Karlsruhe Institute of Technology

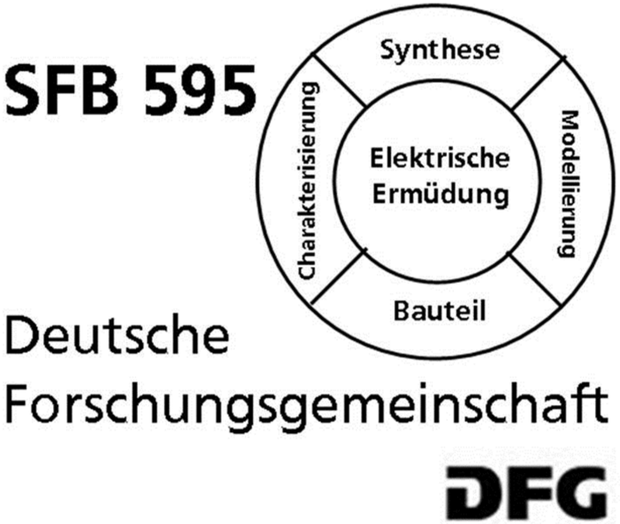
Institut für Angewandte Materialien

Helmholtz Institute Ulm
Electrochemical Energy Storage

TECHNISCHE
UNIVERSITÄT
DARMSTADT

Investigations on Fatigue of Li-ion batteries

HELMUT EHRENBERG INSTITUTE FOR APPLIED MATERIALS – ENERGY STORAGE SYSTEMS (IAM-ESS)



Investigations on Fatigue of Li-ion batteries

HELMUT EHRENBERG INSTITUTE FOR APPLIED MATERIALS – ENERGY STORAGE SYSTEMS (IAM-ESS)

→ **Introduction into Fatigue of Li-ion batteries: General aspects**

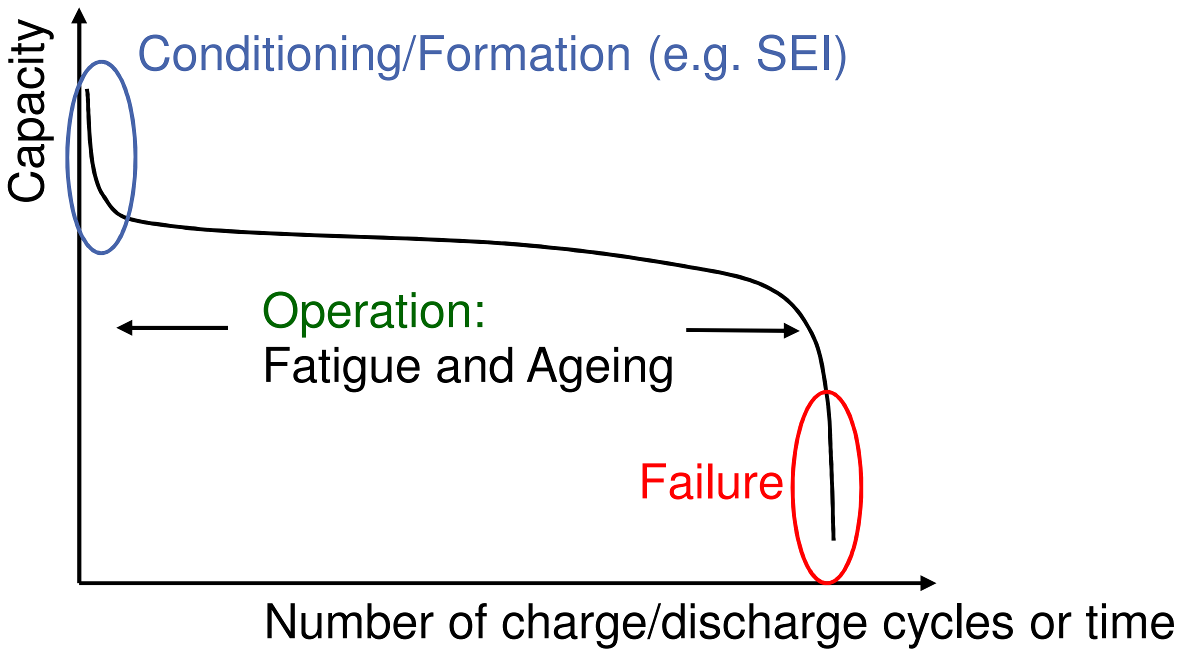
Materials challenges and the cell level

in operando techniques for life-time studies:

Neutron tomography and diffraction on 18650-type batteries

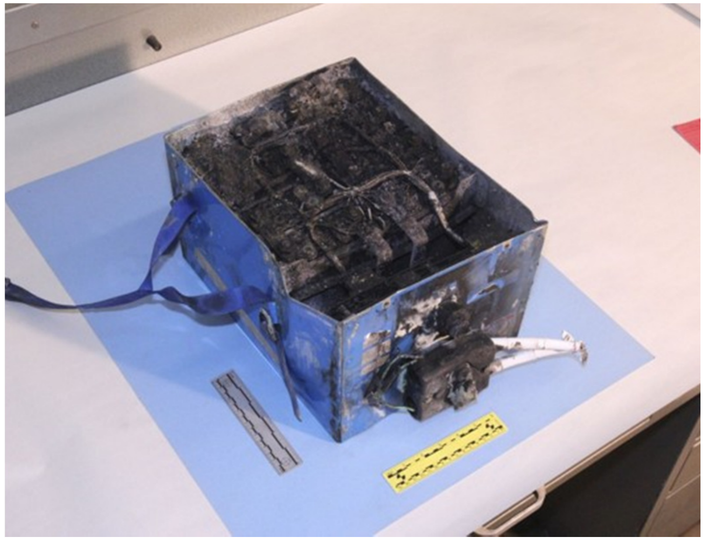
Conclusion

Fatigue:
Degradation of performance with operation



- Loss of capacity
- Increase of internal resistance
- Voltage fade
- …

Failure modes: „Thermal runaway“
Serious safety concerns at the EOL (end of life)



$Li_{1-x}CoO_2$ is intrinsically unstable in the overcharged state ($x > 0.5$)

$$Li_{0.5}CoO_2 \xrightarrow{T \geq 200°C} 1/2\ LiCoO_2 + 1/6\ Co_3O_4 + 1/6\ O_2$$

- Enhanced materials for safer operation (NCM, NCA)
- Design freezing (~7 y in cars, ~10 y in planes)

Safety aspects: energy within a Li-ion battery

A charged Li-ion battery stores about the same energy as a stick of dynamite of the same size!

Safety aspects: energy within a Li-ion battery

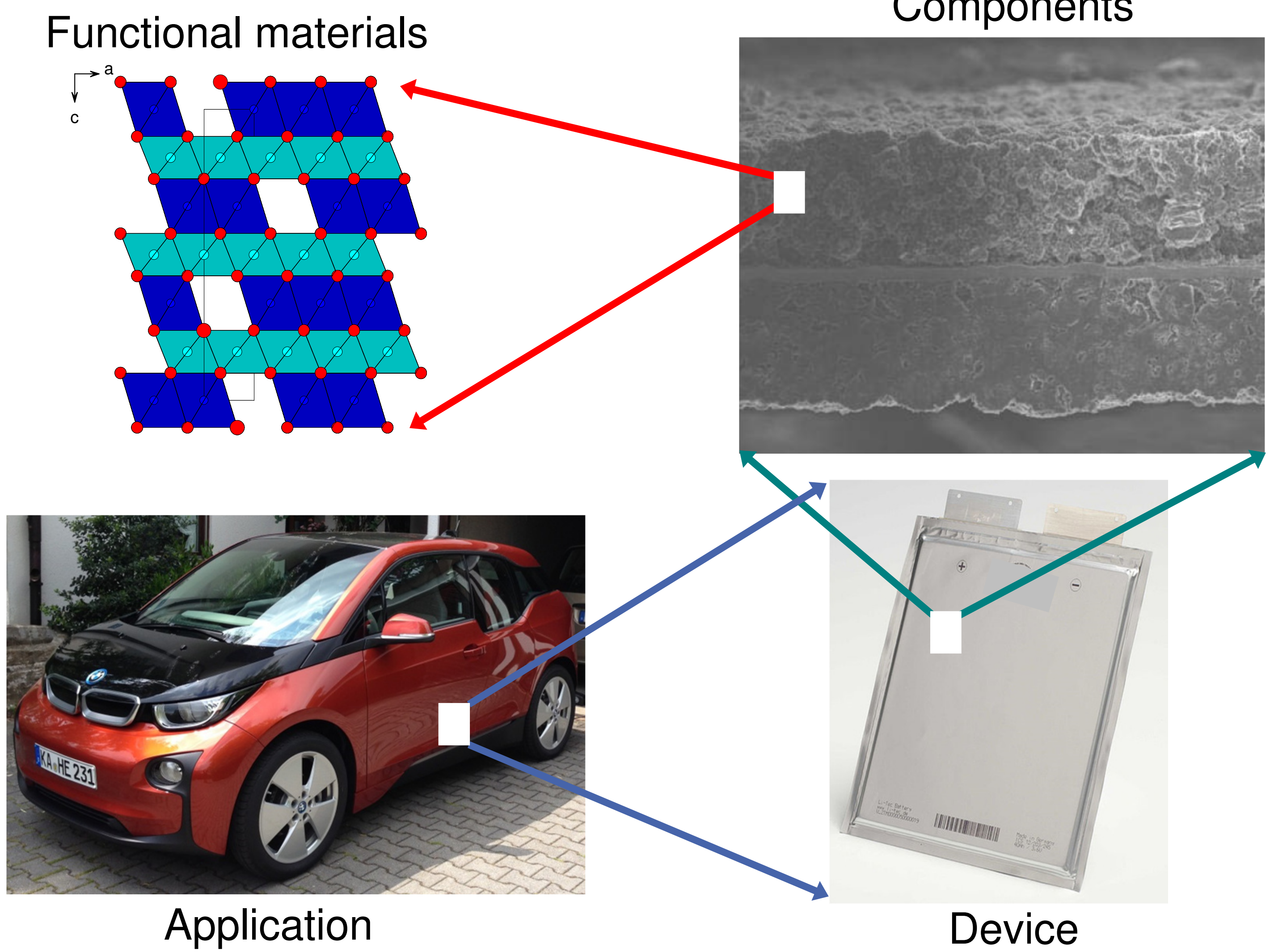
Karlsruhe Institute of Technology

> 2000 Cycles
(80% Capacity)

0.5 Cycle
(0% Capacity)

A charged Li-ion battery stores about the same energy as a stick of dynamite of the same size!

Fatigue: Multi length-scale complexity



Investigations on Fatigue of Li-ion batteries

HELMUT EHRENBERG INSTITUTE FOR APPLIED MATERIALS – ENERGY STORAGE SYSTEMS (IAM-ESS)

Introduction into Fatigue of Li-ion batteries: General aspects

→ **Materials challenges and the cell level**

in operando techniques for life-time studies:

