Karlsruhe Institute of Technology

KNMF Karlsruhe NANO MICRO Facility

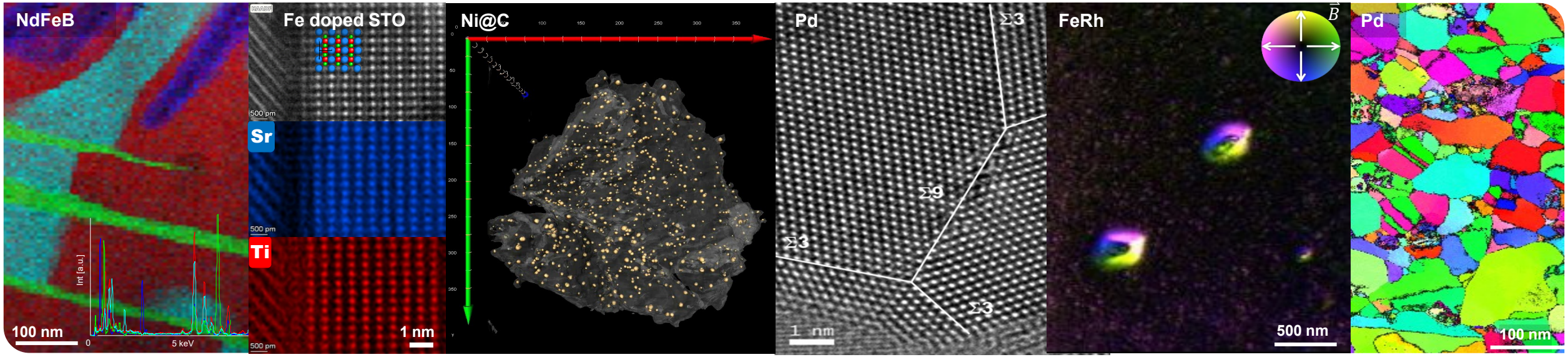
HIU HELMHOLTZ INSTITUTE ULM Electrochemical Energy Storage

TECHNISCHE UNIVERSITÄT DARMSTADT

– Joined Lab MDMC –

Advanced Electron Microscopy to Understand Processes in Batteries

Ziming Ding, Kai Wang, Yushu Tang, Di Wang, Xiake Mu, Ali Ahmadian, Christian Kübel



Joint Lab Model and Data Driven Materials Characterization

Developments

Correlative Characterization

- 2D/3D correlative characterization from mm to nm

New Instrumentation & Methods

- Cross-sector technology transfer
- High-dimensional data driven microscopy
- Integrated multi-modal platform

Meta-Data Management

- Common descriptions
- Meta data exchange

HELMHOLTZ MDMC

Applications

Quantum Materials & Computation

Catalysis

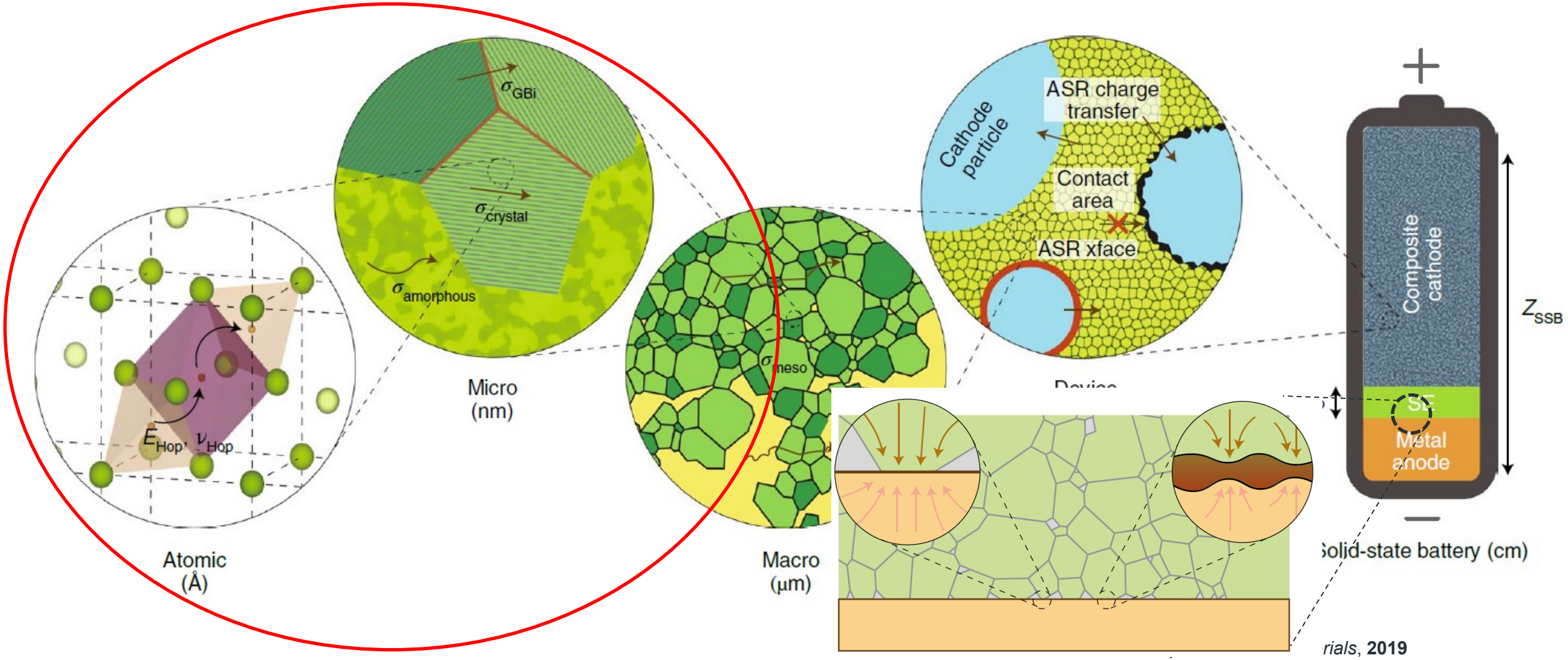
Electrochemical Energy Storage

.. and more …

In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Microstructure and Interfaces in Batteries



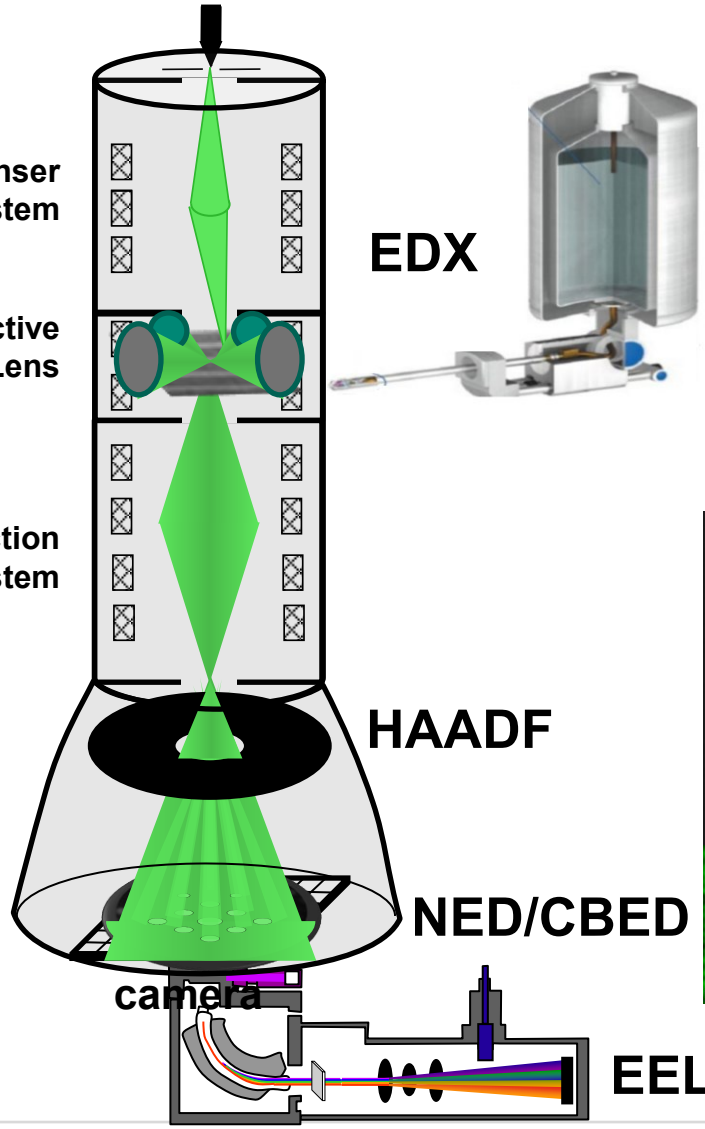
rials, **2019**

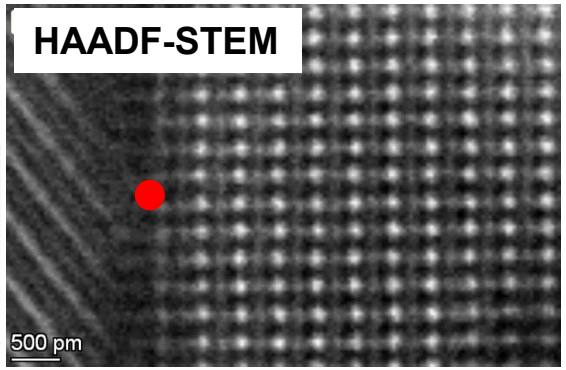
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

