Understanding aging mechanisms in Li-ion batteries with neutrons

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Poster summarises research resulting from collaboration of FRM II with VARTA, ZSW (Groups: M. Wohlfahrt-Mehrens, P. Axmann), TUM (Groups: H. Gasteiger, A. Jossen), Stanford (Z. Bao), HI-Münster (G. Brunklaus)

Relevance of neutrons for battery research

Unique properties of neutrons

- high penetration depth, but non-destructive so operando/*in situ* possible
- sensitive to light elements (eg. Li, H, C) & isotopically senstive
- sensitive to atomic structures and diffusive motions

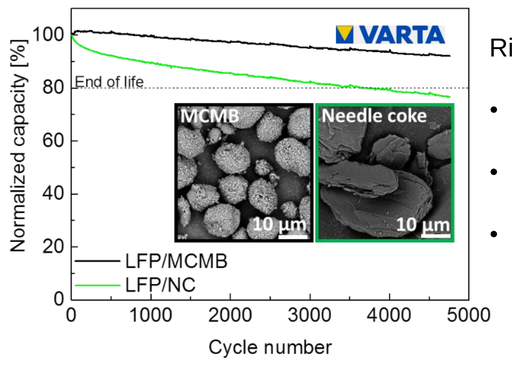
How to apply for neutron beamtime at FRM II ?

Data Evaluation group

- register yourself in the MLZ User office website
- submit a 2 page proposal and wait for approval
- after experiment, for support with data analysis, contact deva evaluation group (deva@mlz-garching.de)

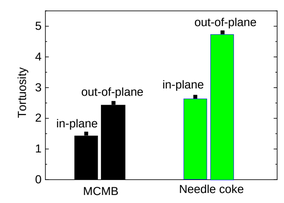
Improve lifetime with a modified anode morphology

Correlation between morphology and aging

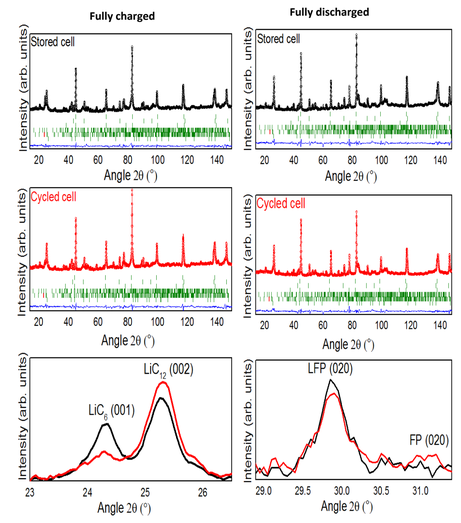


Rietveld analysis of neutron diffractograms

- no material degradation /active material loss
- sole reason for aging was **cyclable Li loss**
- rate dependent loss & calendric aging of NC-based cells



- Why cell with MCMB anode aged much slower than that with NC anode?

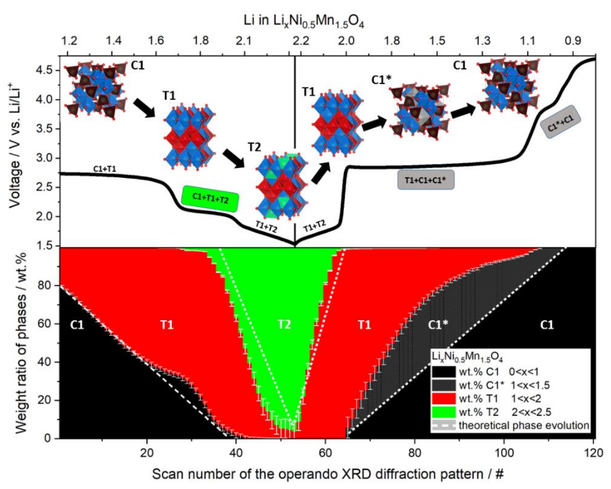


Neutron diffraction

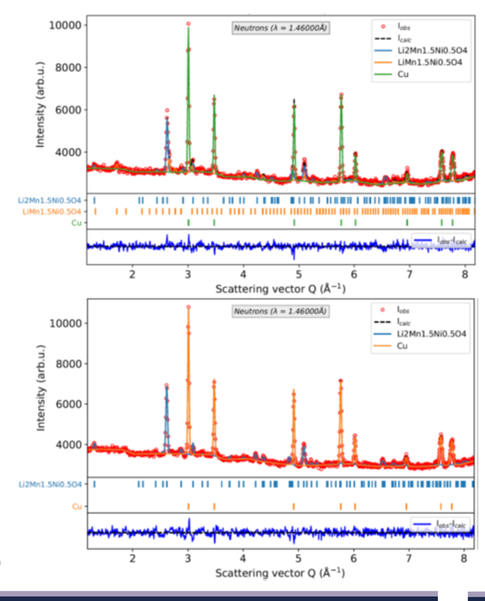
N. Paul, J. Wandt; S. Seidlmayer; S. Schebesta; M. J. Mühlbauer; O. Dolotko; H. A. Gasteiger; R. Gilles, ***J. Power Sources*** 345 (2017) 85