Neutron tomography and diffraction on 18650-type batteries

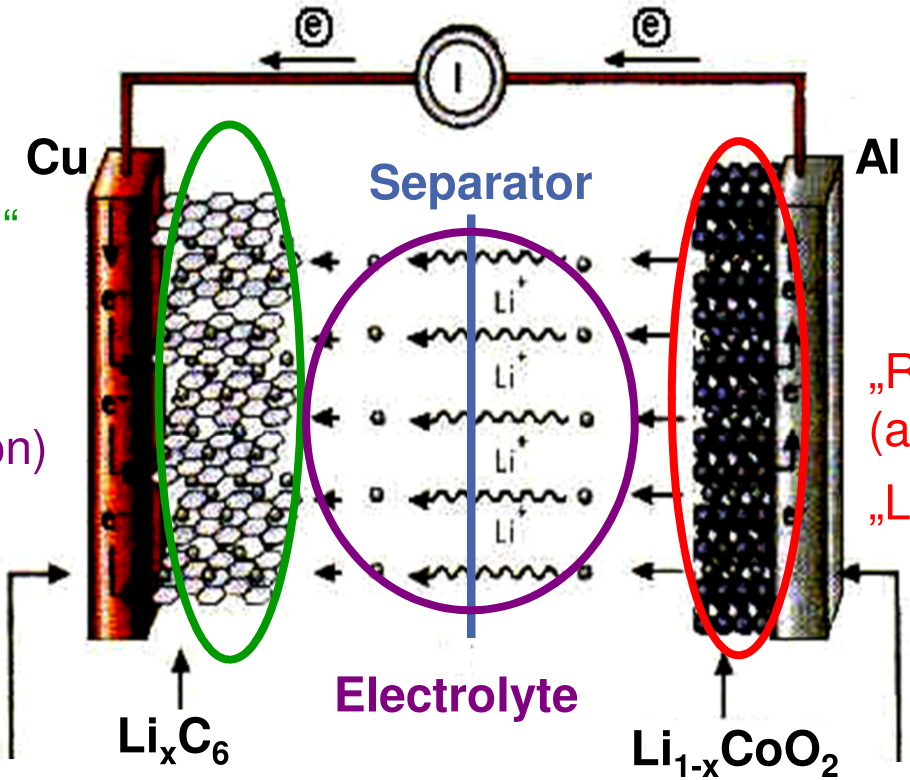
Conclusion

Li-ion batteries: Materials challenges

Karlsruhe Institute of Technology

„Dendrite formation“

„Decomposition“
(oxidation or reduction)
„Ionic conductivity“
„Dissolution“



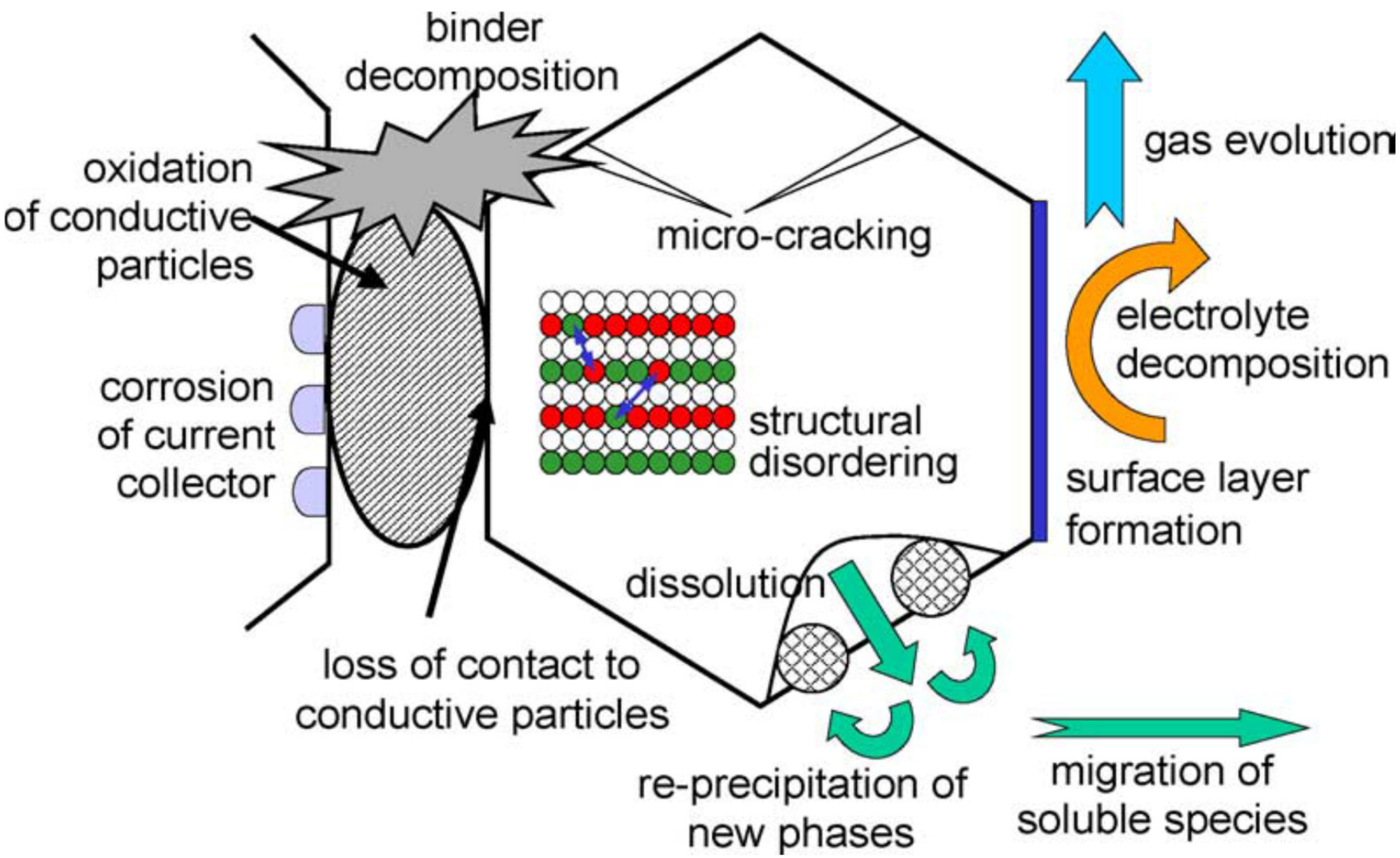
„Short cuts“
„Loss of porosity“

„Redox reactions“
(atomic rearrangements)
„Lattice strain“

„Anode“ „Cathode“

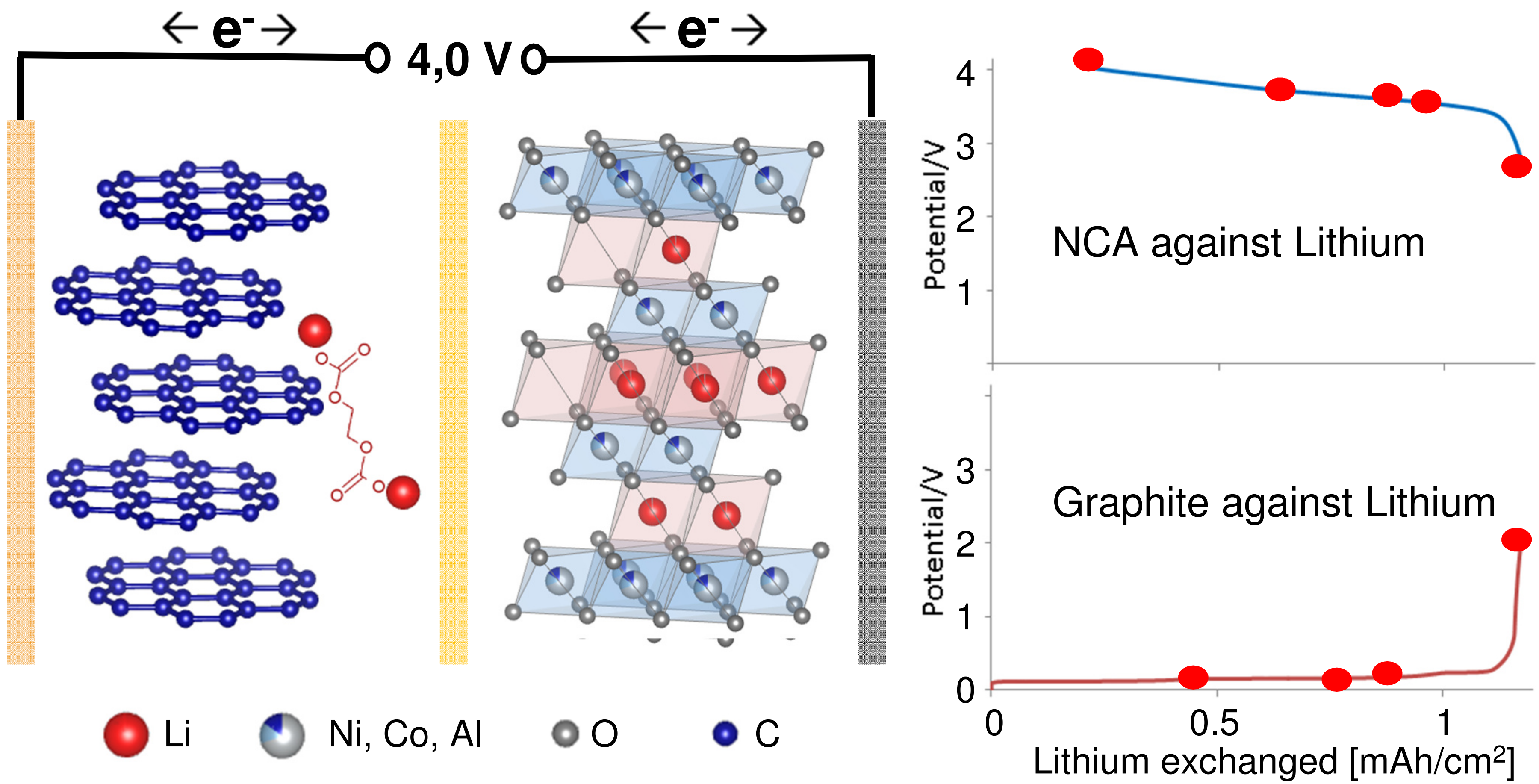
- All components suffer from „Ageing“ & „Fatigue“
- Materials interactions: „Solid Electrolyte Interface/Interphase“, SEI
  „Metal dissolution“, „Loss of adhesion“

Li-ion batteries: contributions to fatigue



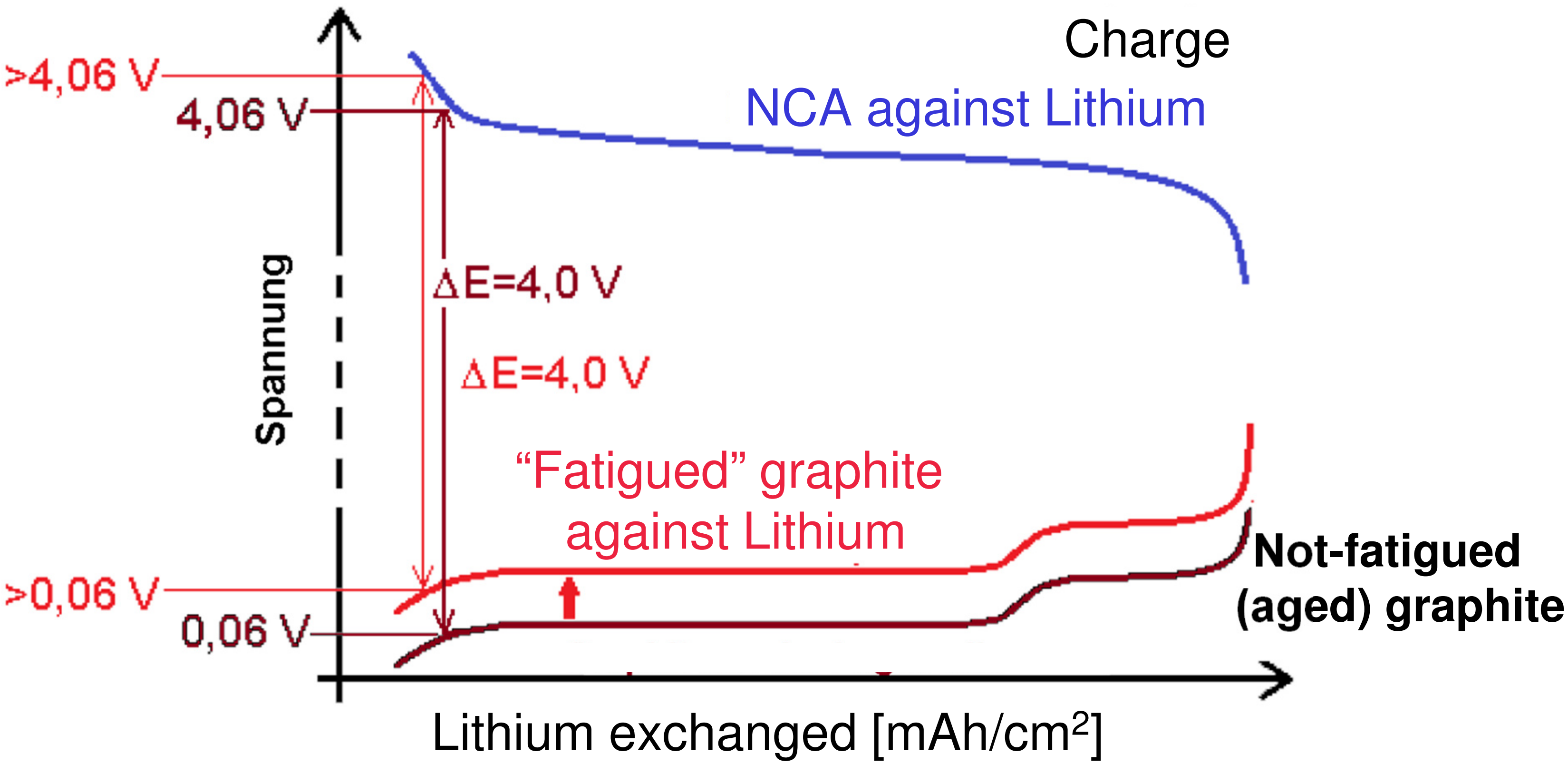
Vetter, J., et al., *Ageing mechanisms in lithium-ion batteries.*
J. Power Sources **147** (2005) 269-281.