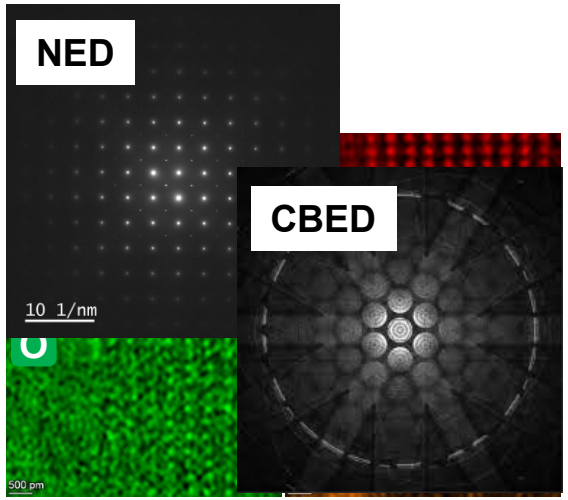
Methodology

Advanced (S)TEM Techniques



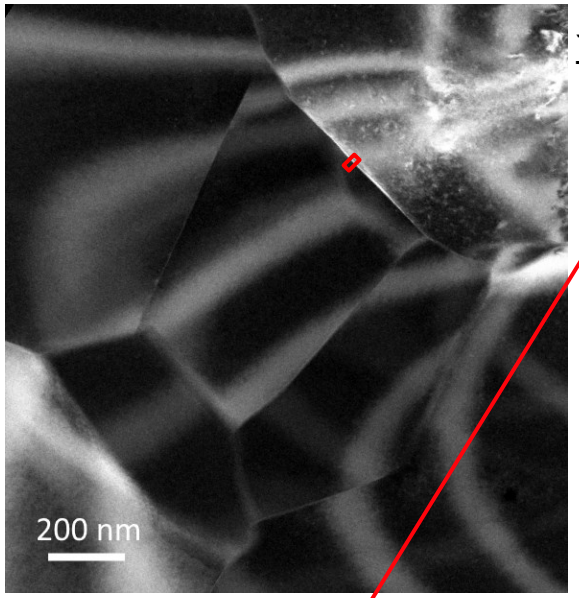


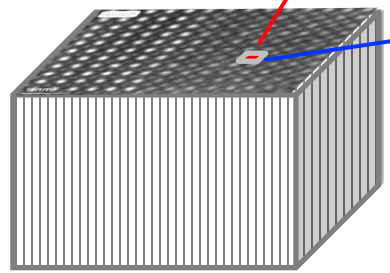
atomic structure I ~ $Z^{1.7}$

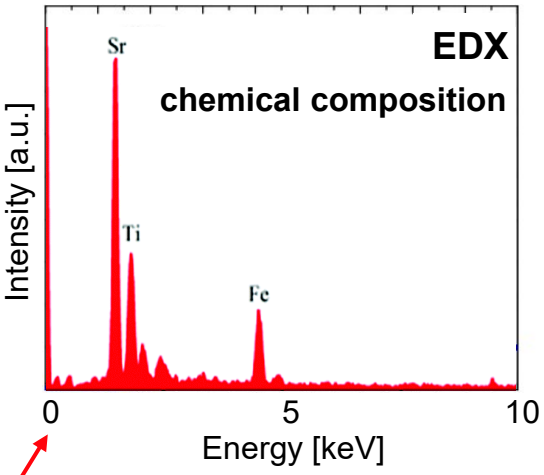


elemental distribution

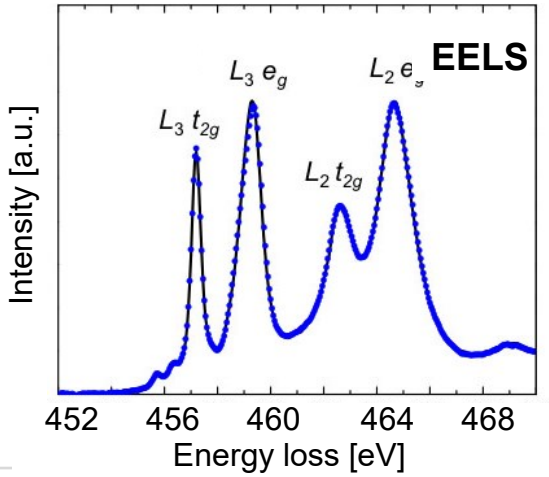
STEM







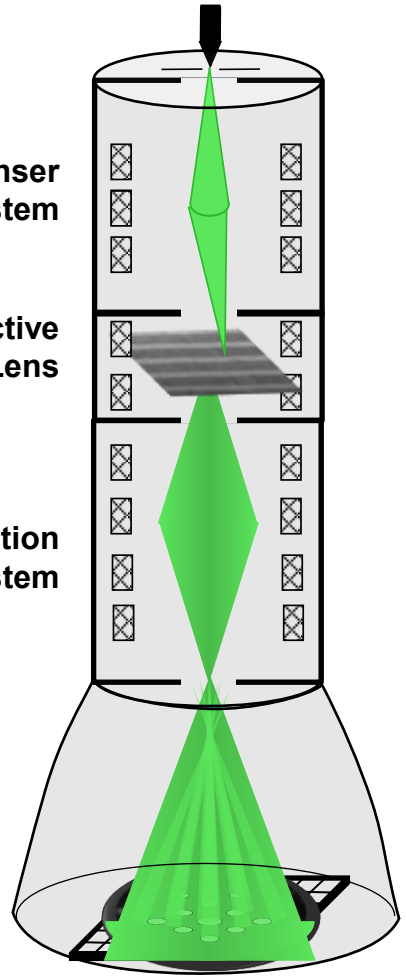
chemical composition
oxidation state
band gap



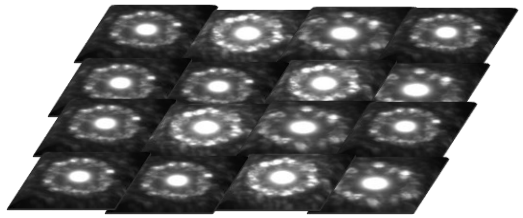
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

