



Glow Discharge Mass Spectrometry in Lithium Ion Batteries – The Jack of All Trades for Analyzing Solid Battery Materials?

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Lifecycle of a Battery





Lithium Ion Battery – Basic Principles

- Standard Setup of LIB
- Materials:

Anode - Carbonaceous Materials (Graphite)
Cathode - Lithium Transition Metal Oxides (e.g. LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂, NCM622)
Electrolyte – Conducting Salt (Lithium

Hexafluorophosphate) in organic Carbonate Mixture







Aging Effects of LIBs



Vortmann-Westhoven, B. et al.; J. Power Sources 2017, 346, 63-70.

Motivation



- Elucidation of elemental distribution and (Li-)migration mechanisms
- Measurement of challenging sample matrices (especially Si/C anodes) and next generation materials





Lithium Migration Mechanisms Using Isotopic Labeling







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Ageing Experiments



- Comparison of ⁶Li-abundances indicate differences on the surface (≈0-5 min)
- Closer consideration of ^{6/7}Li intensities independently
 - First indications of an increased
 ⁷Li uptake after longer cycling

MÜNSTER



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Determination of the Lithium Distribution

- Agglomeration of ⁶Li on the first hundreds of nm after 1st formation step
- Effect is lowered after longer aging procedure
- Initial decomposition contact to the anod
- Trend is apparent the
- Almost instant mixing of the different isotopic species in all measured cell components
- Still, cycling experir numbers need to be
 - So far not pos
- Enriched NCM cathousured in first experiments

Only GD measurements show stronger differences of the isotopic fractions

Pristine

20 -



20

Pristine

10 Cycles

1st Formation

10 Cycles

1st Formation









Pre-Lithiation Analyses for Cand C/Si-Electrodes





Why Pre-Lithiation?







Comparison of Different Pre-Lithiation Techniques





Influence of Si Particle Size on Pre-Lithiation





a)

- All electrodes with same amount (20 wt.%) Si in active material
- All electrodes pre-lithiated for 10 min with direct contact method
- Pre-lithiation time has an impact on the homogeneity, depth-distribution and relative intensity of lithium









Conclusion

- ⁶Li-isotope labeled conducting salt showed accumulation of ⁶Li on the top surface of carbonaceous anode
 - insertion of electrolyte lithium into cathode host structure
- ⁶Li-isotope labeled conducting salt also confirmed exchange of lithium from the conducting salt with lithium in the cathode material
 - insights into formation of protective SEI layer
- Different influence factors for lithium homogeneity and accumulation of prelithiated carbonaceous and C/Si composite electrodes could be determined
- BUT, only elemental information can be gathered and no spatial information are accessible

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Outlook: Li-Metal – Proof of Principle



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- Major problems:
 - no possibility of inert sample transfer \rightarrow sputter-coating of Cu on surface (least reactivity and alloying)
 - Thermal stress, plasma ignition and sustaining stable conditions







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