Electrode-specific contributions to fatigue



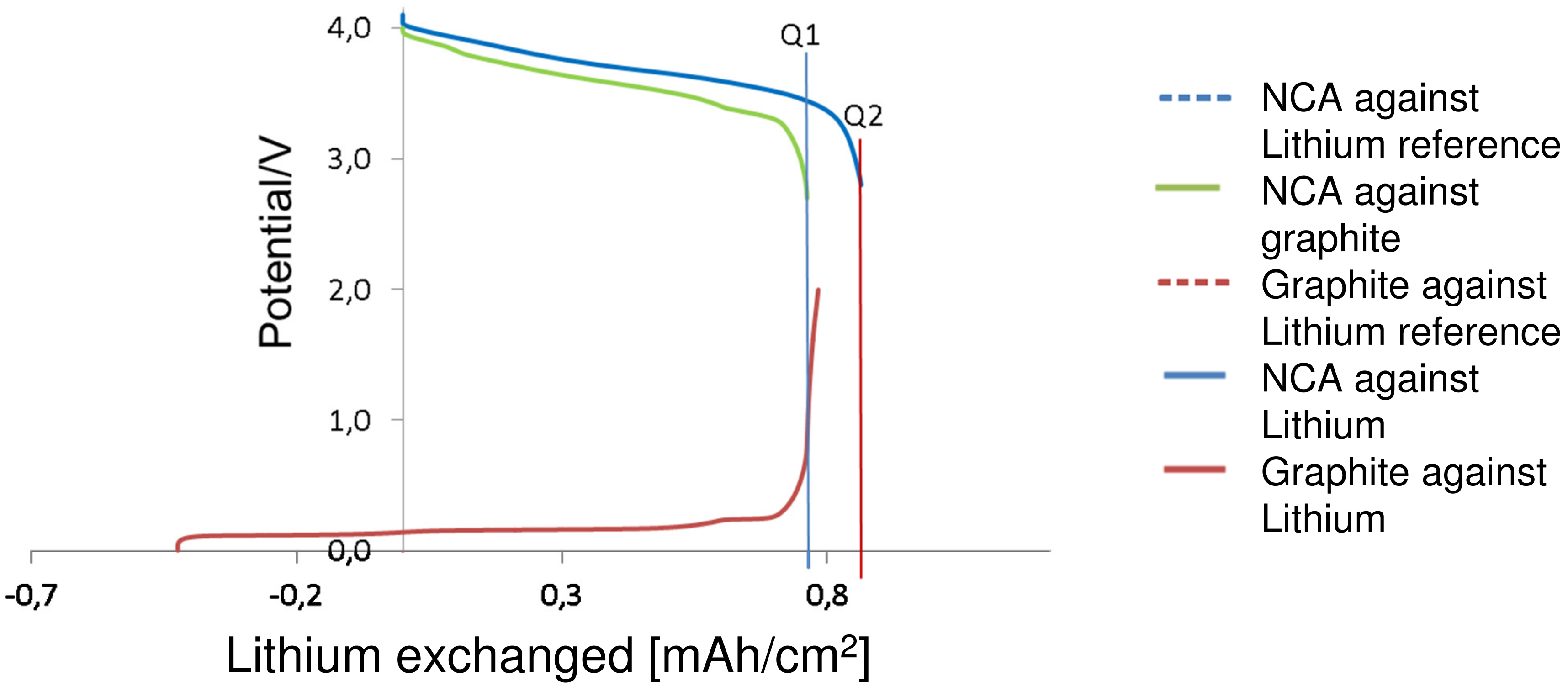
- Relative shift of the states-of-charge of cathode and anode results in capacity losses on full-cell level (example: NCA against graphite)

Electrode-specific contributions to fatigue



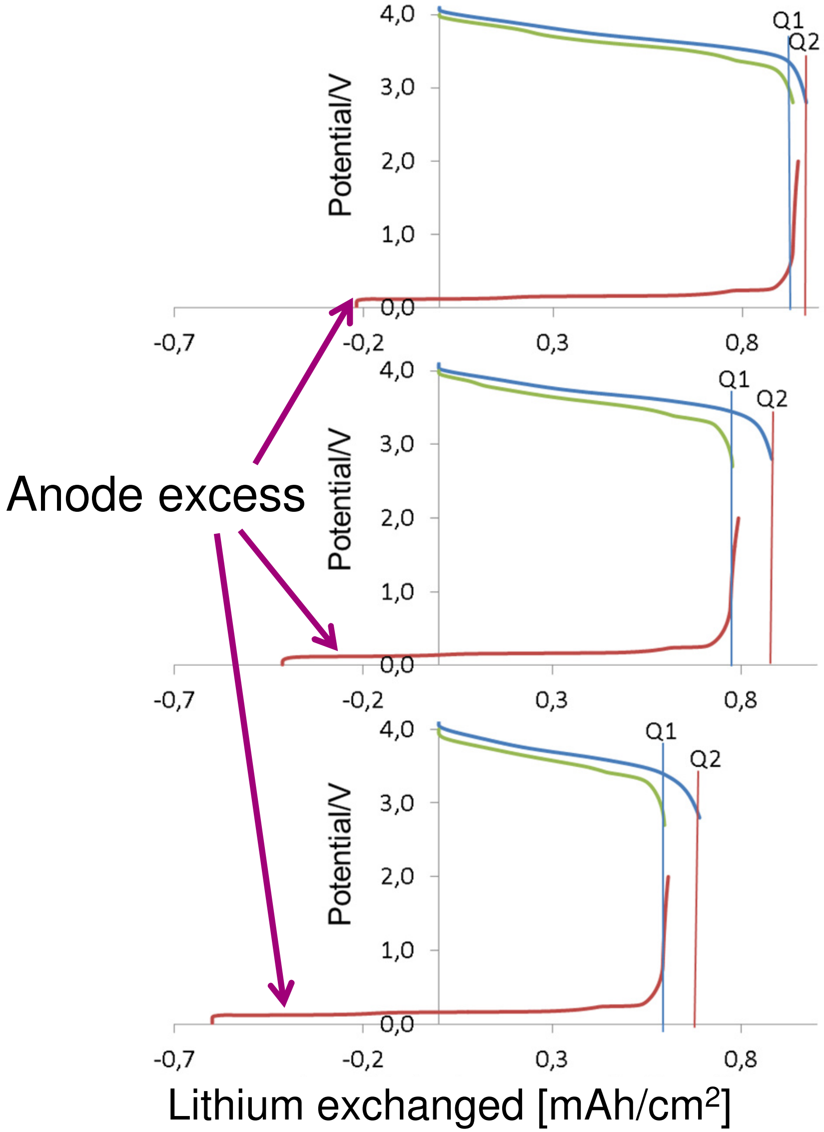
- Overvoltages from the negative electrode result in a higher level of Li-extraction from the positive electrode and, therefore,
- more pronounced fatigue.

Electrode-specific contributions to fatigue



- Cyclovoltamograms of full cells with reference electrode (NCA against graphite) in combination with half-cell data (NCA and graphit against Li).

Electrode-specific contributions to fatigue



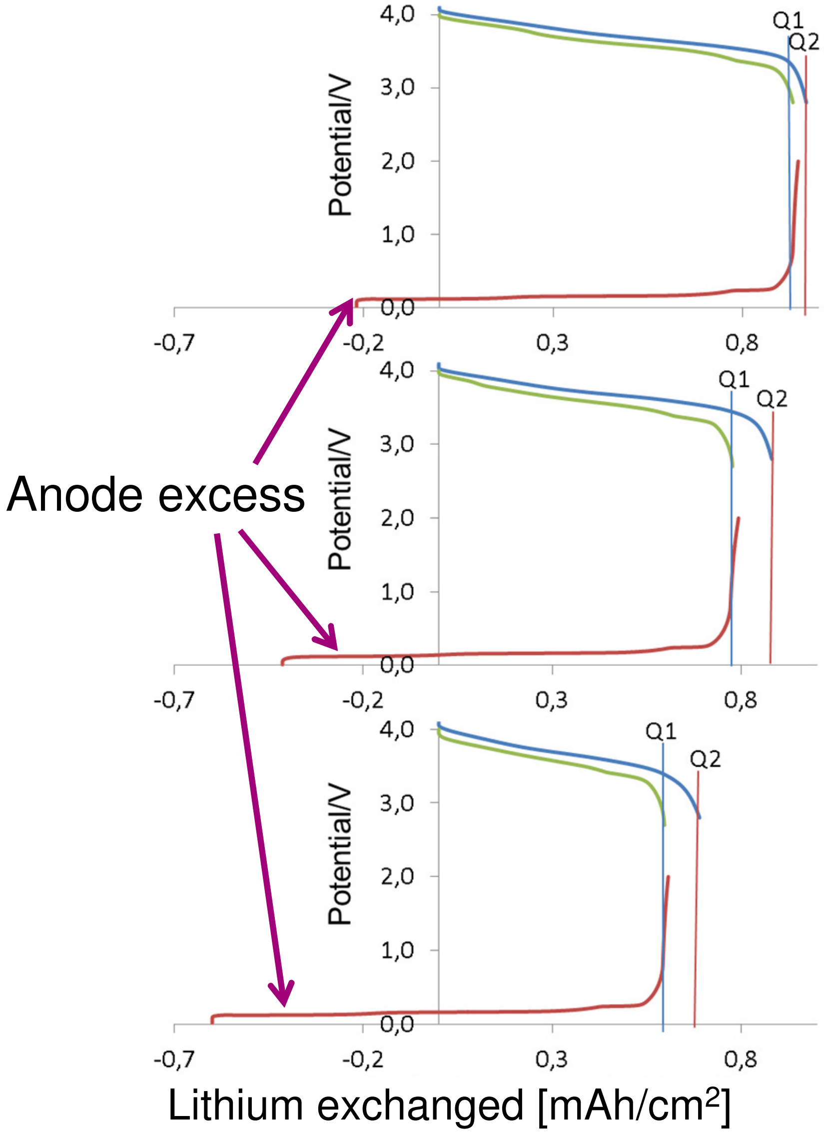
Aged cell	Capacity loss
Cathode	-
Cell balancing	2,1 % ± 0,01 %1)

Fatigued	Capacity loss
Cathode	9,0 % ± 1,3 %1)
Cell balancing	10,0 % ± 2,0 %1)

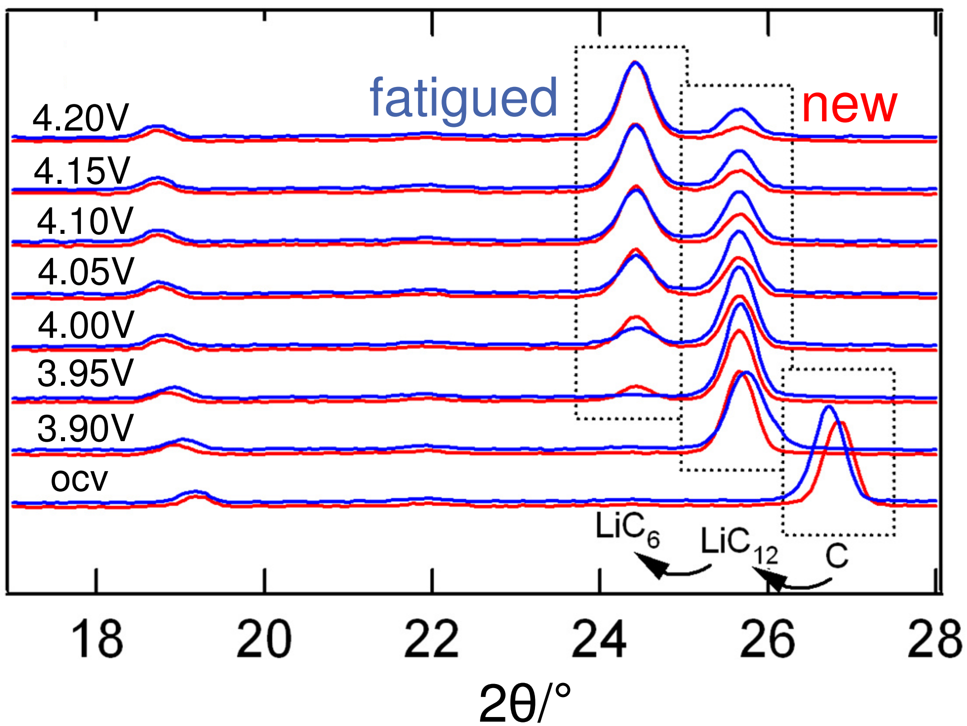
Highly fatigued	Capacity loss
Cathode	28,5 % ± 1,3 %1)
Cell balancing	9,7 % ± 0,7 %1)

1) Maximum deviation within three experiments

in operando observation of anode excess



Neutron diffraction:



- More intermediate LiC_{12} in the „fully“ charged state due to fatigue, i.e.
- less Li in the anode in fatigued state due to „anode excess“.