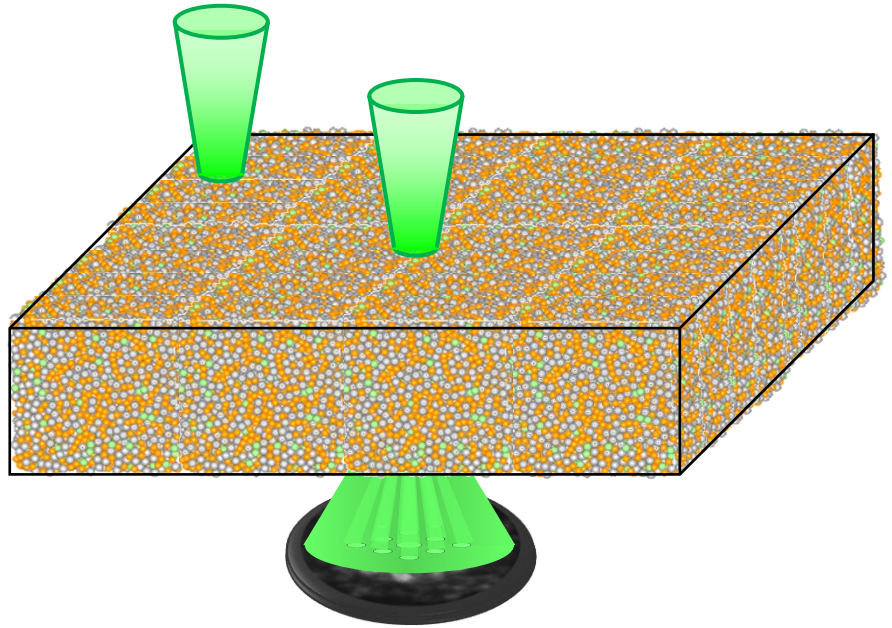
Advanced (S)TEM Techniques – 4D-STEM

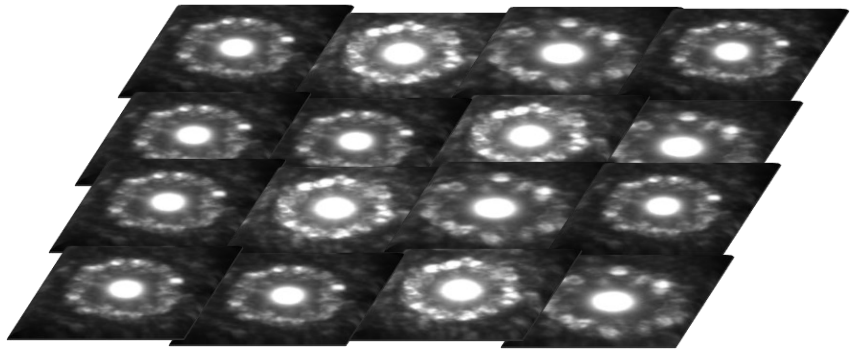


Diffraction Array



512x512 pixel
18000 fps

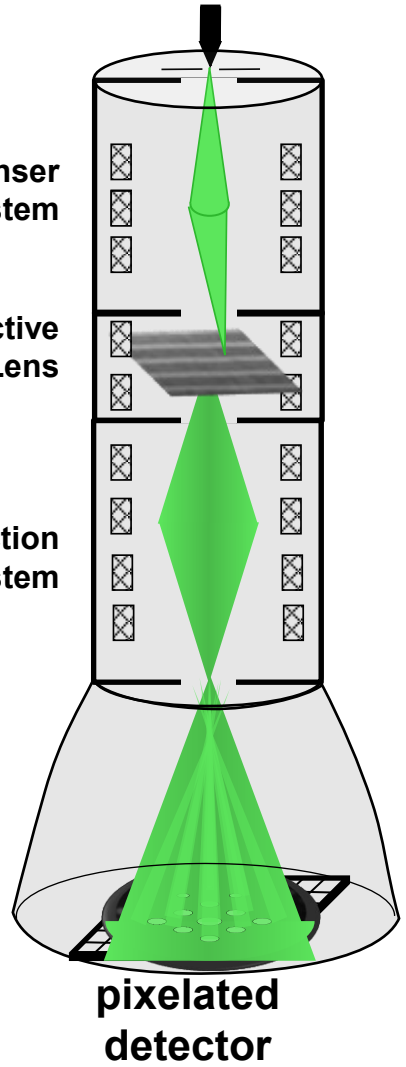




In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

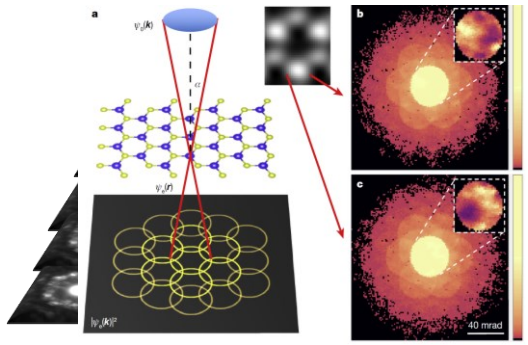
Advanced (S)TEM Techniques – 4D-STEM



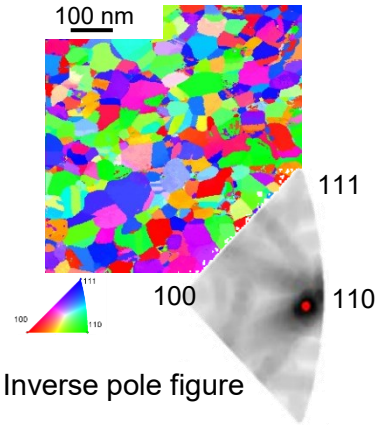
Diffraction

Ptychography

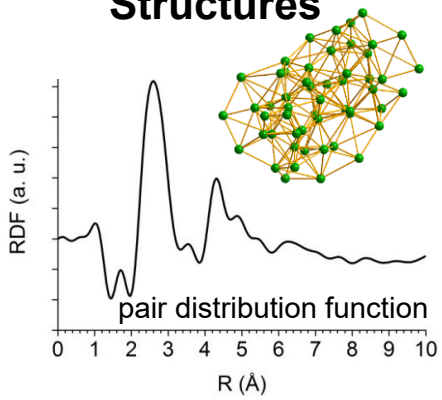
Array



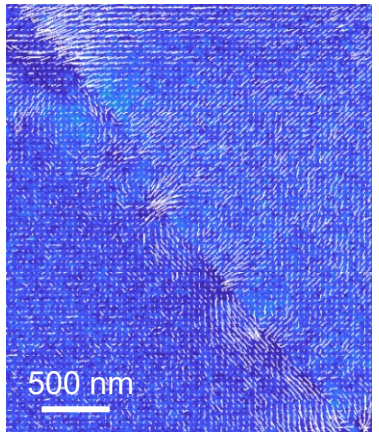
Crystal Orientation



Amorphous Structures



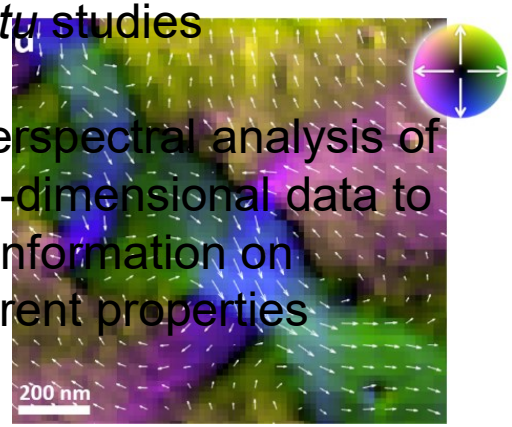
Strain Distribution



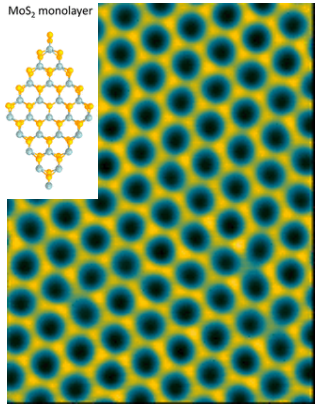
can be combined with *in-situ* studies

hyperspectral analysis of high-dimensional data to get information on different properties

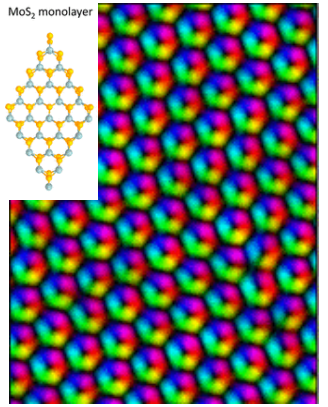
Magnetic Orientation



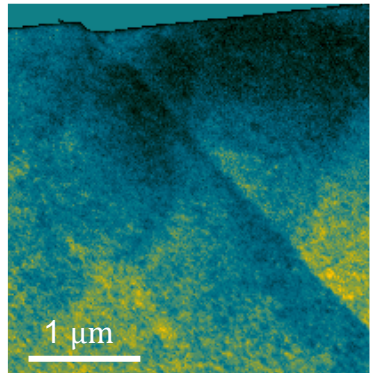
Charge Density



Electric Field



Atomic Packing Density



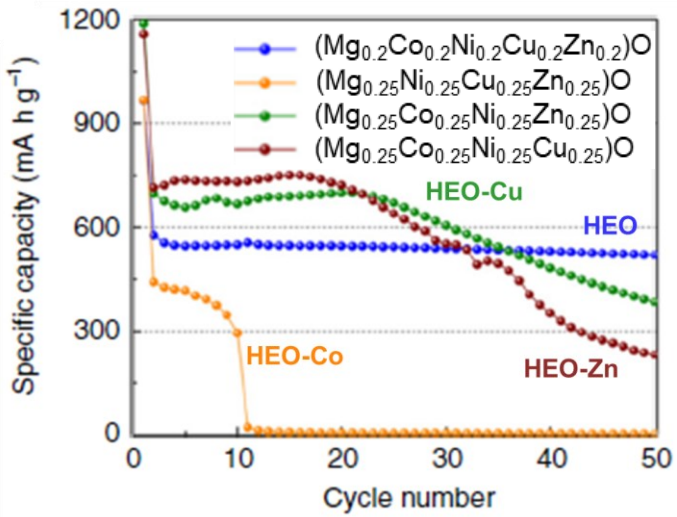
Cation Synergy in a CCO Electrode for LIBs


B. Breitung


A. Sarkar

Karlsruhe Institute of Technology

Understanding the Principle Processes in CCO Lithium Ion Batteries



A. Sarkar et al., Nat Commun 9 (2018) 3400

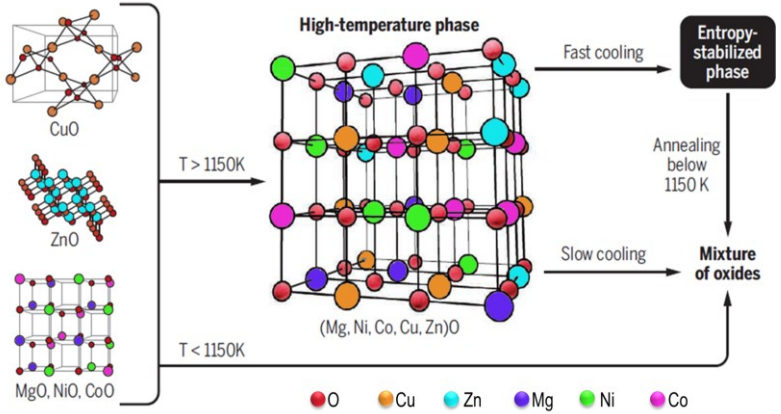
5 element CCO exhibits significantly improved battery performance of any 4 element MEO.

High entropy effect?

- CCO is metastable at RT
- Cycling should be irreversible

Cocktail effect

- Understand interaction of elements
- Clarify individual elemental contribution



N. Dragoe et al., Science 366 (2019) 573-574

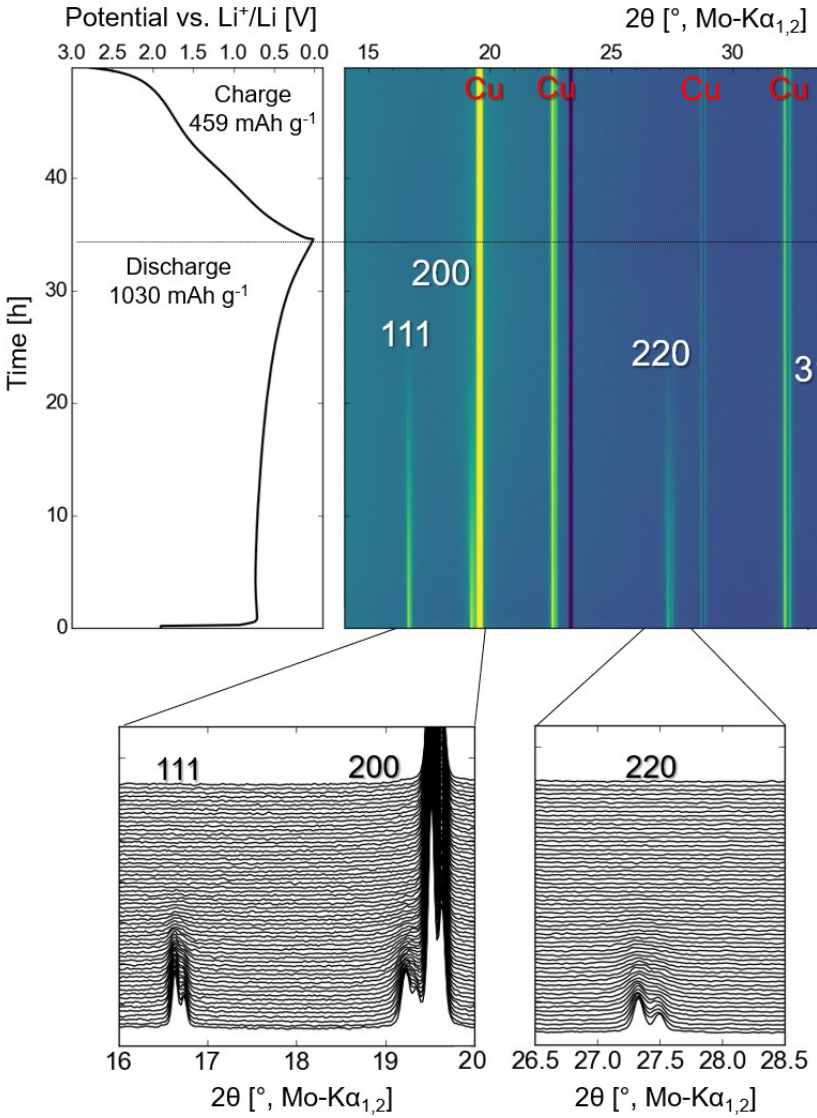
HEO formation at high temperatures,
but mixed oxides at low synthesis temperatures.