Follow structural evolution in high voltage spinel LNMO for new phases and Li positions

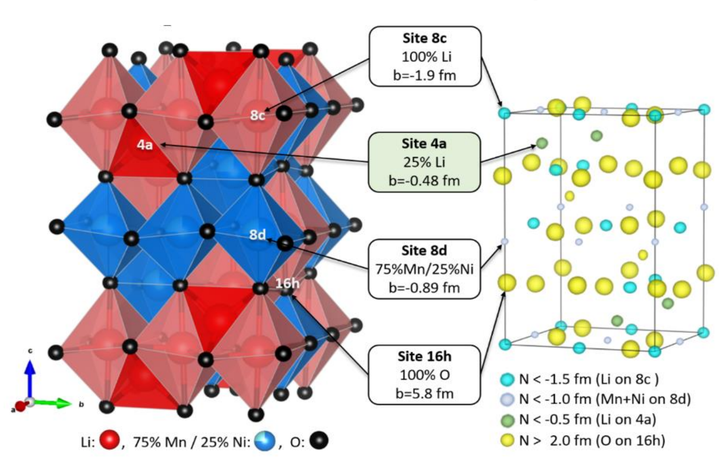
Operando XRD reveals a kinetically favored distorted phase



- kinetically favored formation of T2 phase in low voltage region observed after refinement of operando XRD data
- all octahedral 8c sites are occupied in $Li_{2.0}Ni_{0.5}Mn_{1.5}O_4$
- MEM analysis of neutron diffractograms identified additional Li on 4a sites



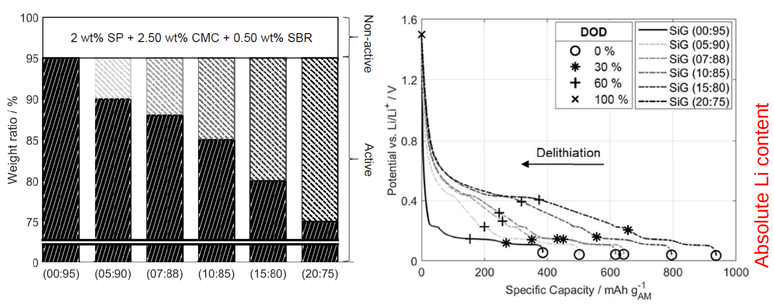
Ex-situ neutron diffraction reveals Li positions



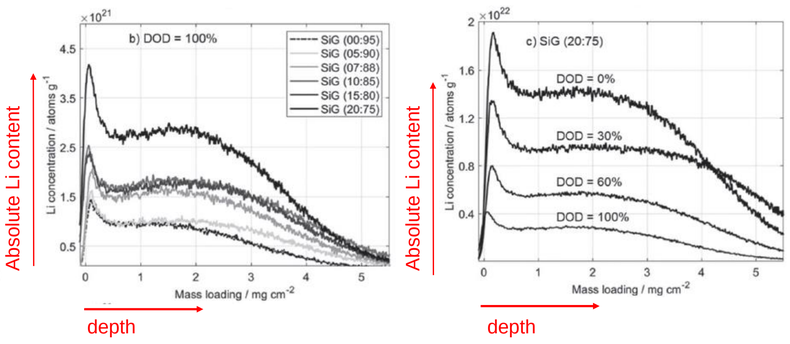
N. M. Jobst, N. Paul, P. Beran, M. Mancini, R. Gilles, M. Wohlfahrt-Mehrens and P. Axmann, ***J. Am. Chem. Soc.*** 145, 8 (2023) 4450

Notice Li within SEI with increase in Si content in SiG anodes

specific capacity increases with silicon content



neutron depth profiling shows Li content Vs depth



- **increased SEI** formation with **higher silicon** content SiGs (fully discharged electrodes)
- increase in Li content with decreasing depth of discharge (DOD) in every electrodes - uniform and complete electrode bulk utilization - **no limiting transport phenomena for higher Si** contents

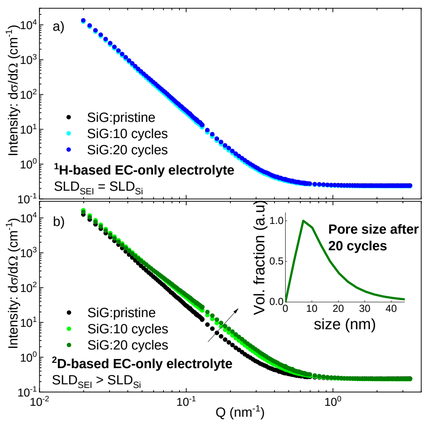
N. Paul, M. Wetjen, S. Busch, H. Gasteiger, R. Gilles, ***J. Electrochem. Soc.***166(6), (2019) A1051