Reveal working and degradation mechanisms

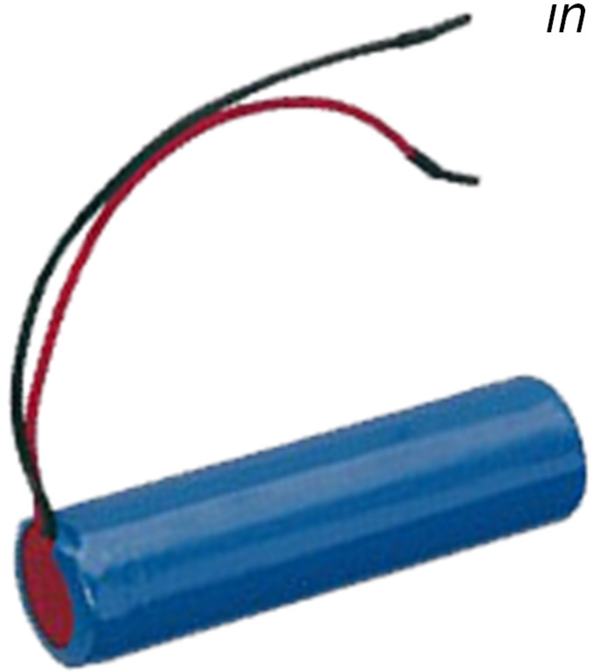
Karlsruhe Institute of Technology

Idealized model systems
(Single processes)

Real energy storage devices
(high level of complexity)

e.g. UHV conditions
XPS, TEM

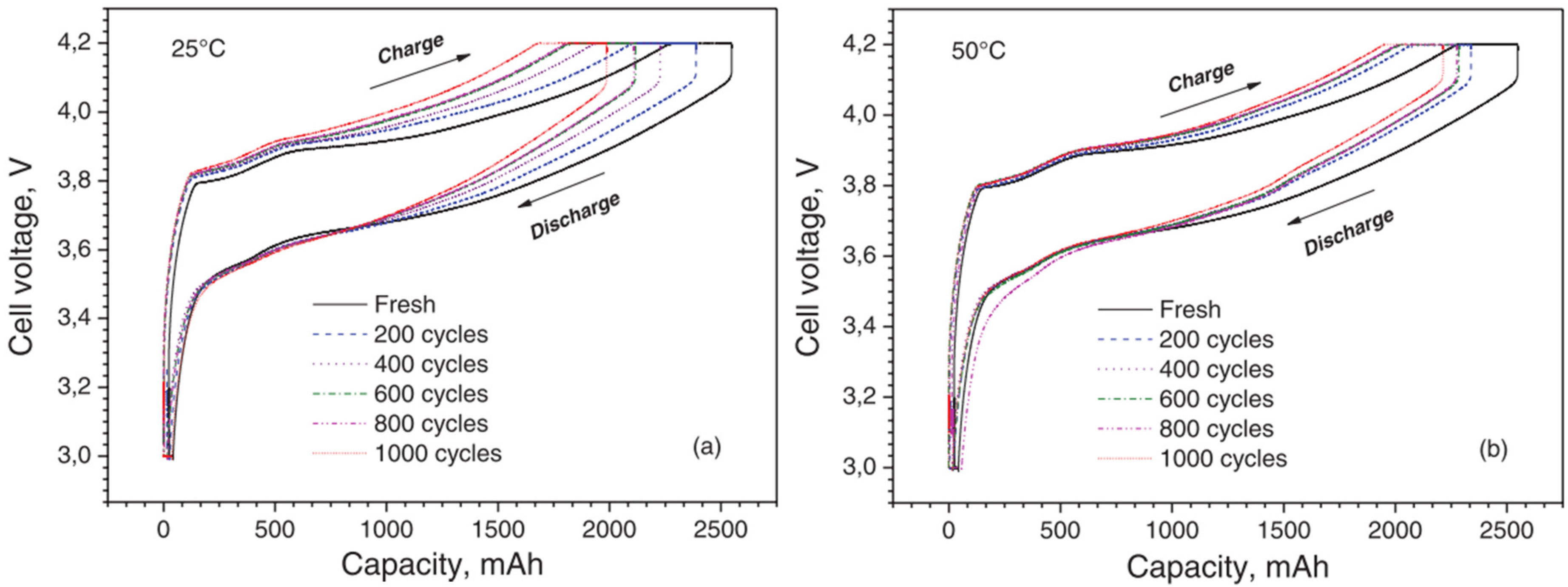
in operando studies



Cycle life testing and fatigue analysis

KIT
Karlsruhe Institute of Technology

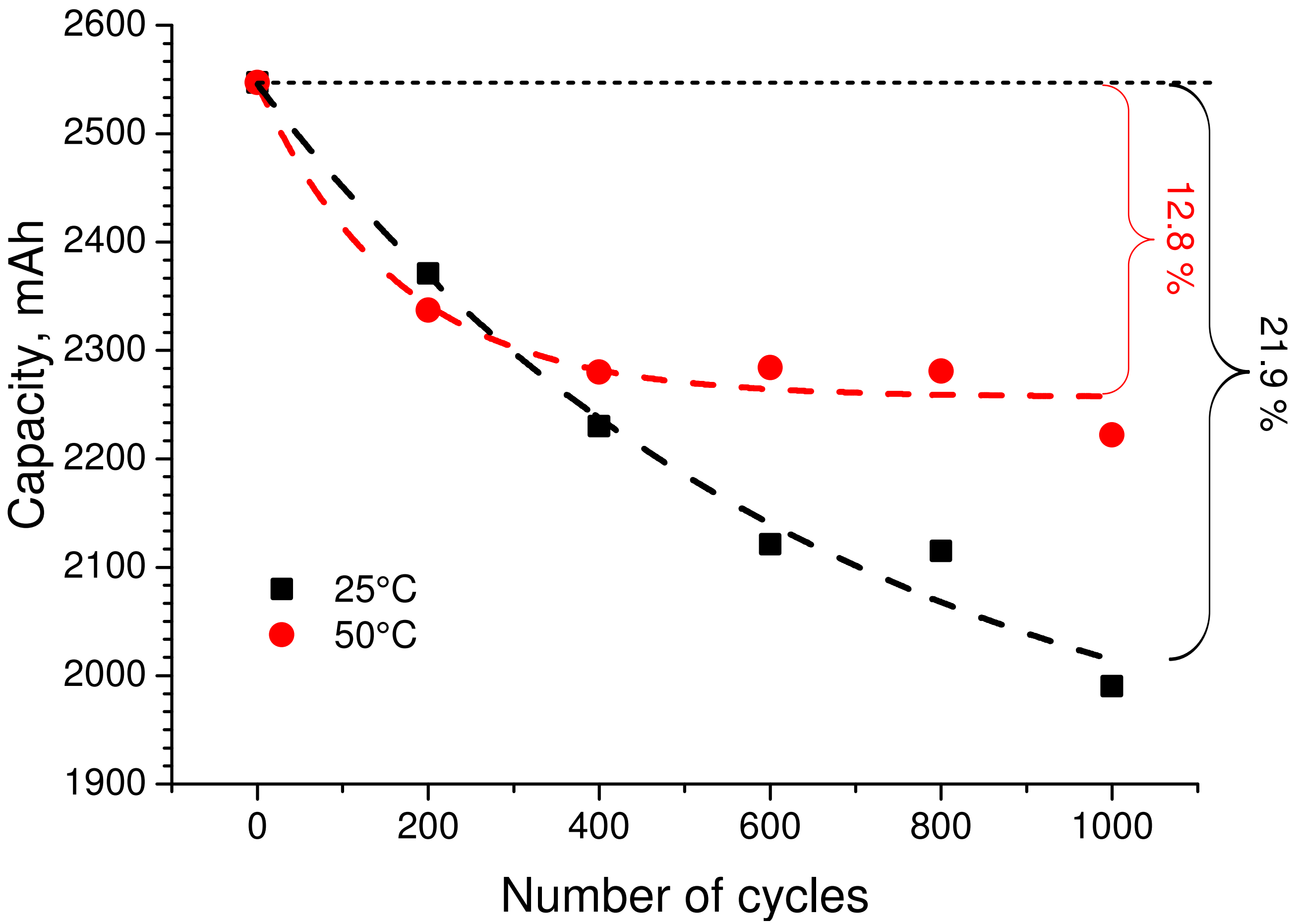
- Commercial Li-ion cell of 18650-type (2600 mAh, 3.0 - 4.2 V)
  - „Fresh“ - single cycle
  - „Fatigued“ at 25°C and 50°C (200, 400, 600, 800, 1000 cycles)
  - Cycling 3.0 - 4.2 V, CCCV, 1C



O. Dolotko, *J. Electrochem. Soc.* **159** (2012) A2082

Cycle-life testing and fatigue analysis

- Commercial Li-ion cell of 18650-type (2600 mAh, 3.0 - 4.2 V)



O. Dolotko, *J. Electrochem. Soc.* **159** (2012) A2082

Karlsruhe Institute of Technology

Institut für Angewandte Materialien

Helmholtz Institute Ulm
Electrochemical Energy Storage

TECHNISCHE
UNIVERSITÄT
DARMSTADT

Investigations on Fatigue of Li-ion batteries

HELMUT EHRENBERG INSTITUTE FOR APPLIED MATERIALS – ENERGY STORAGE SYSTEMS (IAM-ESS)

Introduction into Fatigue of Li-ion batteries: General aspects

Materials challenges and the cell level

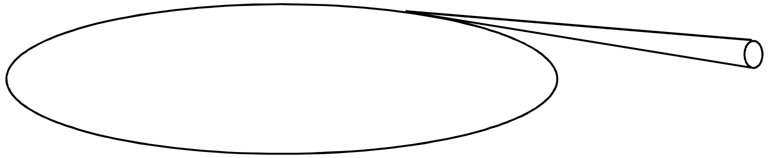
→ ***in operando* techniques for life-time studies:**

Neutron tomography and diffraction on 18650-type batteries

Conclusion

in operando techniques for life-time studies

- Pronounced materials interactions: real battery conditions essential
- Specific degradation mechanisms:
  - Correlation between effects and cause
  - Influence of load profile
- Proceeding of fatigue
- Cell design concepts

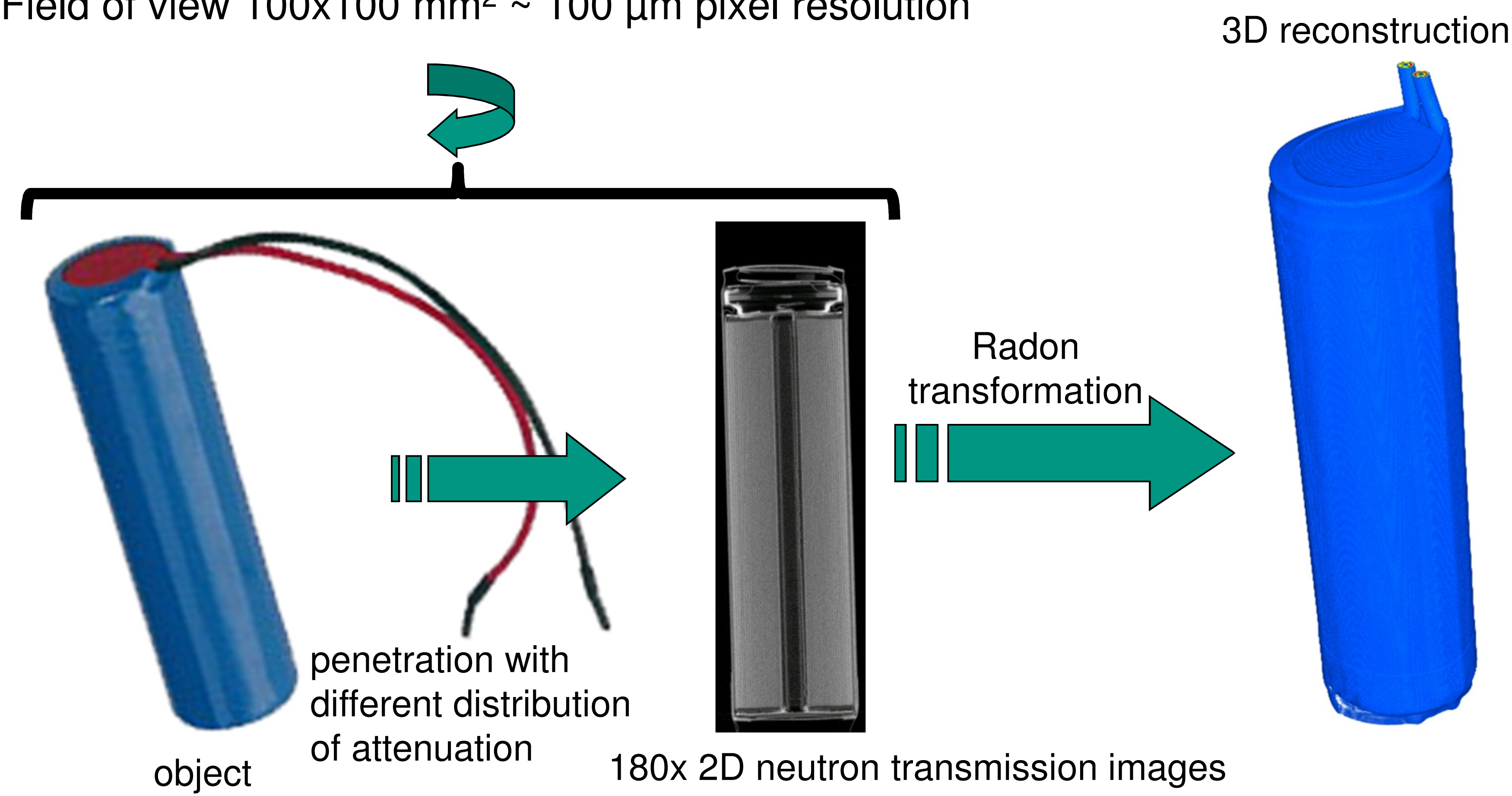


High-energy synchrotron & neutron radiation

- Non-destructive methods
- Penetration capability
- Time- and spatial resolution
- Detailed information (minor changes)
- Sensitivity to light elements (H, Li, C, O)
- Complementary *post mortem* analysis