In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Cation Synergy in a $(Mg_{0.2}Co_{0.2}Cu_{0.2}Ni_{0.2}Zn_{0.2})O$ Electrode for LIBs

In-situ XRD and XAS



Cu^0 Ni^0 $Co^{0/2+}$ Zn^{2+} Mg^{2+}

cycling

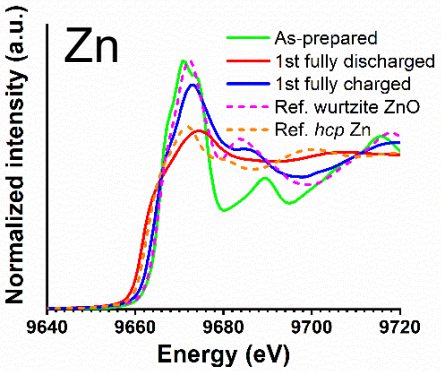
electrochemically active

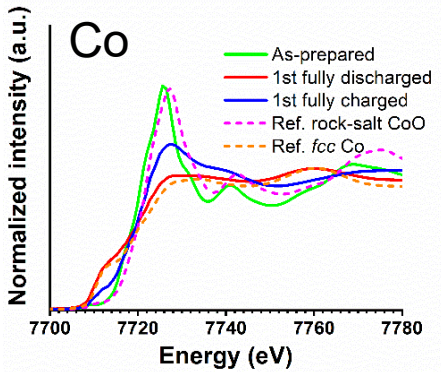
Cu^0 Ni^0 Co^0 $Zn^{0/1-}$ Mg^{2+}

first discharging

Cu^{2+} Ni^{2+} Co^{2+} Zn^{2+} Mg^{2+}

- **X-ray amorphous**





X-ray absorption spectroscopy

A. Sarkar et al., *Nature Comm.*, **2018**, *9*, 3400

In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

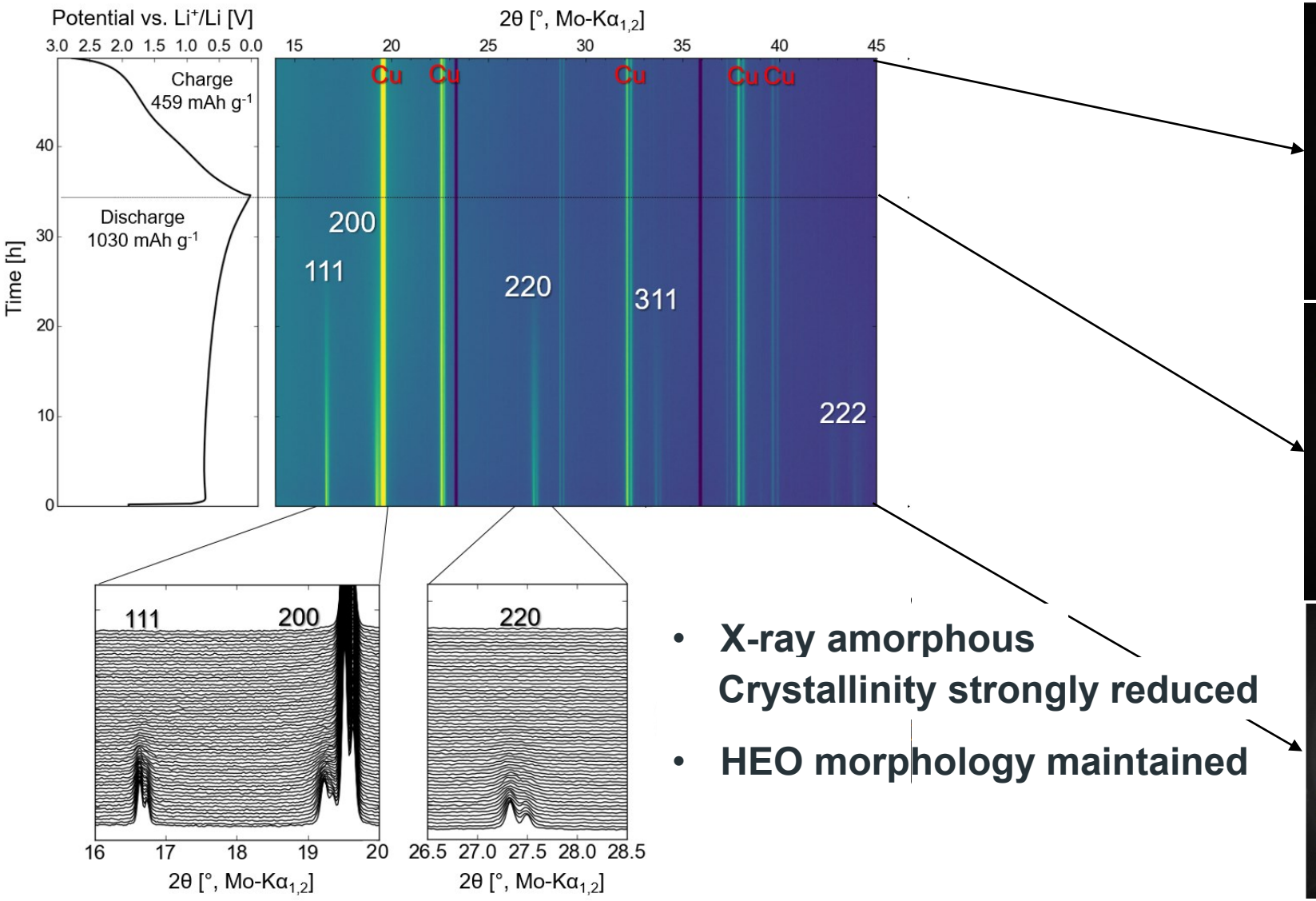
Cation Synergy in a $(Mg_{0.2}Co_{0.2}Cu_{0.2}Ni_{0.2}Zn_{0.2})O$ Electrode for LIBs

In-situ XRD and SAED/TEM Analysis

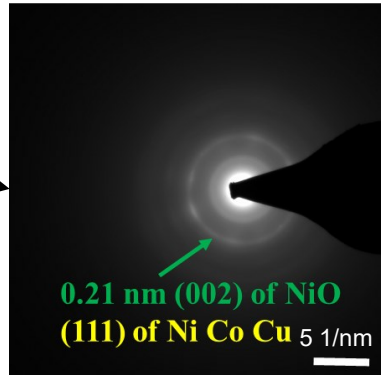

W. Hua

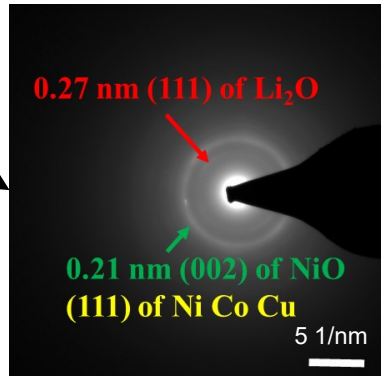

K. Wang

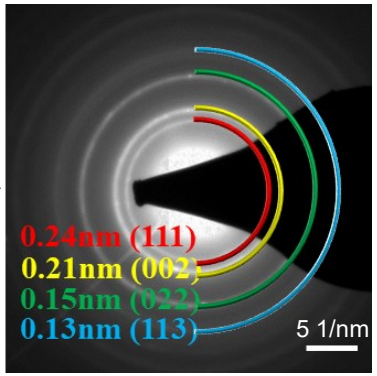
Karlsruhe Institute of Technology

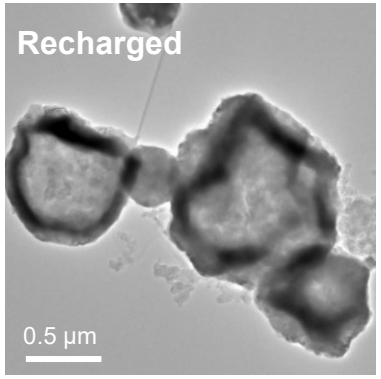


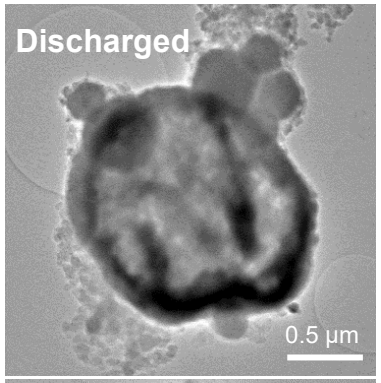
- **X-ray amorphous**
  Crystallinity strongly reduced
- **HEO morphology maintained**

