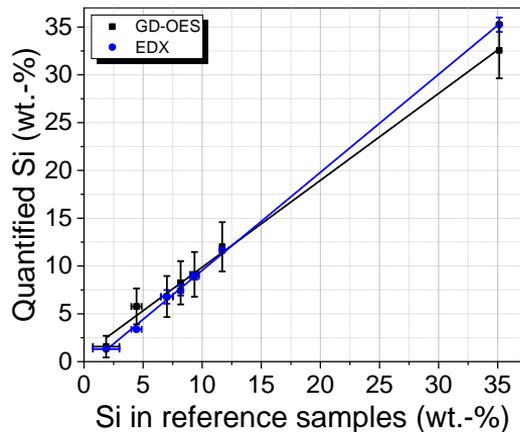
Silicon, $\text{Li}_{15}\text{Si}_4$: 3579 mAh g^{-1}



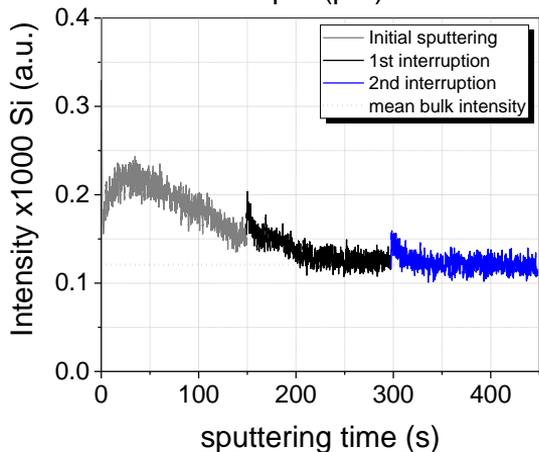
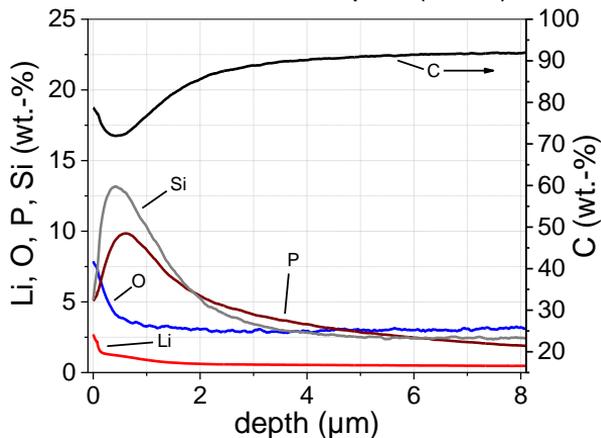
[3] M. N. Obrovac, L. Christensen, D. B. Le, J. R. Dahn, *J. Electrochem. Soc.* **2007**, *154*, A849. [4] M. N. Obrovac, V. L. Chevrier, *Chem. Rev.* **2014**, *114*, 11444–11502.

[5] P. Limthongkul, Y.-I. Jang, N. J. Dudney, Y.-M. Chiang, *Acta Mater.* **2003**, *51*, 1103–1113. [6] N. Delpuech, N. Dupre, P. Moreau, J.-S. Bridel, J. Gaubicher, B. Lestriez, D. Guyomard, *ChemSusChem* **2016**, *9*, 841–84

Si in LIB anodes – GD-OES approach

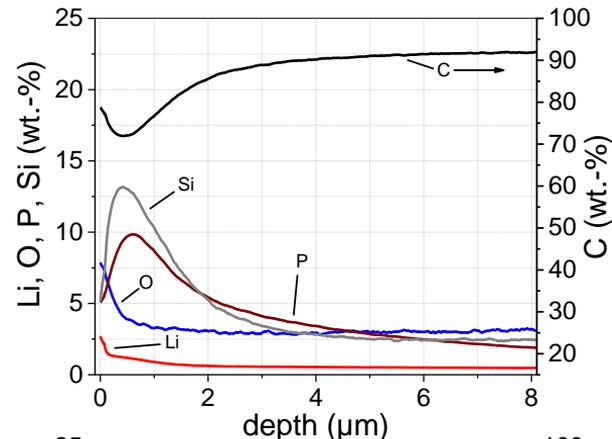


- covering 0-100 wt.-% Si to analyse graphite and Si dominant composite electrodes