Neutron radiography and tomography

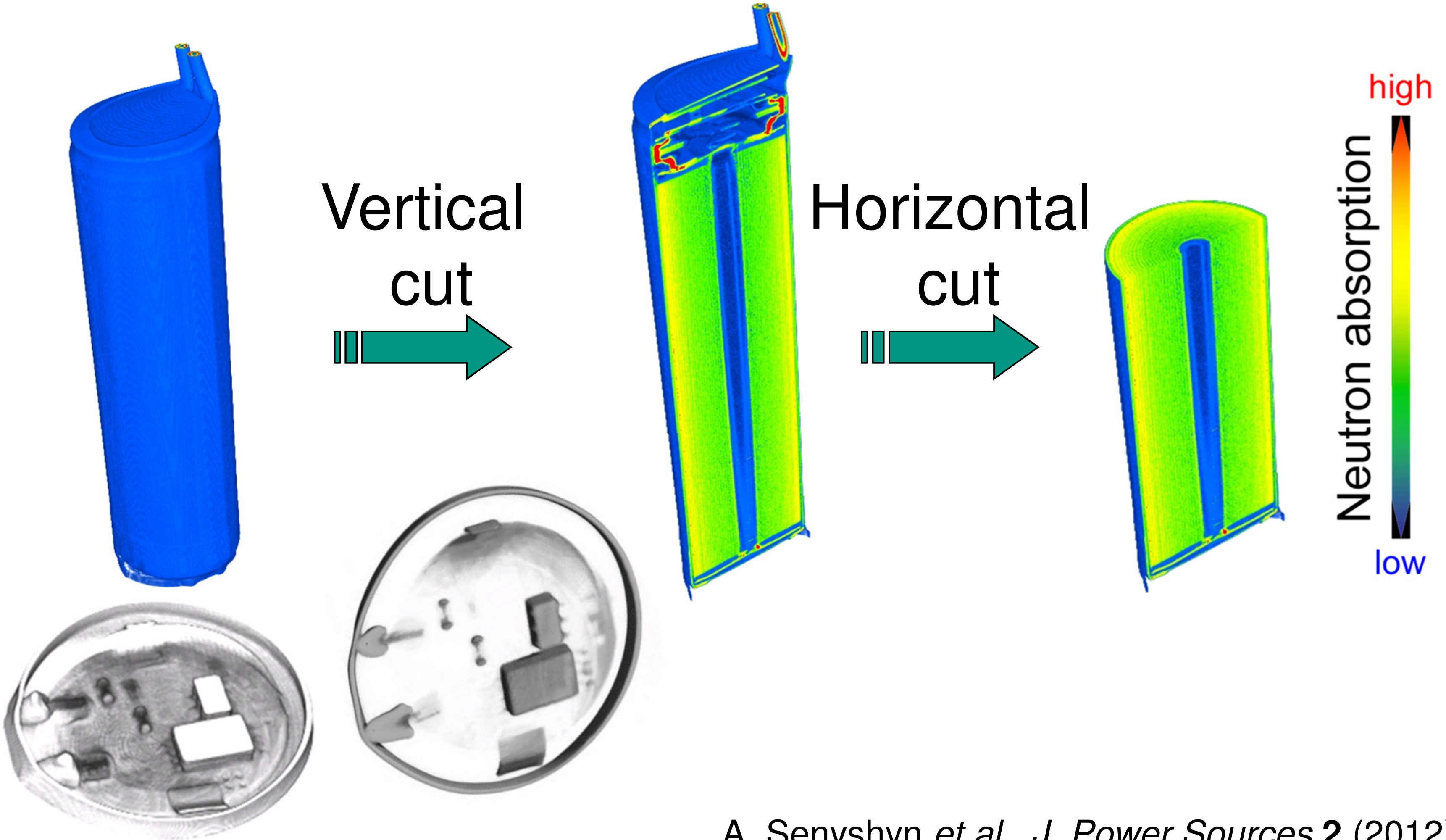
ANTARES (research reactor FRM-II), L/D=800
Field of view 100x100 mm^2 ~ 100 µm pixel resolution



A. Senyshyn *et al.*, *J. Power Sources* **2** (2012) 126

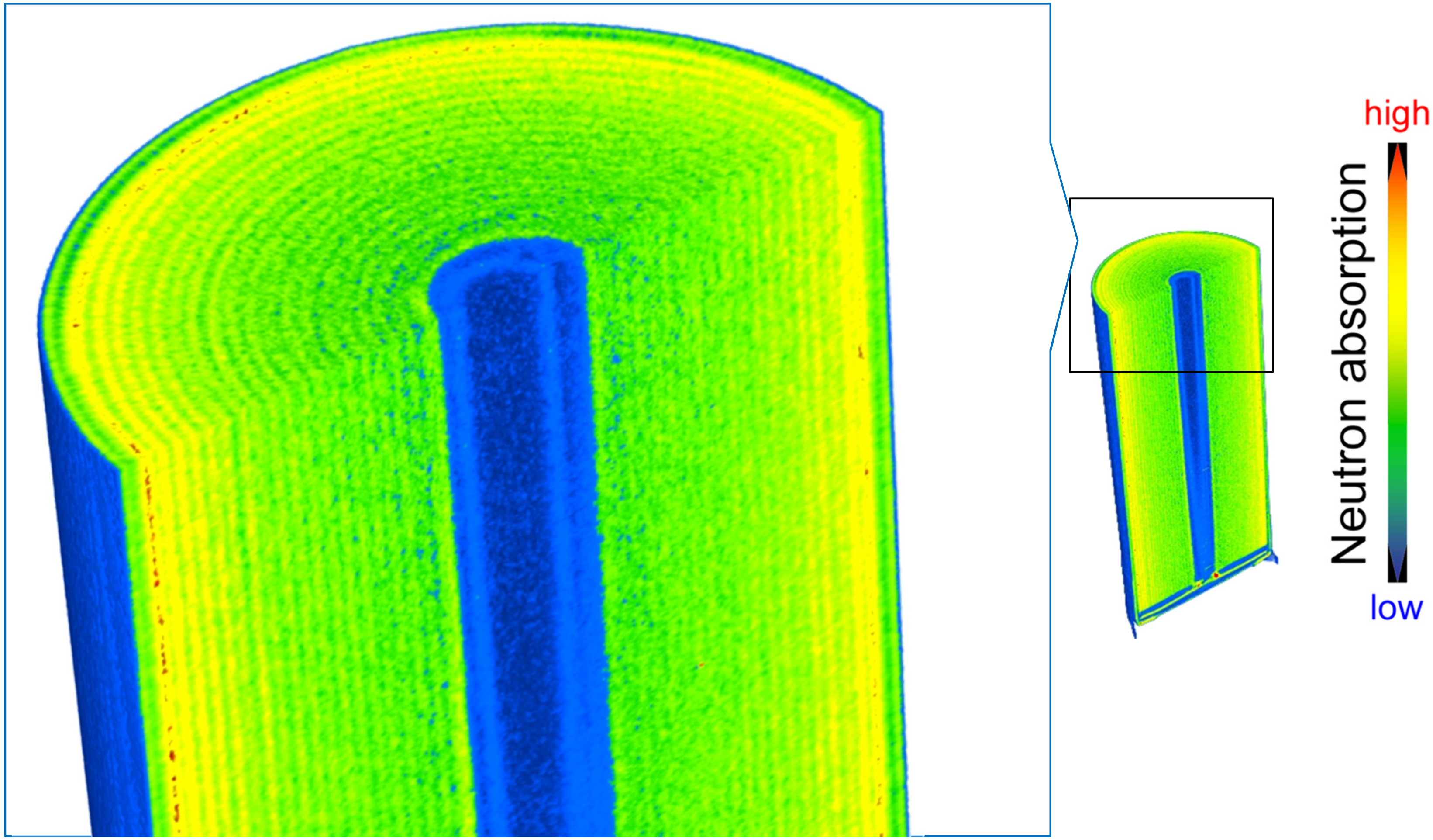
Neutron radiography and tomography

Visualisation by assignment of absorption levels to a false-color scheme



A. Senyshyn *et al.*, *J. Power Sources* **2** (2012) 126

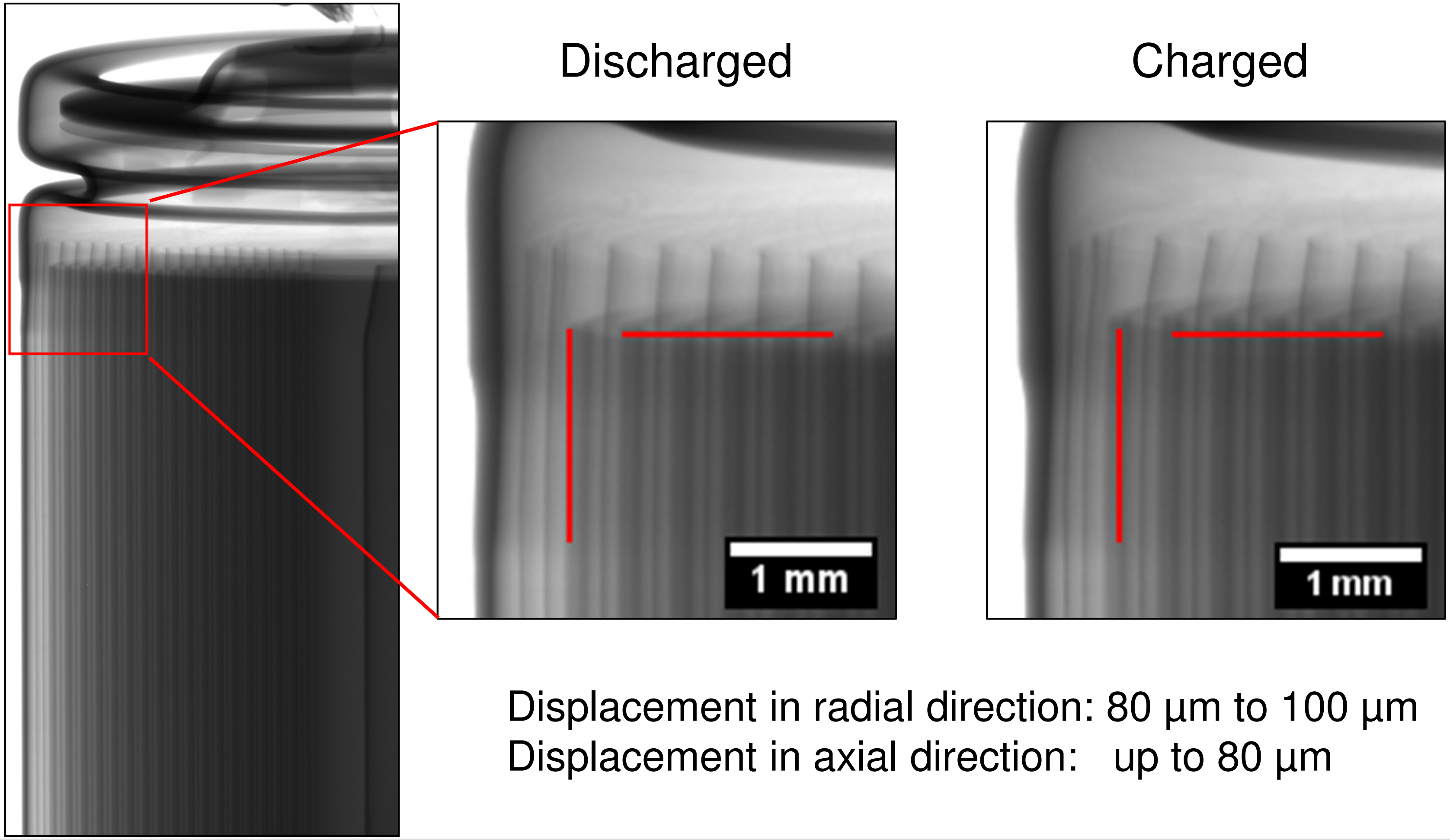
Neutron radiography and tomography



A. Senyshyn *et al.*, *J. Power Sources* **2** (2012) 126

Selected examples

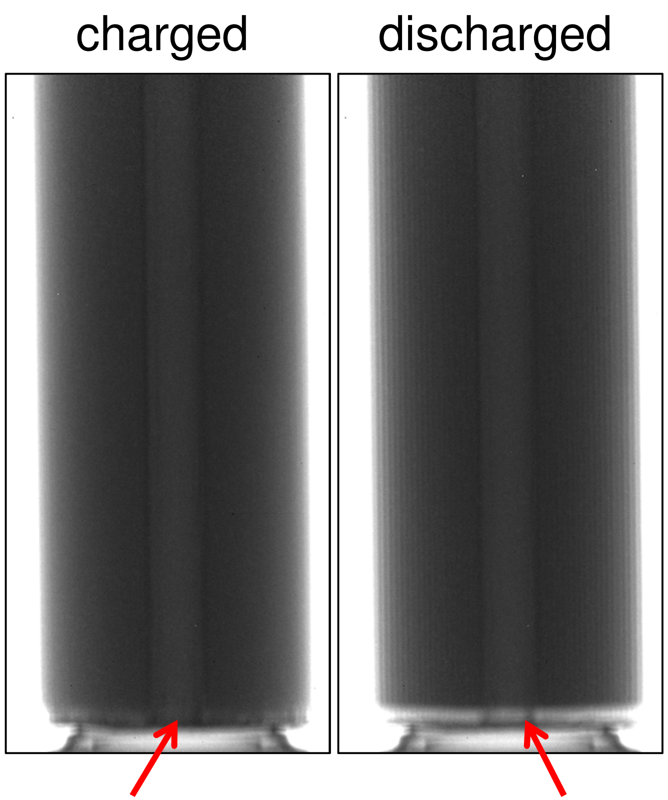
- X-ray tomography reveals shifts with SOC