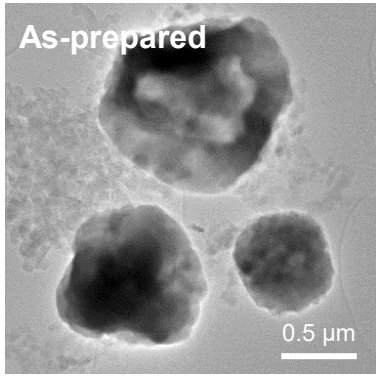












A. Sarkar et al., *Nature Comm.*, **2018**, *9*, 3400

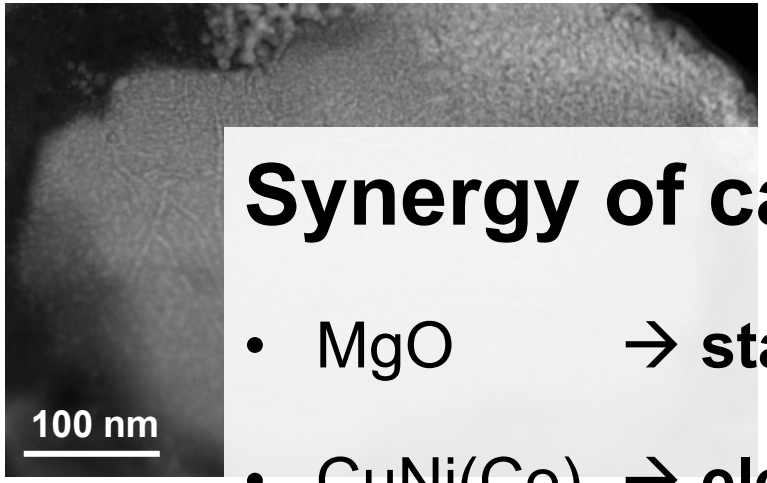
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Complex Metal/Oxide Composite Formation

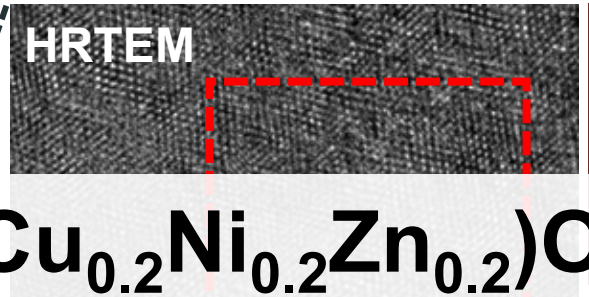
K. Wang Karlsruhe Institute of Technology

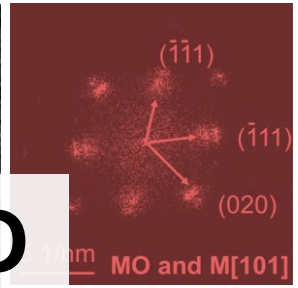
HAADF-STEM

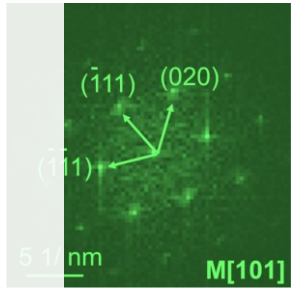


3D distribution of metallic alloy

HRTEM

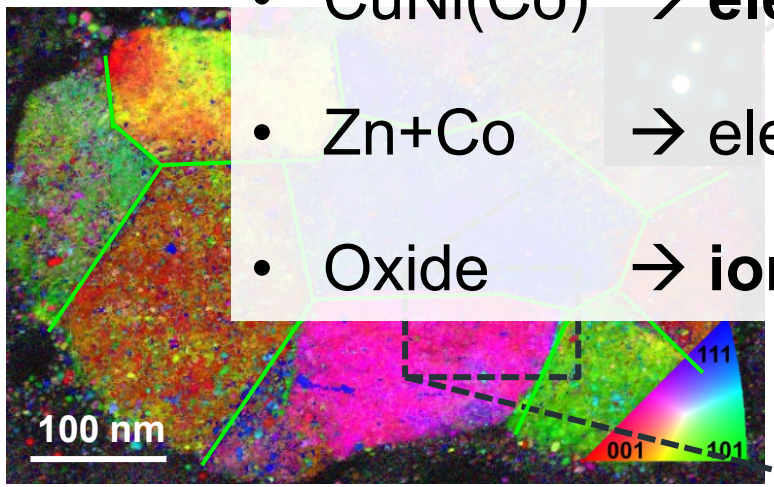




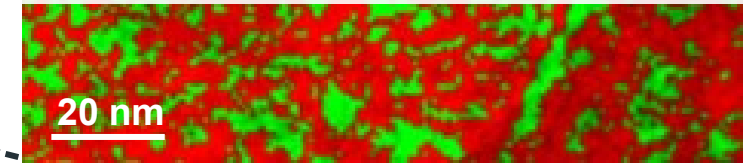


Synergy of cations in $(Mg_{0.2}Co_{0.2}Cu_{0.2}Ni_{0.2}Zn_{0.2})O$

- MgO → **stabilization** of microstructure (semicoherence)
- CuNi(Co) → **electrical conductivity** (GB + nanoparticles)
- Zn+Co → electrical **capacity**
- Oxide → **ionic conductivity**



crystal orientation map



phase map (alloy, oxide)

- CuNi(Co) alloy segregation at GB and as nanoparticles
  → electron conductive network
- **semicoherent interface of CuNi(Co) and MgO matrix**

→ **structural stability**

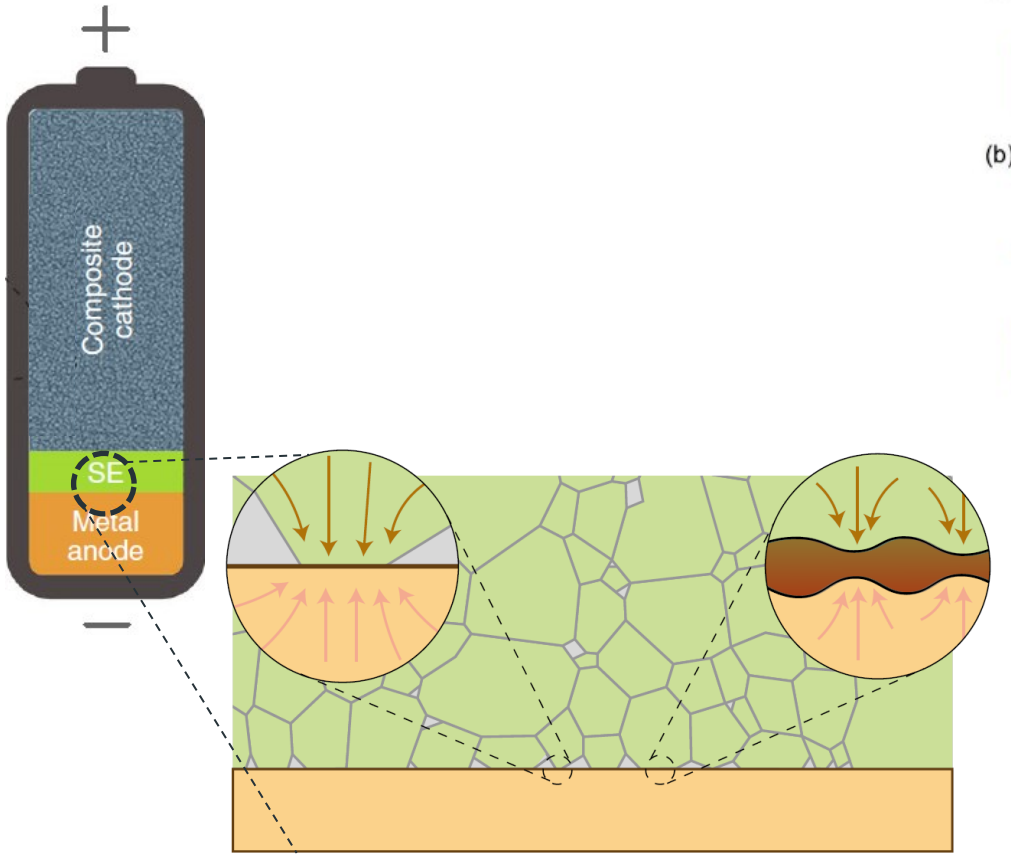
K. Wang et al., Nature Communication. **2023,** *14*, 1487

In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

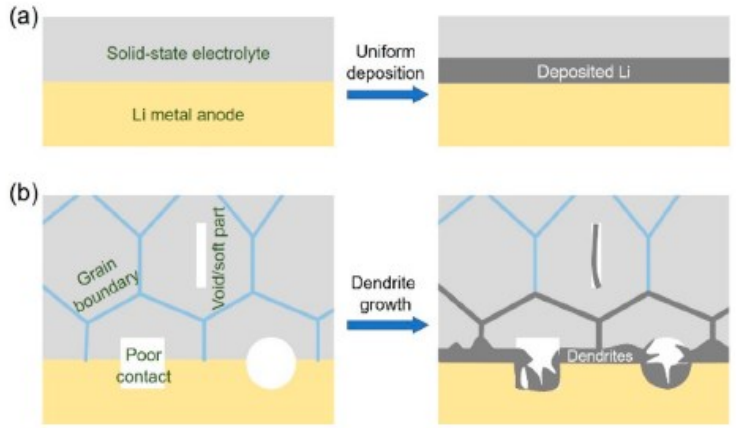
Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Microstructure and Interfaces in Solid State Batteries