E. Moyassari, L. Streck, N. Paul, M. Trunk, R. Neagu, C.-C Chang, S.-C. Hou, B. Märkisch, R. Gilles, A. Jossen, ***J. Electrochem. Soc.*** 168 (2020) 020519

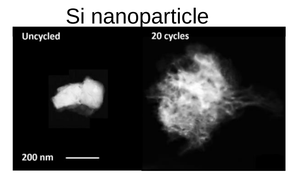
Nanopore filling in SiG anodes

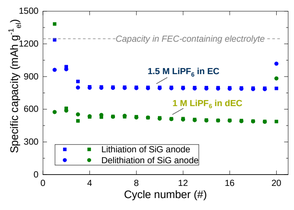
Size of nanopores? **Are pores filled with SEI or air** (empty)?

Contrast matching with **small-angle neutron scattering**



Si nanoparticle

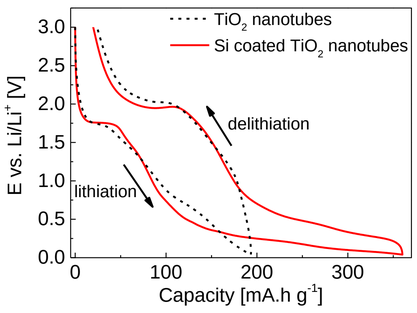


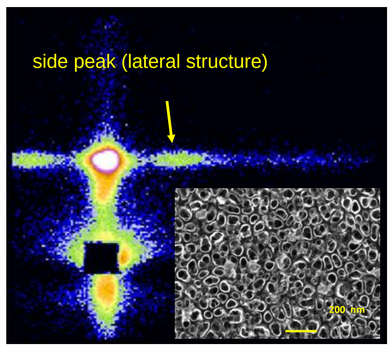


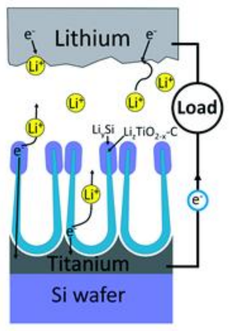
- aged SiG electrodes are nanoporous with a mean **pore size 8 nm**
- pores within Si nanoparticle **completely filled with SEI**

Notice incomplete coating on interfaces in anodes

How good is the Si coating?





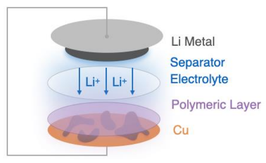


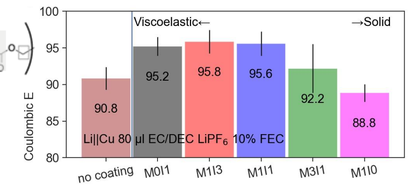
- a nanotubular TiO_2 array successfully prepared with radius **46 nm** with volume averaged porosity 46 %
- on **Si** coating, **wall thickness** of tube **increase** and radius **reduces to 23 nm** at surface – depth resolved **GISANS showed incomplete coating** of the lower part tube

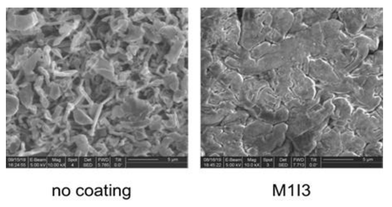
N. Paul, J. Brumbarov, A. Paul, Y. Chen, J. F. Moulin, P. Müller-Buschbaum, J. Kunze-Liebhäuser, R. Gilles, ***J.Appl.Cryst.*** 48 (2015) 444

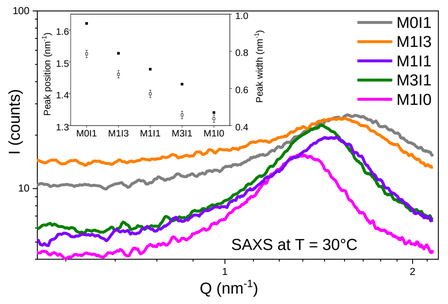
Use viscoelastic polymer coatings to prevent dendrites

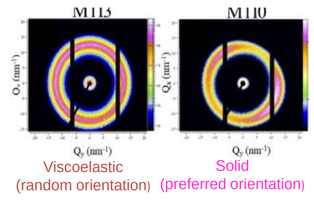
Interplay polymer mechanics and coulombic efficiency (CE)











Lithium metal deposition morphology changed from **dendritic to homogenous** with coating

- SAXS peaks correspond to inter-block distances between units - indicate faster dynamics for lower M-units
- WAXS peaks reveal stable H-bonded groups for all, and random or preferred orientation depending on M units

Z. Huang, S. Choudhury, N. Paul, J. H. Thienenkamp, P. Lennartz, H. Gong, P. Müller-Buschbaum, G. Brunklaus, R. Gilles, Z. Bao ***Adv. Energy Mater.*** 12 (2022) 2103187

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