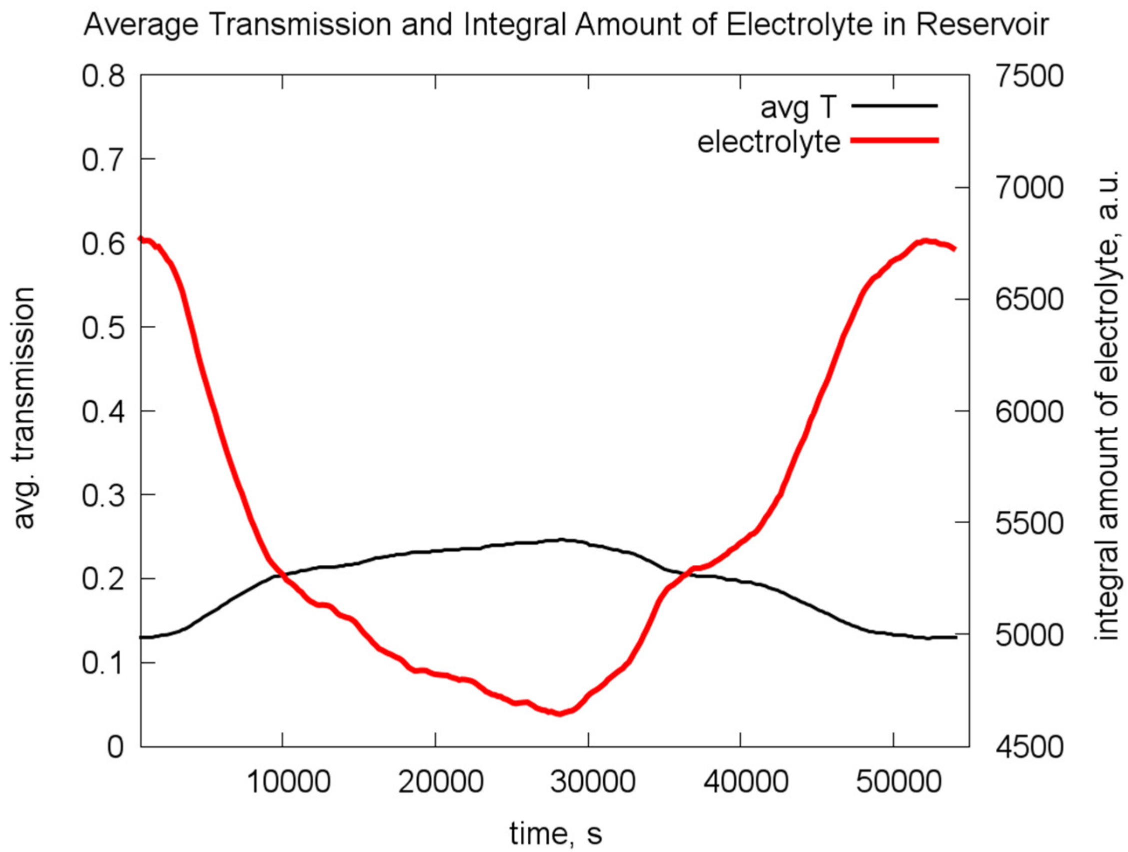


Displacement in radial direction: 80 µm to 100 µm
Displacement in axial direction: up to 80 µm

Selected examples

- Neutron tomography: electrolyte level changes during charge/discharge



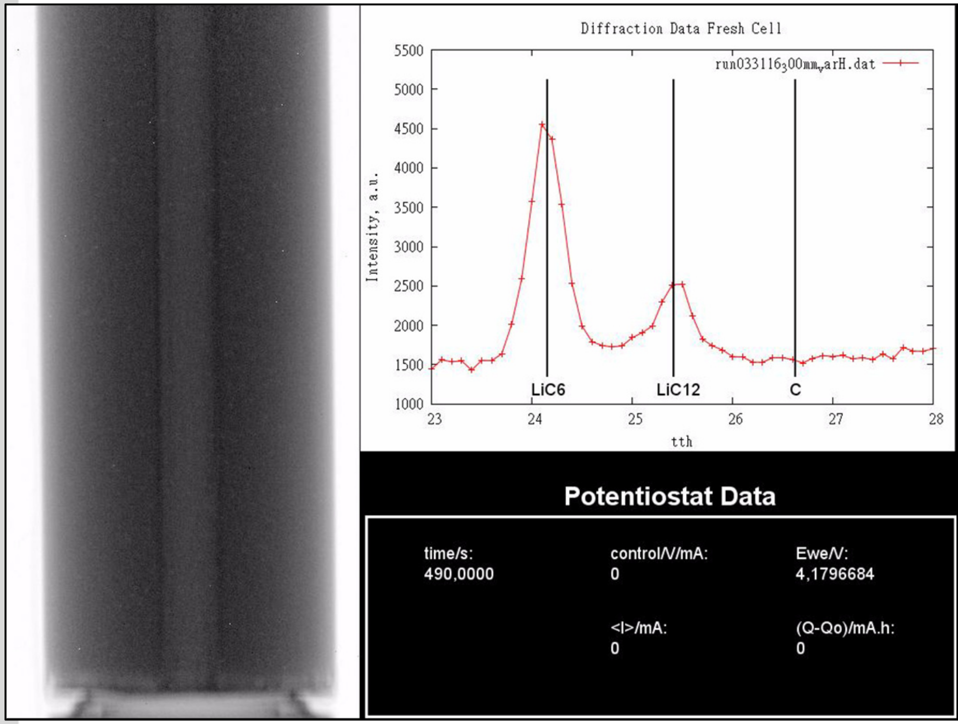


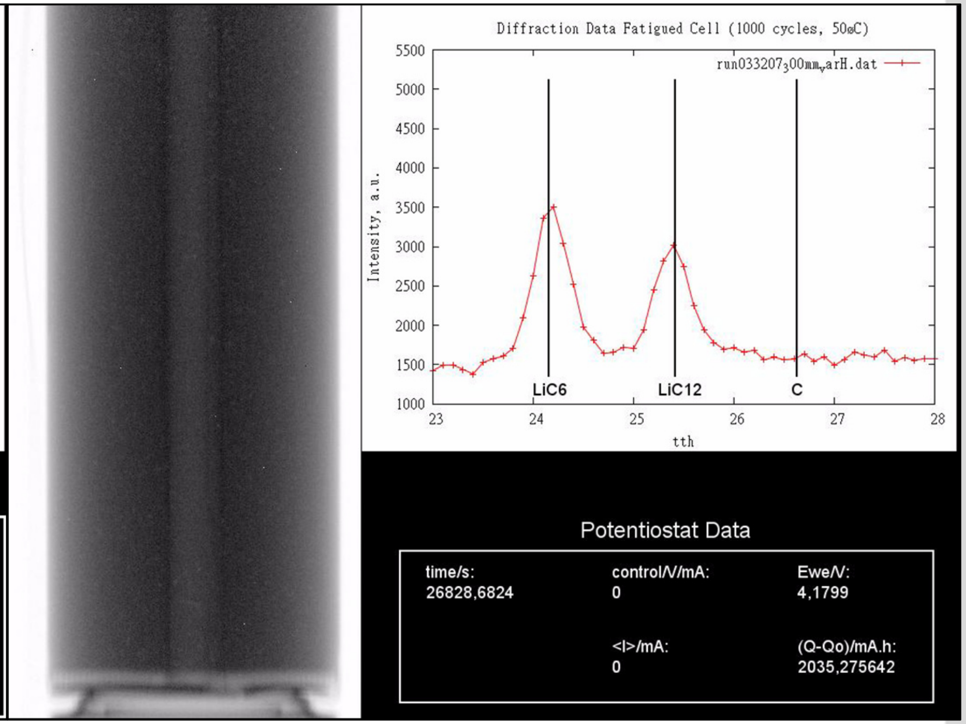
Selected examples

- Combined neutron tomography & diffraction

Fresh Cell

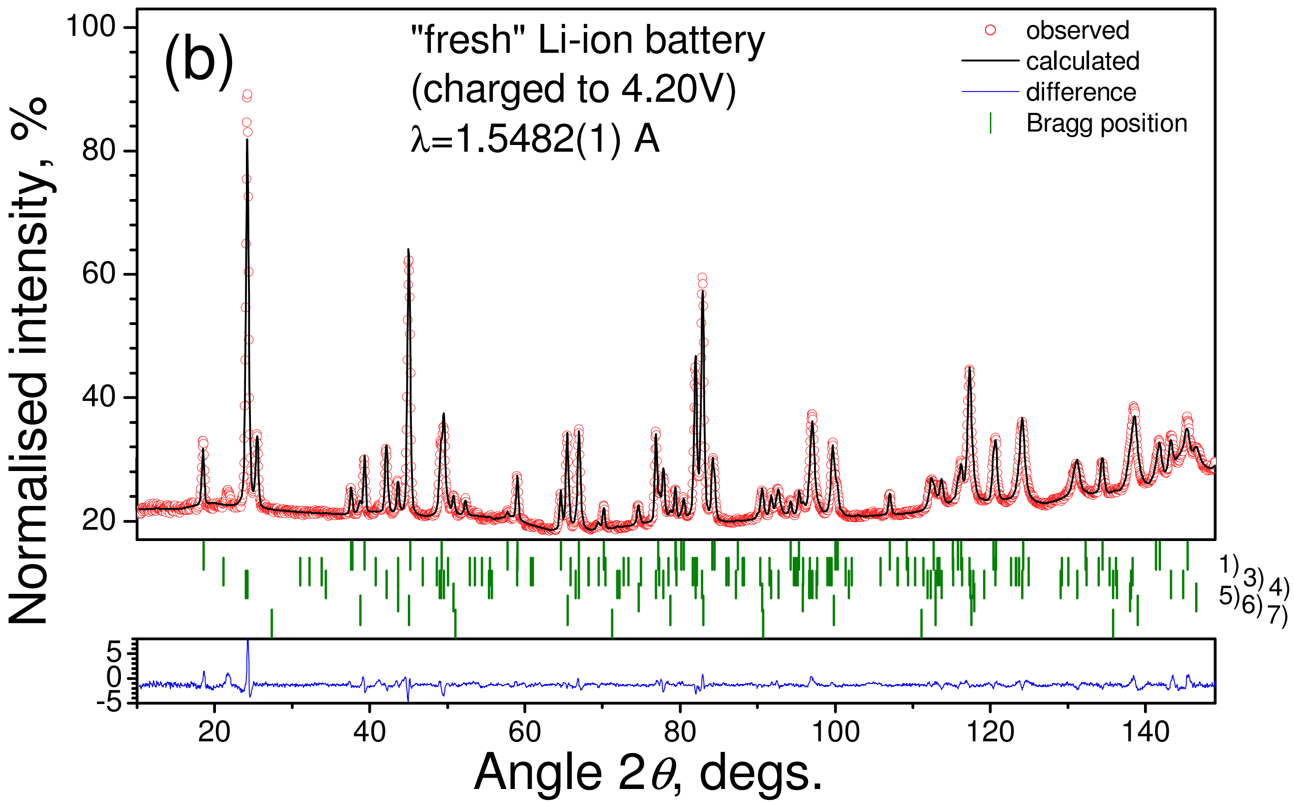
Fatigued Cell (1000 cycles)





see „Highlights“ @ http://www.iam.kit.edu/ess

Neutron Powder Diffraction



(1) - cathode (Li_xCoO_2)

(2) - anode (graphite)

(3) - anode (LiC_{12})

(4) - anode (LiC_6)

(5) - current collector (Cu)

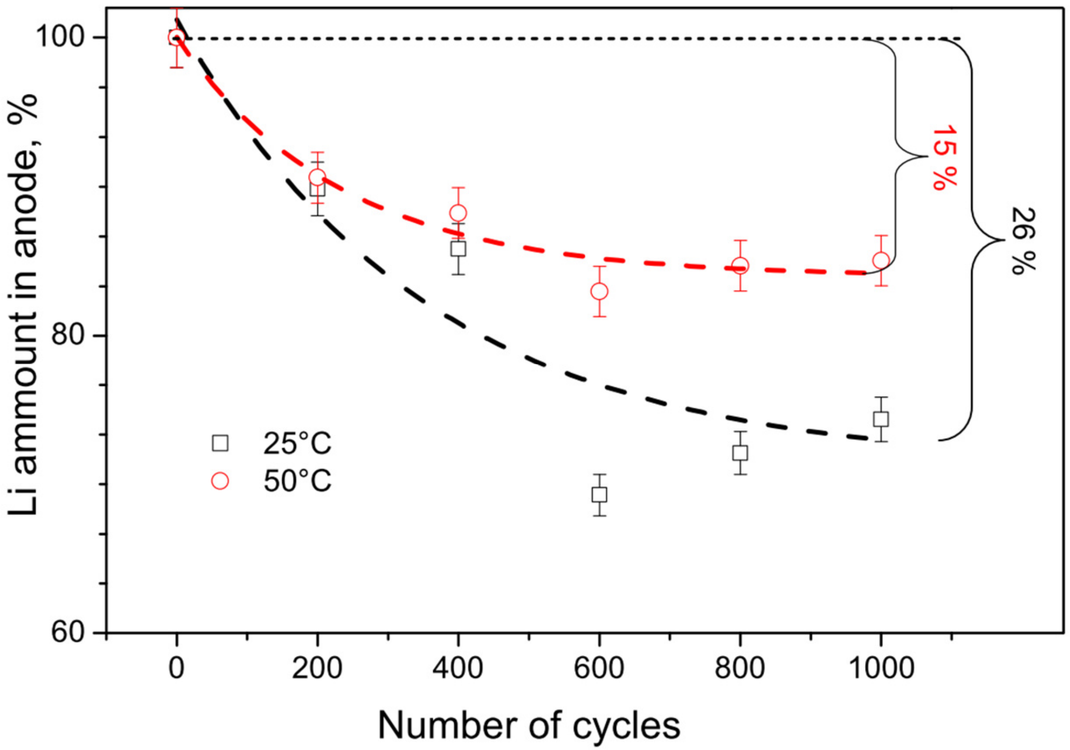
(6) - current collector (Al)

(7) - steel housing (Fe)

- Measured at SPODI, FRM II, Garching

O. Dolotko, *J. Electrochem. Soc.* **159** (2012) A2082

Anode: Ratio of LiC_6 and LiC_{12} in charged state



Phase fraction of LiC_6 is lower for the fatigued 25 °C cell, while the LiC_{12} value is higher.