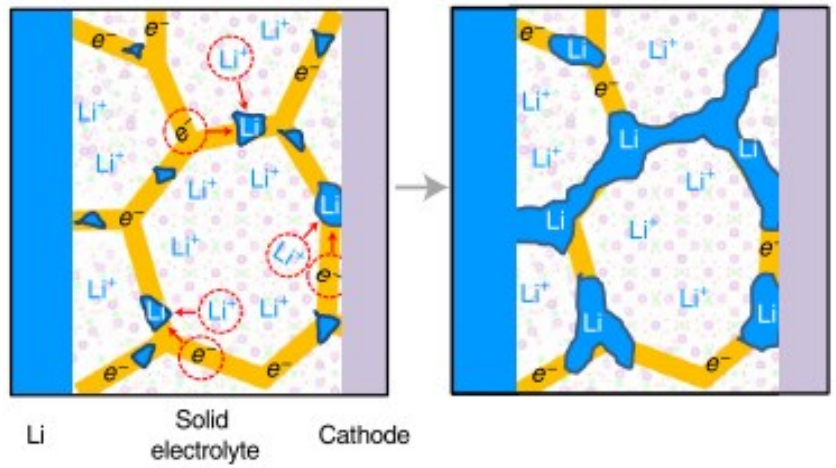
Dendrite Formation in Solid State Batteries



T. Famprikis, *Nature Materials*, **2019**



ACS Energy Lett. 2020, 5, 833−843



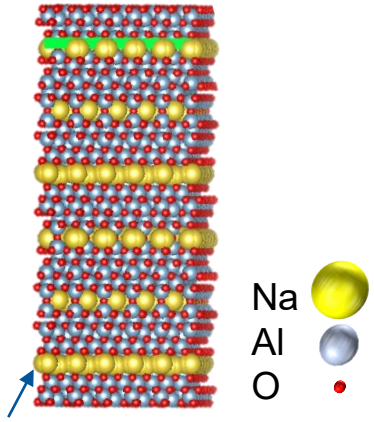
Liu, X., et. al.; Nature Material, 2021

Anisotropic Na^+ Ion Transport

- Role of orientation distribution in polycrystals?
- Role of GBs?

→ Na-β”-Al_2O_3
excellent stability against metallic Na
electron beam stable

anisotropic transport within grains
(Na-β”-Al_2O_3)

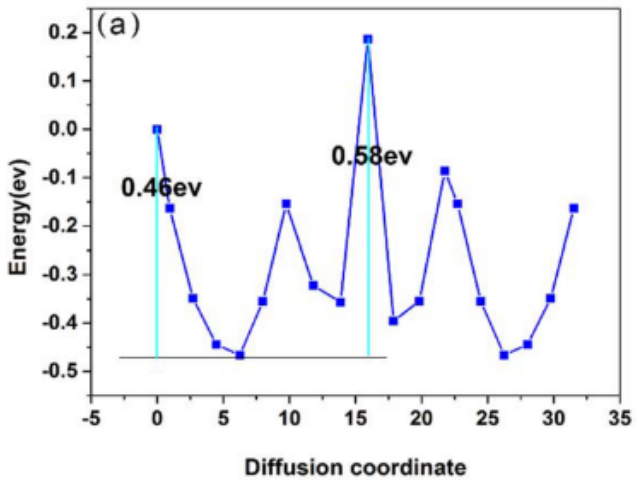


Na conductive layer

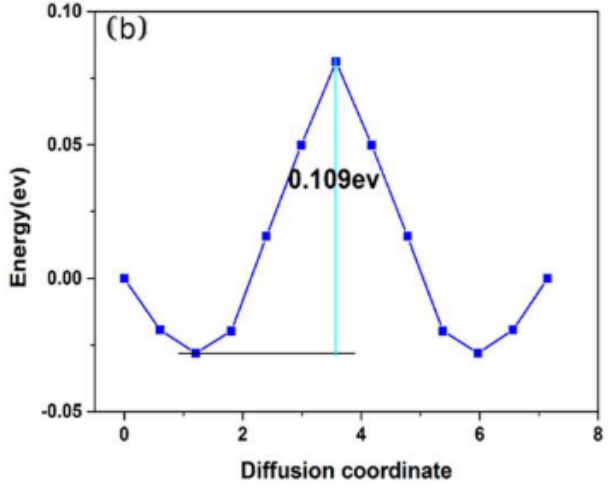
ACS Appl. Mater. Interfaces 2016, 8, 28216−28224

transport across/along grain boundaries
(in Na_3PS_4)

activation energy across GB



activation energy along GB

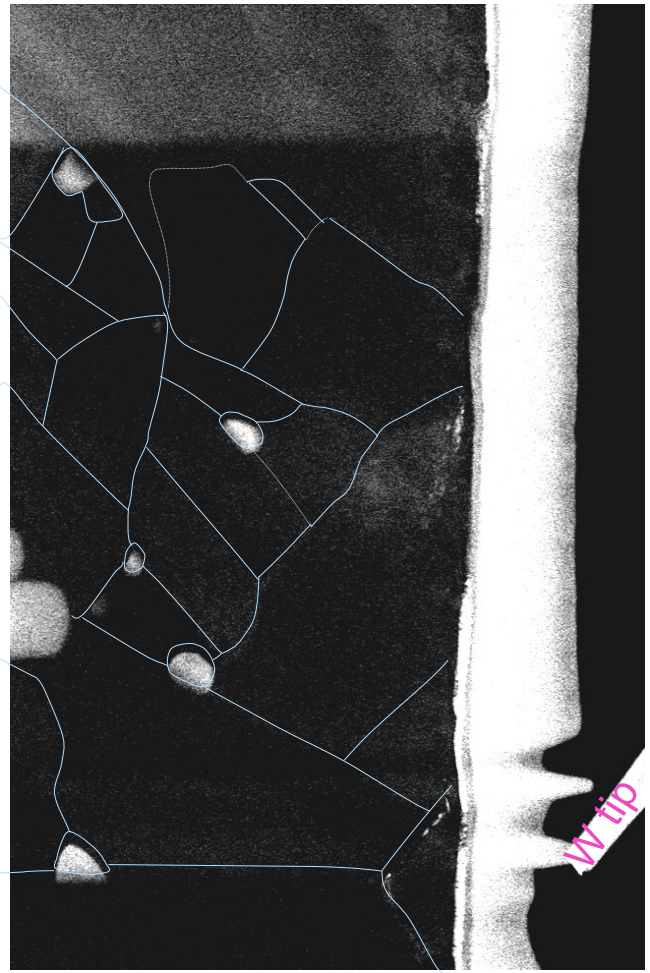


Yixuan Wang et. al. 2021 Mater. Res. Express 8 025508

In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

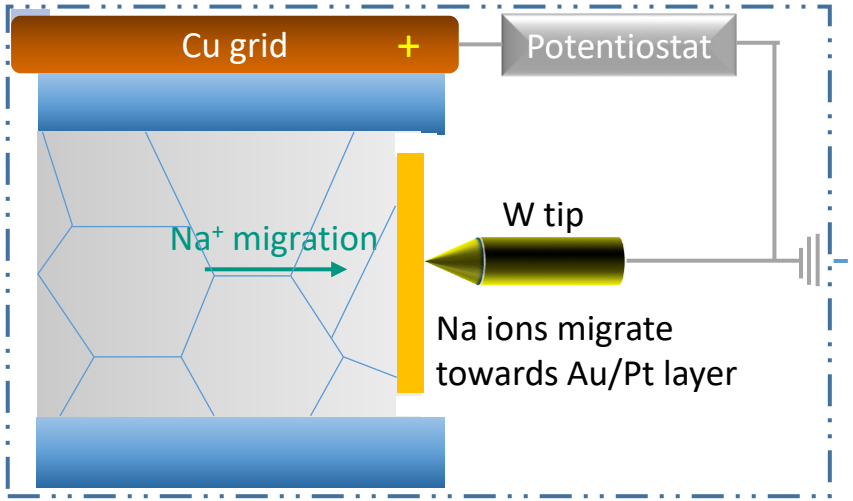
Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

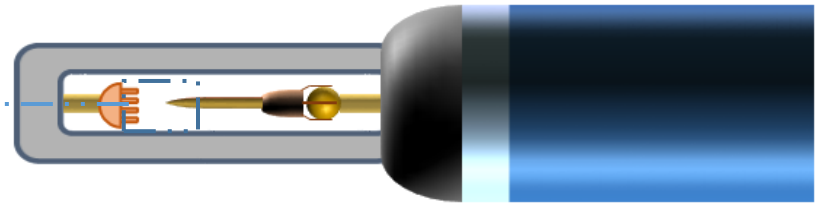
STM based *in-situ* TEM Measurement Setup



ADF-STEM image

FIB prepared metal coated TEM lamella on Cu half-grid for *in-situ* contacting with W tip.