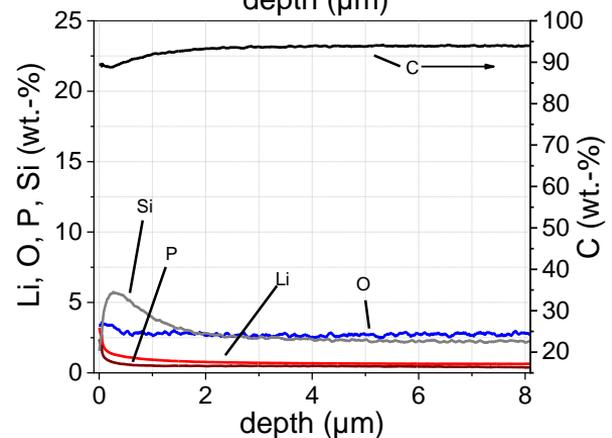


- unexpected Si distribution observed

Si related aging mechanism – revealed by GD-EOS



3x 60s dip washed
with DMC

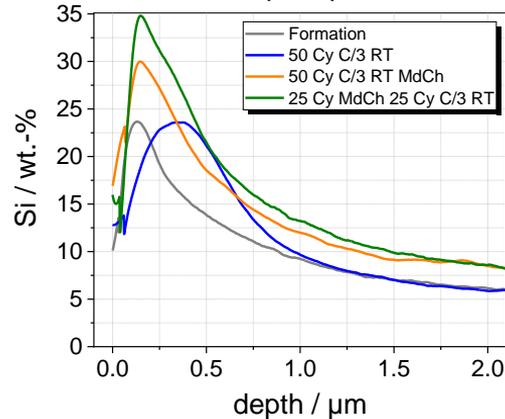
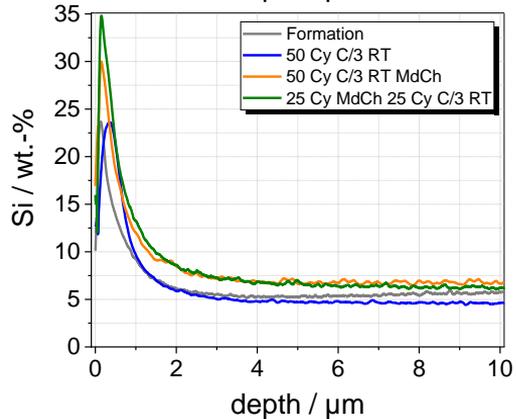
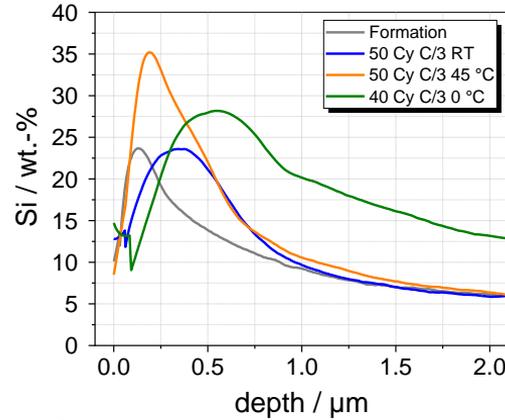
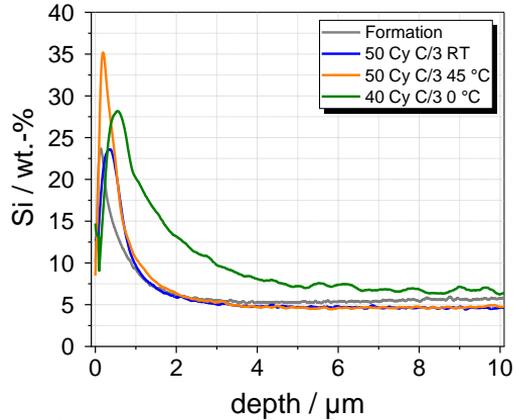


- Si detectable in DMC with ICP-OES



→ Side reaction of active material
with electrolyte, consumes Li.
Additional film formation and
dissolution.

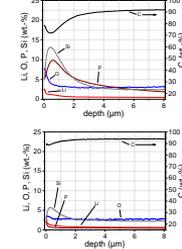
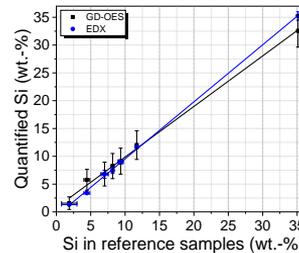
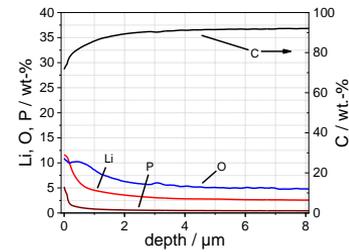
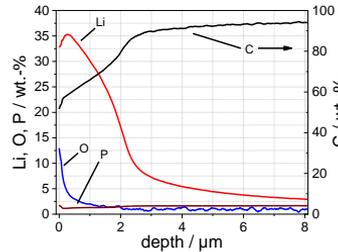
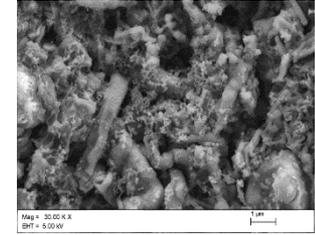
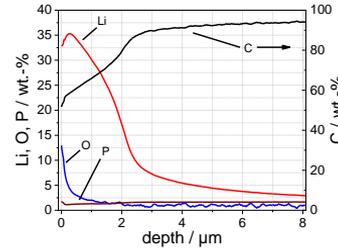
Si related aging mechanism – revealed by GD-EOS



- Si distribution depends on physical and electrochemical operation conditions
- 45 °C enhances film formation, containing Si-rich species
- 0 °C shifts the Si distribution to deeper levels of the electrode
- lower cut off potential increases Si species on surface
- Enhanced side reactions during discharge

Conclusions

- GDOES provides spatially resolved elemental distribution
 - Covering the plating behaviour over the jelly roll
- GDOES provides information about the aging mechanism regarding cell operation conditions
 - Differentiation between, e.g. Li metal deposition or electrolyte decomposition
- GDOES can be calibrated to novel battery materials revealing material specific aging mechanism
 - Film formation and dissolution on Si/C composite materials



electrode
washing

// Energy with a future

// Zentrum für Sonnenenergie- und Wasserstoff-
Forschung Baden-Württemberg (ZSW)

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Policy and Energy
Carriers, Central
Division Finance,
Human Resources
& Legal

Widderstal:
Solar Test Facility



Ulm:
Electrochemical Energy Technologies - Main Building & eLaB

ZSW:

Niloofar Ghanbari (now Bosch)

Thomas Waldmann

Michaela Memm

Michael Kasper

Peter Axmann

Margret Wohlfahrt-Mehrens

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