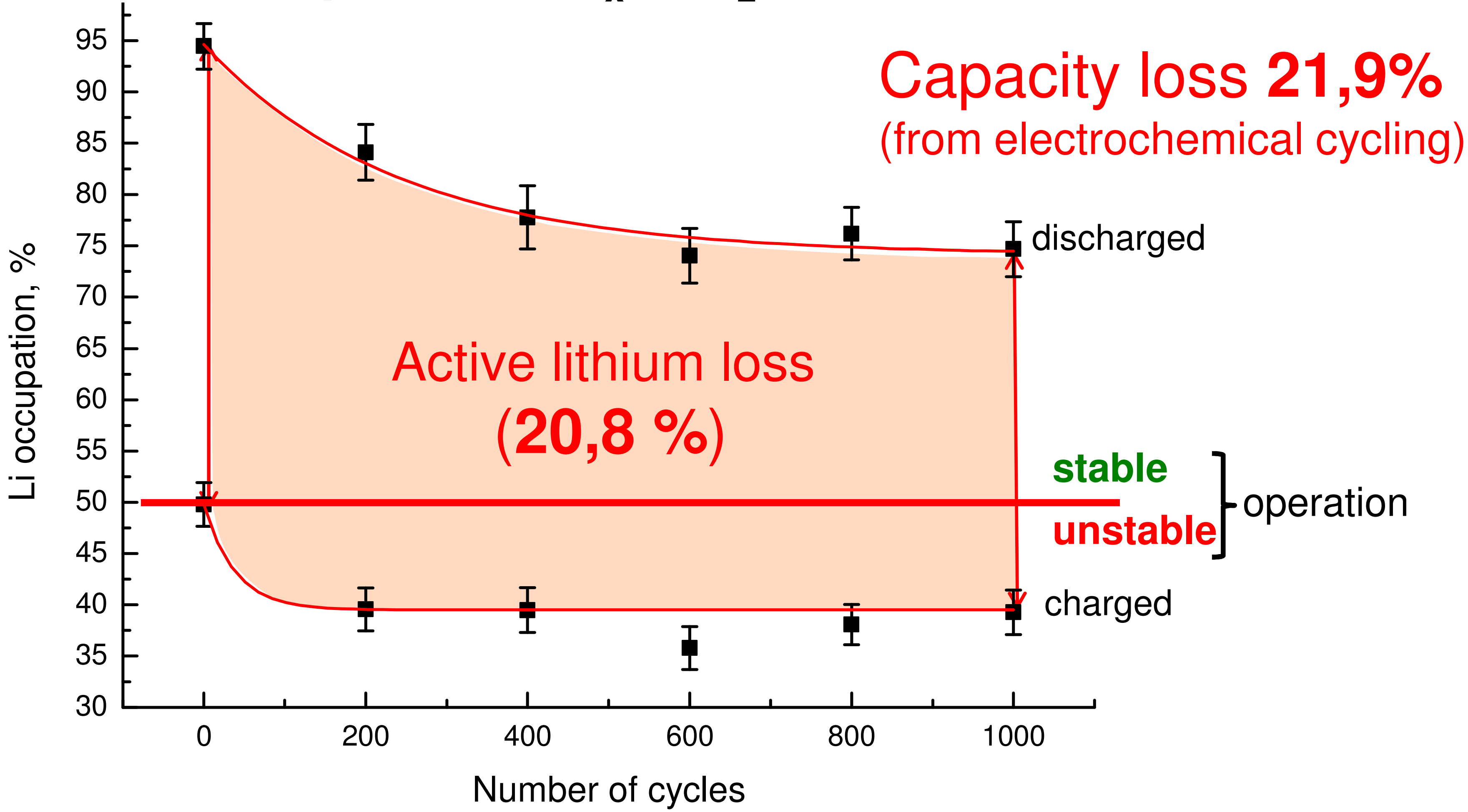
Reduction of lithium inside the anode:
25 °C → 26 %
50 °C → 15 %

- More intermediate LiC_{12} in the „fully“ charged state due to fatigue, i.e.
- less Li in the anode in fatigued state due to „anode excess“ by shift of the voltage window.
- Elevated temperature: less overvoltage and less fatigue.

O. Dolotko, *J. Electrochem. Soc.* **159** (2012) A2082

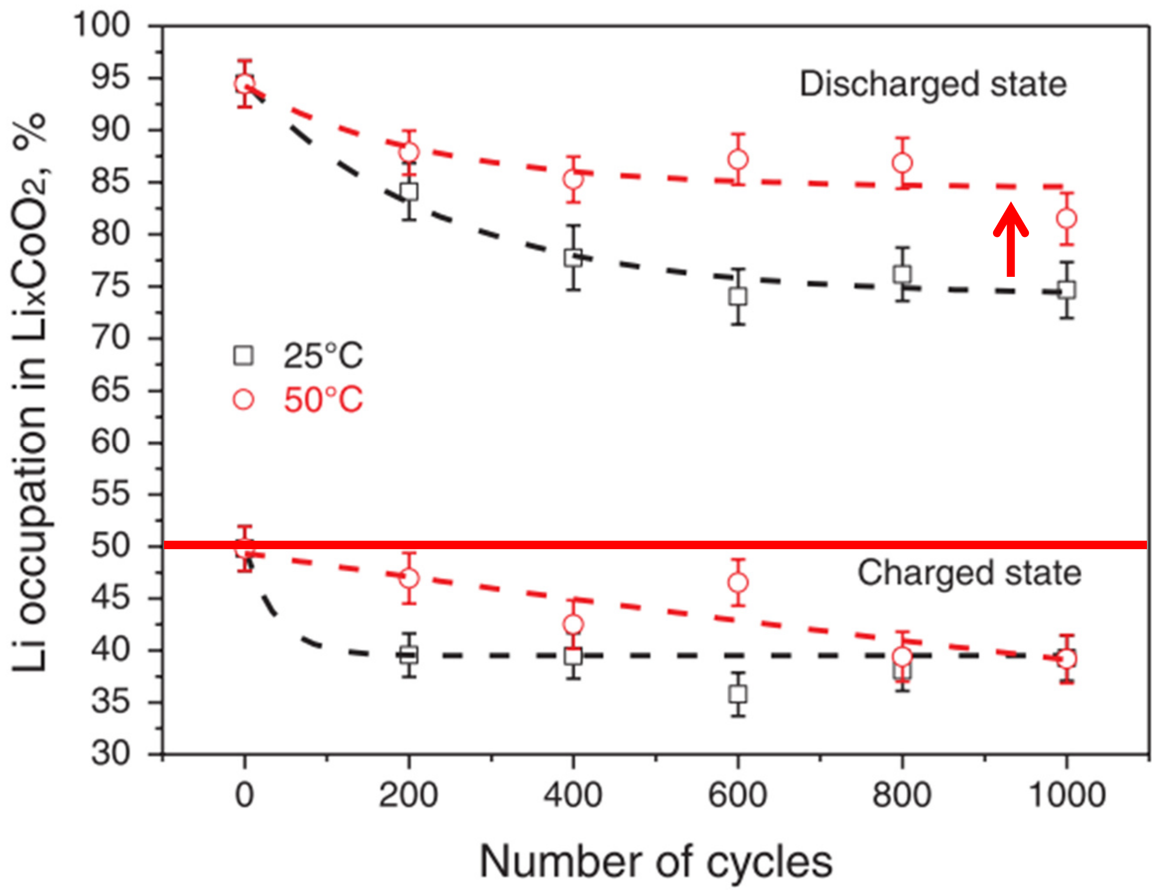
Lithium occupation in Li_xCoO_2 (cathode)

KIT
Karlsruhe Institute of Technology



- 18650 cell, cycling at 1C, 4.2 – 2.0 V, 25 °C

Lithium occupation in Li_xCoO_2 (cathode)



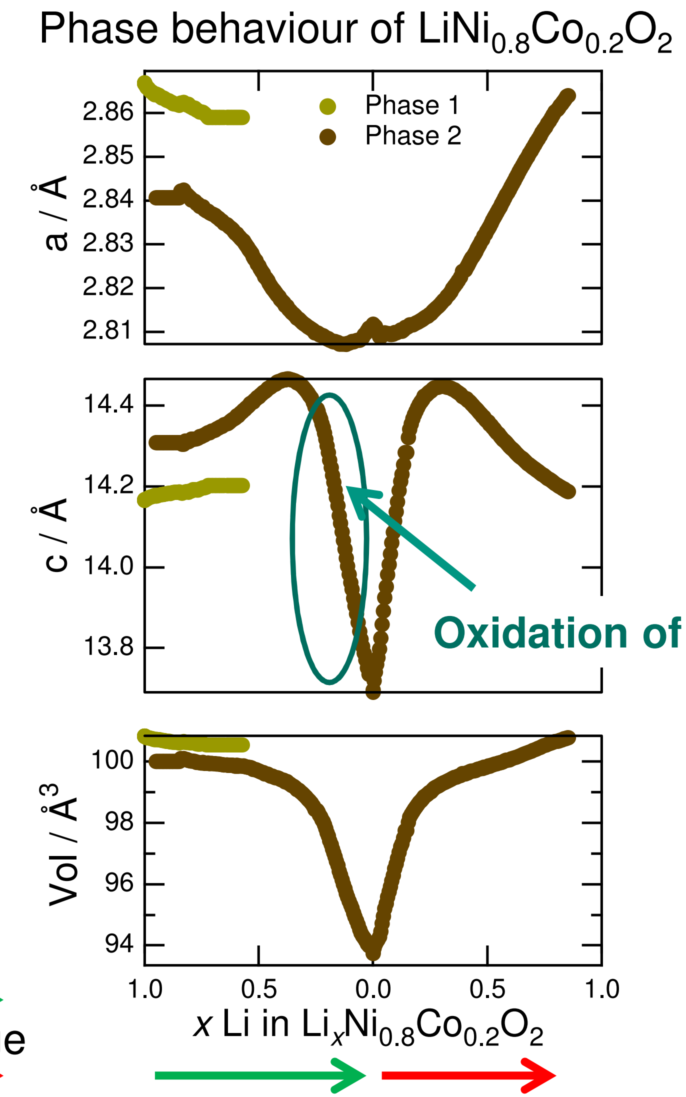
- 18650 cell, cycling at 1C, 4.2 – 3.0 V, 25 °C and 50 °C

unstable operation

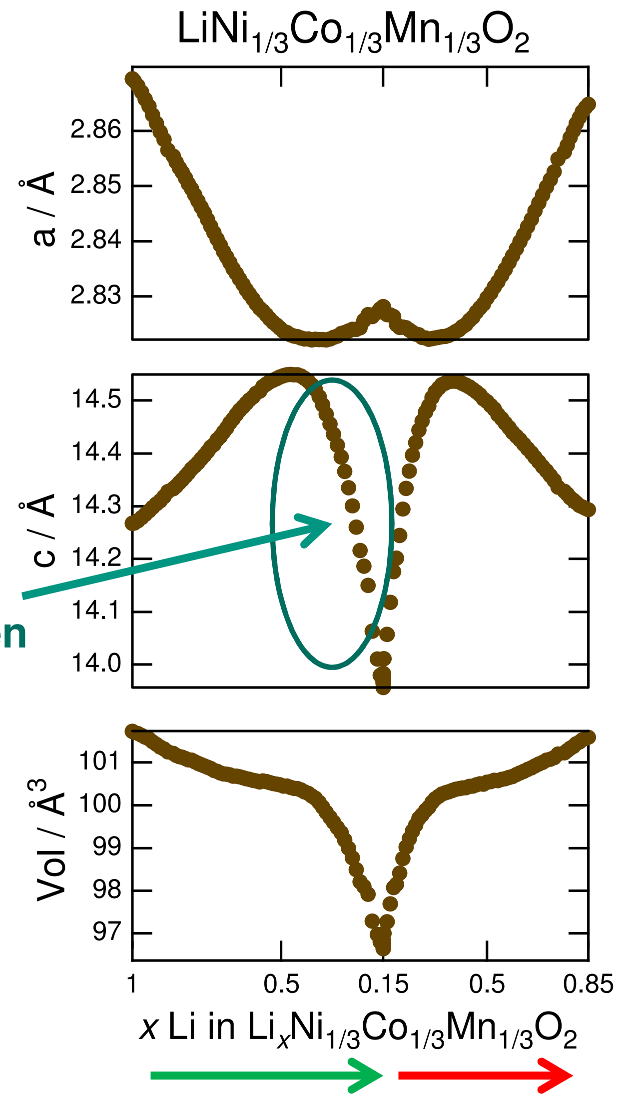
- Li occupation in the discharged state higher at 50°C.
- Safety problems due to low Li-content in the carged state also at higher temperature!