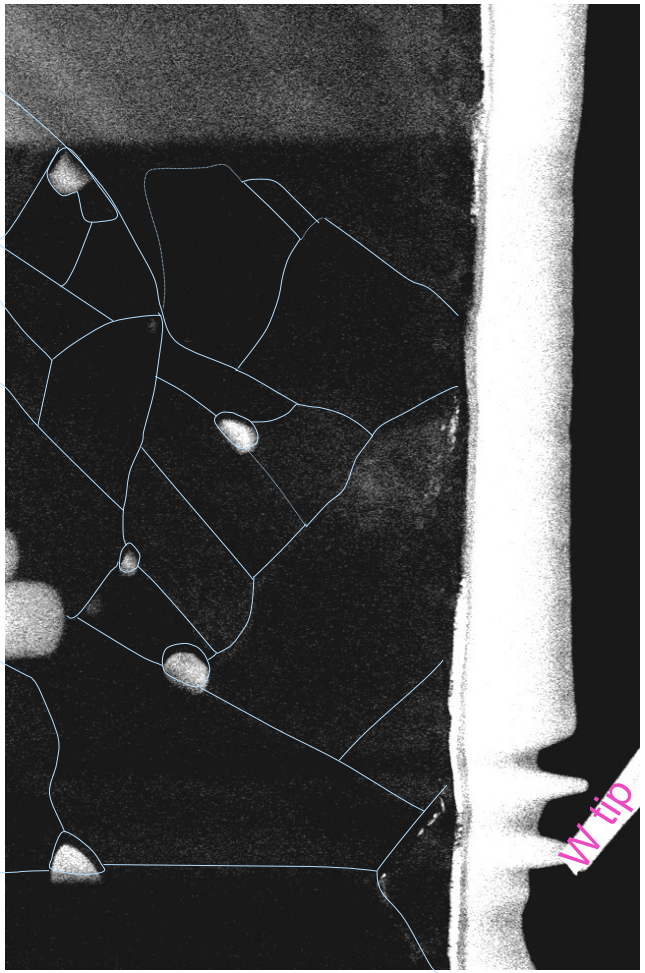


Large contact area through Au/Pt layer

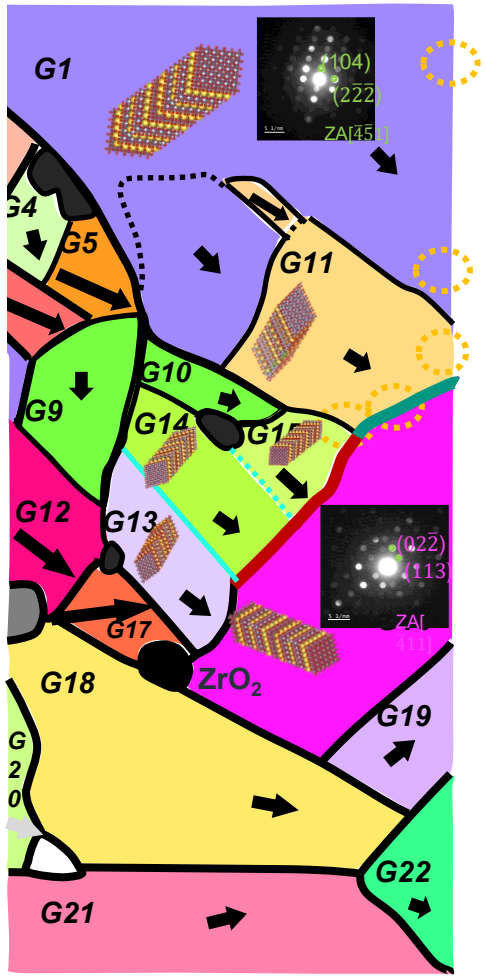
Z. Ding
Karlsruhe Institute of Technology

Z. Ding et al., *Advanced Energy Materials*, **2023**, *online*

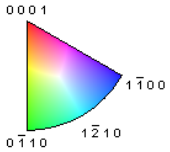
4D-STEM based Crystal Orientation Mapping



ADF-STEM image



simplified microstructure model



— large angle boundary

····· small angle boundary

ZrO_2

- Random orientation of grains
- Random orientation of GBs
- Mostly HAGBs

Z. Ding et al., *Advanced Energy Materials*, **2023**, *online*

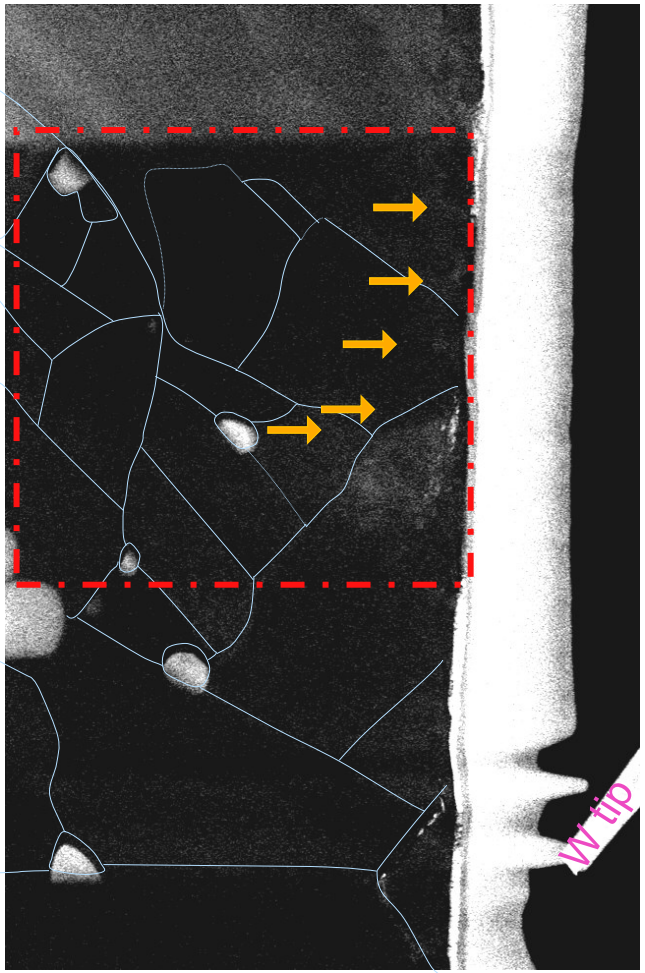
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

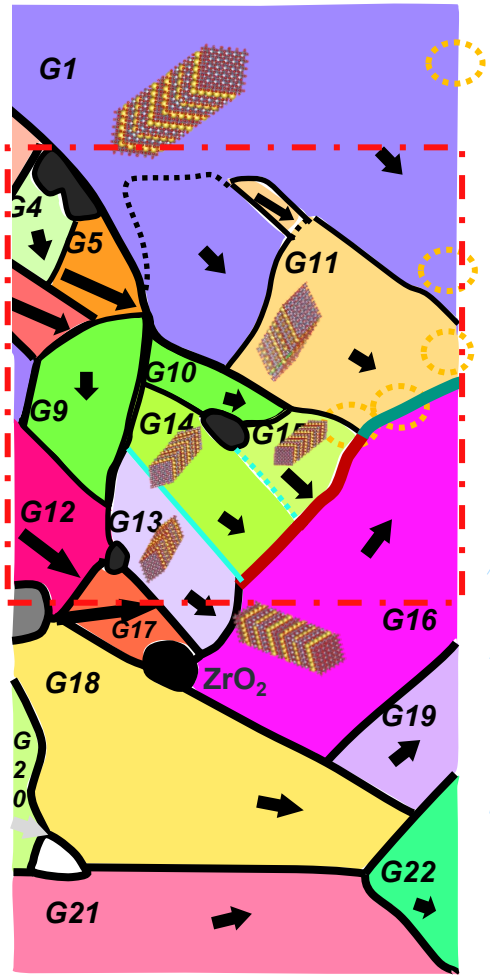
Z. Ding
Karlsruhe Institute of Technology

Na Filament Formation during *in-situ* Biasing

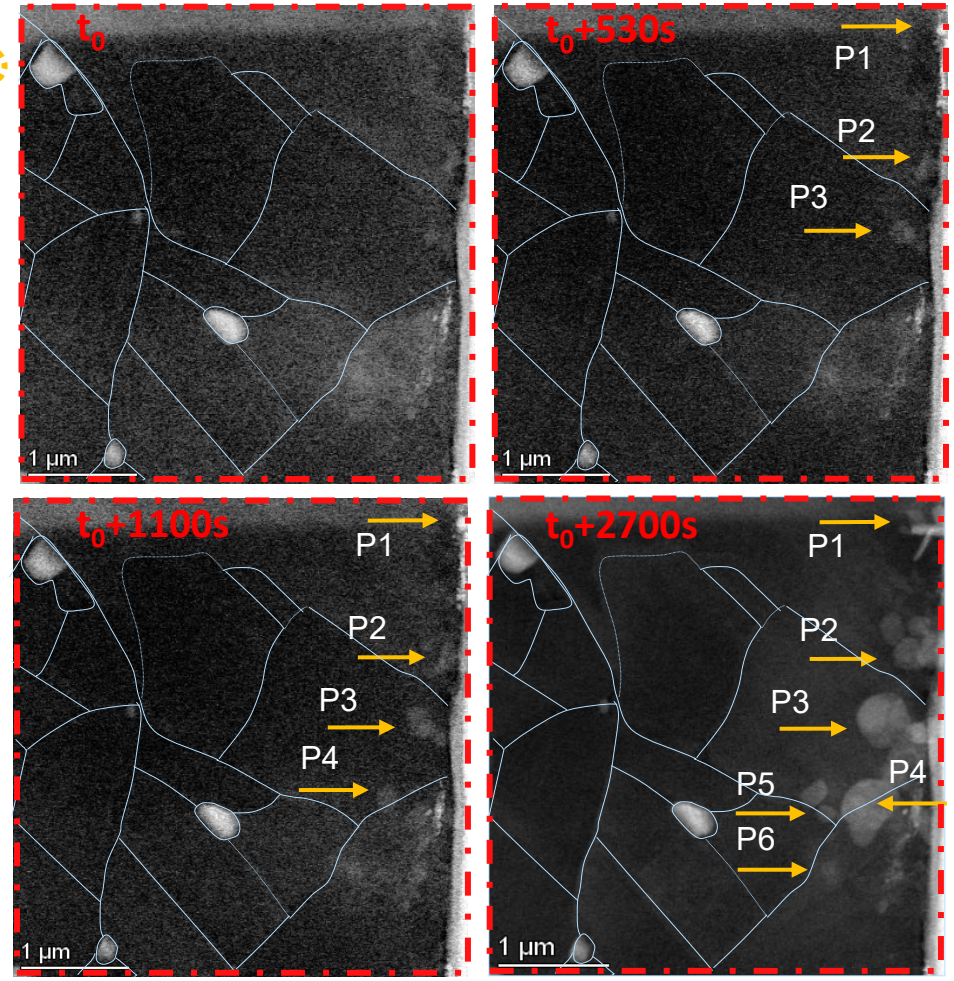
Z. Ding
Karlsruhe Institute of Technology