O. Dolotko, *J. Electrochem. Soc.* **159** (2012) A2082

Lattice strain in layered oxides LCO, NCM, NCA



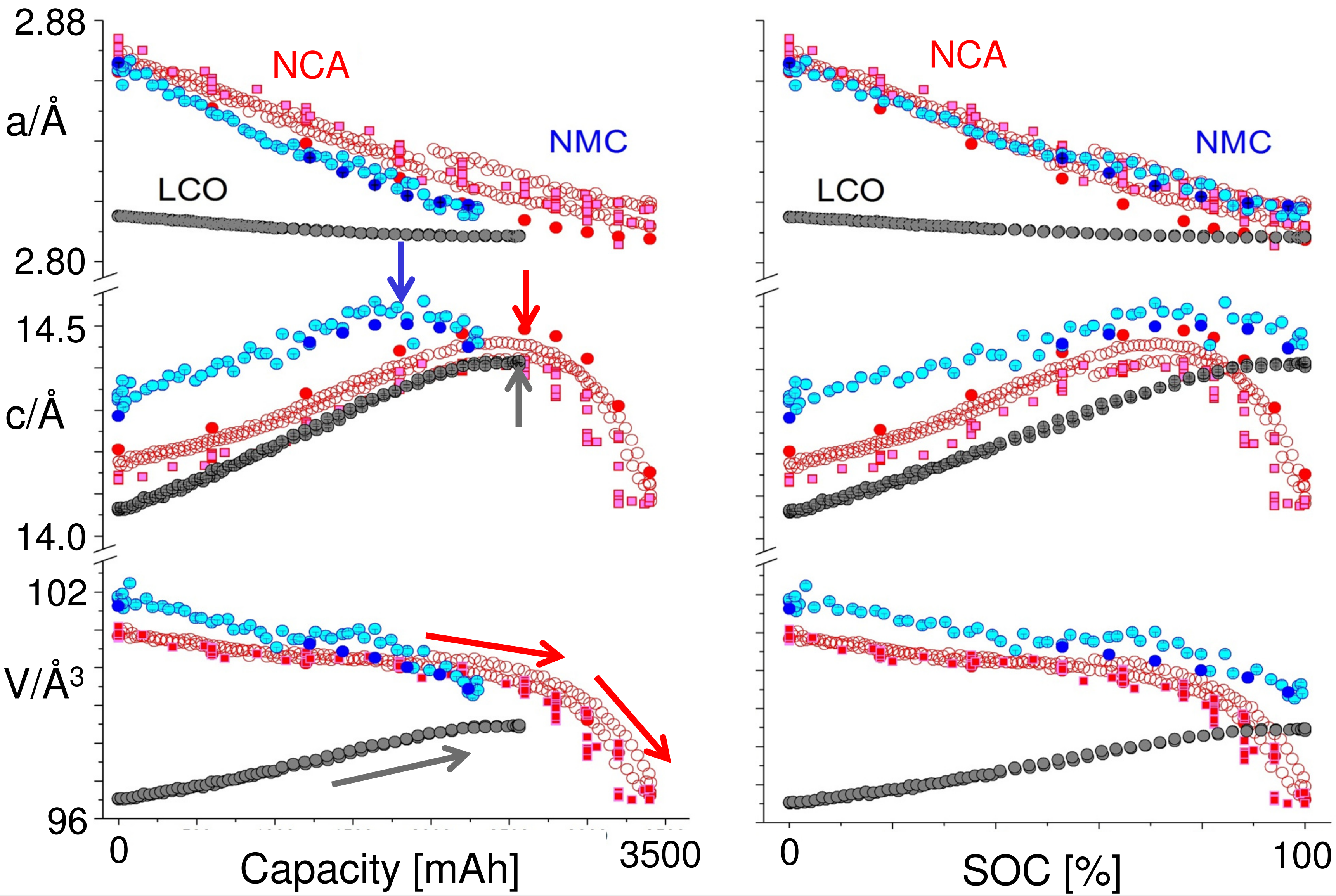
Oxidation of oxygen



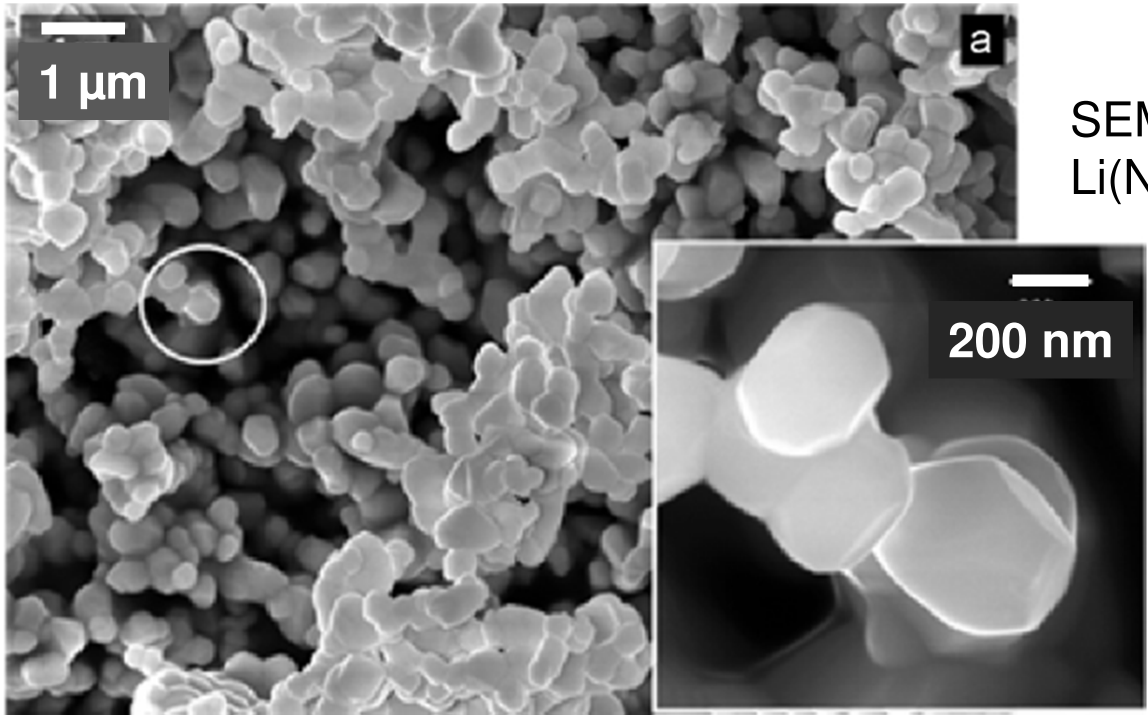
charge

discharge

Comparison of lattice strain in LCO, NCM, NCA



Lattice strain and microstructure: NCM



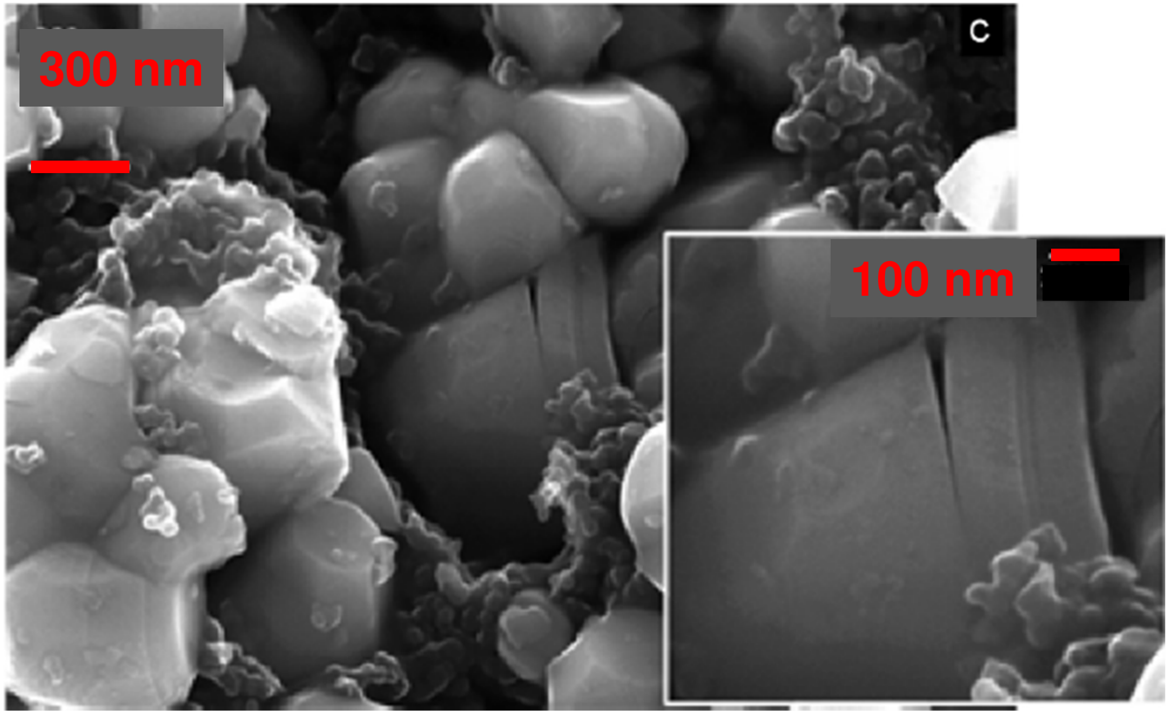
SEM images of as-prepared $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powder

N. Kiziltas-Yavuz et al.,
Electrochim. Acta. **113** (2013) 313

Lattice strain and microstructure: NCM

SEM images of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$
after cycling between 3.0 and 4.2 V

N. Kiziltas-Yavuz et al.,
Electrochim. Acta. **113** (2013) 313



Cathode fatigue

- Positive electrode materials are the only source of exchanged Li.
- Most serious limitation for the energy density of a cell.
- Restricted stability with respect to the Li-content (except $LiFePO_4$).
- Details of the electronic structure play a crucial role for
  - cell voltage,
  - electronic conductivity,
  - stability range, band overlap: oxidation of oxygen,
  - activitiy of specific ions (energy levels)
  - and more…
- Structure and composition gradients within one particle/crystallite, for example a NiO-type surface layer in NCA.
- One-phase or two-phase mechanisms.
- Significant structural distortions and volume changes.
- High probability for cracks, especially in blend cathodes, working over a broad voltage range.

Karlsruhe Institute of Technology

IAM
Institut für Angewandte Materialien

HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

TECHNISCHE
UNIVERSITÄT
DARMSTADT

Investigations on Fatigue of Li-ion batteries

HELMUT EHRENBERG INSTITUTE FOR APPLIED MATERIALS – ENERGY STORAGE SYSTEMS (IAM-ESS)

Introduction into Fatigue of Li-ion batteries: General aspects

Materials challenges and the cell level

in operando techniques for life-time studies:

Neutron tomography and diffraction on 18650-type batteries

→ **Conclusion**

Conclusions

- Fatigue of Li-ion batteries has to be addressed on cell level.
- Capacity losses and internal resistance are determined by materials and balancing.
- Materials interactions are very pronounced in batteries.
- No individual optimization of materials, only within specific cells!

- Dedicated methods are needed to investigate fatigue under real operation conditions.
- Data analysis is a specific challenge.
- Complementary methods are essential.
- Probably not all basic physical parameters can be measured.

- Complex functionalities have to be considered
- Too many degrees of freedom: only knowledge-based approaches are promising.

Acknowledgement

Karlsruhe Institute of Technology

Natalia Bramnik
Susana Darma
Oleksandr Dolotko
Markus Herklotz
Karin Kleiner
Michael Lang
Martin Mühlbauer
Kristian Nikolowski
Lars Riekehr
Anatoliy Senyshyn
Florian Sigel

&

all SFB members

TECHNISCHE UNIVERSITÄT DARMSTADT

SFB 595

Synthese
Modellierung
Bauteil
Charakterisierung
Elektrische Ermüdung

Deutsche Forschungsgemeinschaft

DFG