ADF-STEM image



simplified microstructure model



snapshots from *in-situ* series

Na filament formation

- Interface between electrolyte and metallic layer
- Selected grain boundaries

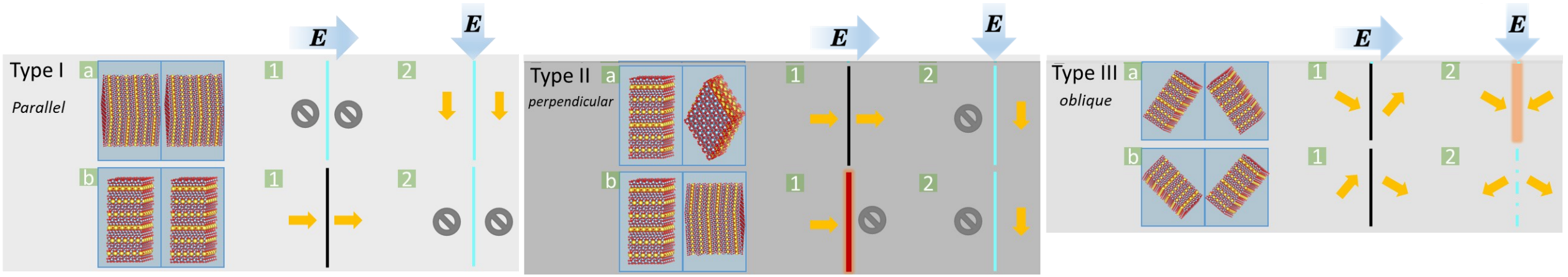
Z. Ding et al., *Advanced Energy Materials*, **2023**, *online*

In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Simplified Transport Model at Grain Boundaries

Z. Ding
Karlsruhe Institute of Technology



Unaffected GBs

ion migration across GBs

Blocking GBs

Blocking GBs; potential ion migration along GBs

- Preferential sodium filament formation at blocking boundaries
- Filament formation (mostly) follows GBs with electrical contact to electrode

Z. Ding et al., *Advanced Energy Materials*, **2023**, *online*

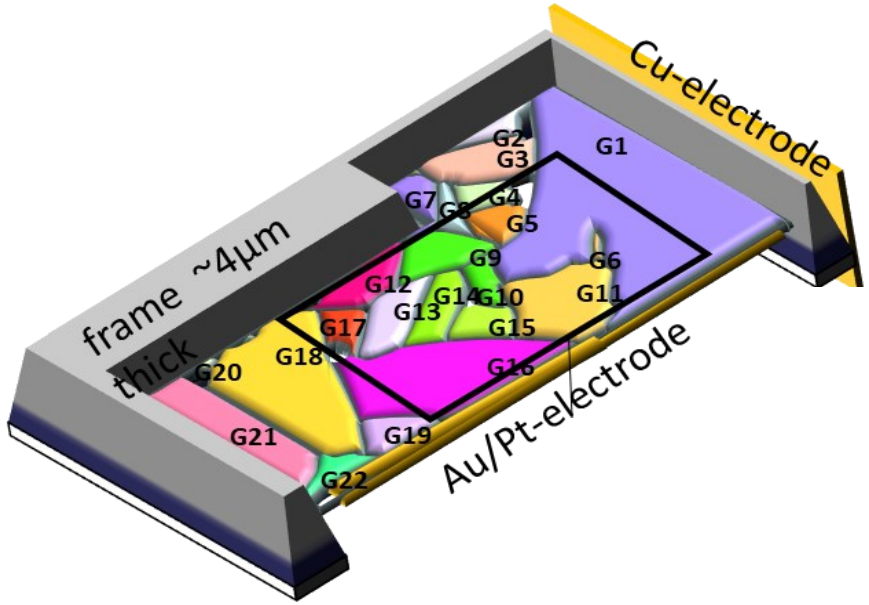
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Modelling Ion Transport


J. Janek

JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN



transport parameters:

σ_{ip} = 1 S/m, σ_{op} = 10^{-3} S/m,

δ_{GB} = 1 nm, σ_{GB} = 10^{-3} S/m

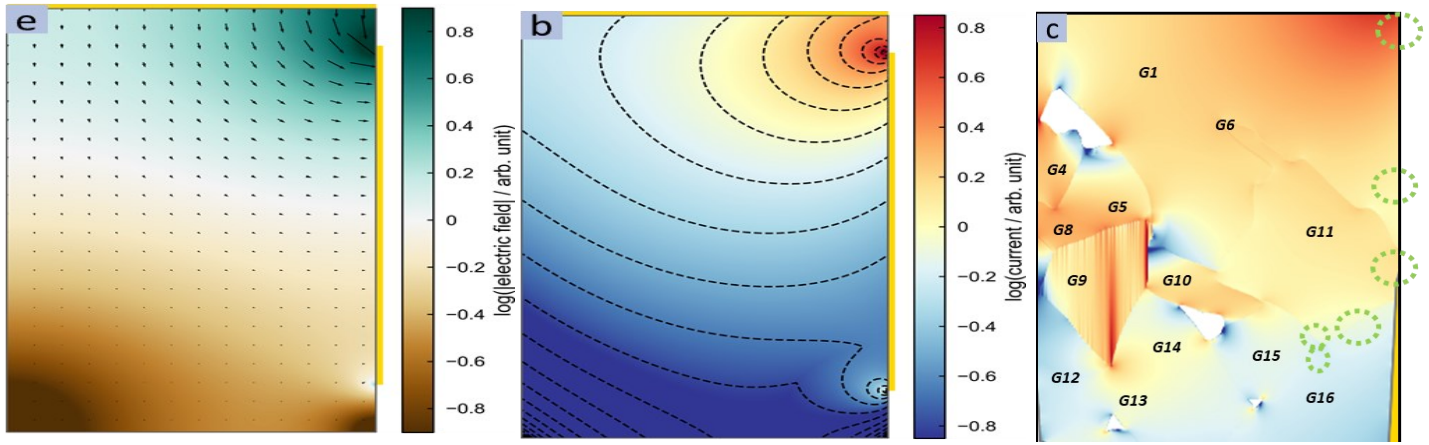
texture & grain boundary engineering

Electric Field

Sodium Ion Current Density

isotropic microstructure

experimental microstructure



- Broad distribution of currents (1–2 orders of magnitudes)
- GB conductivity effects transport pathways
- Sodium filament formation at boundaries between high and low conductivity
- Filament formation (mostly) follows GBs with electrical contact to electrode

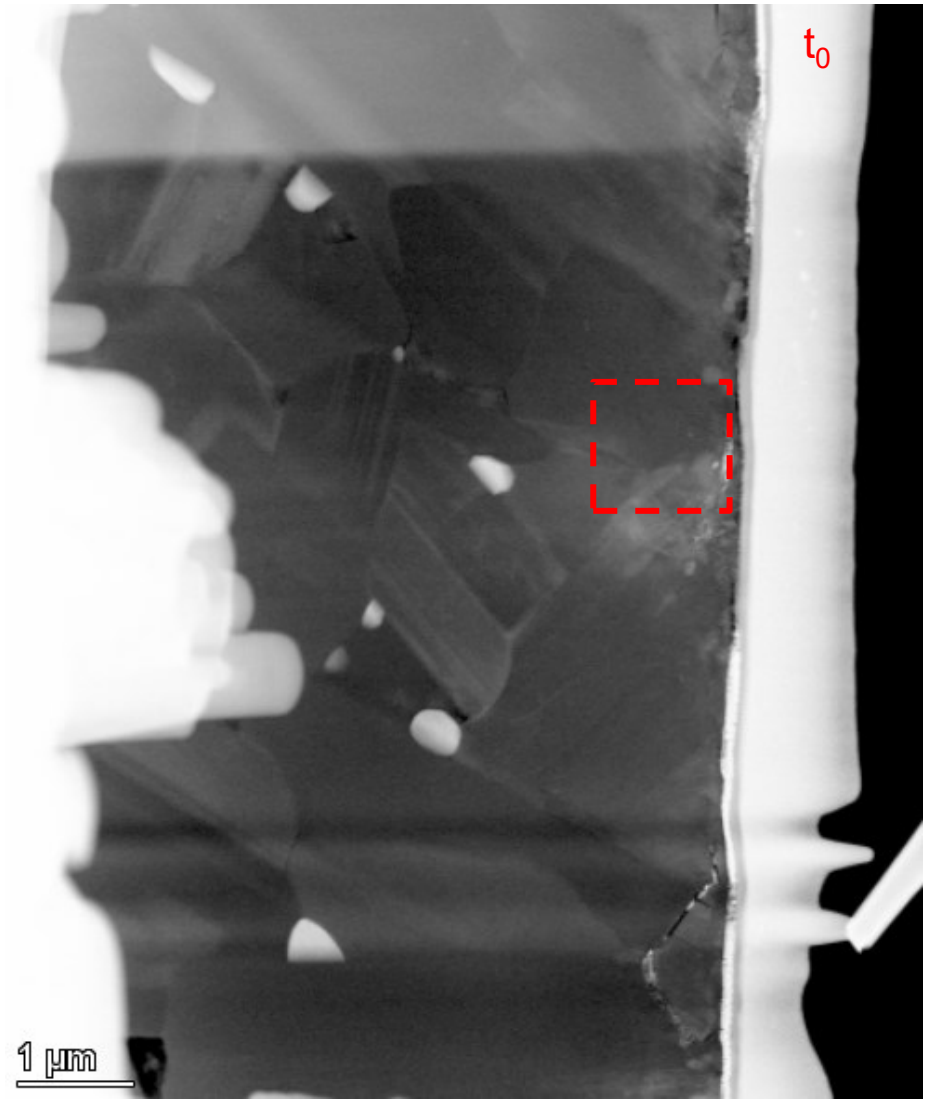
Z. Ding et al., *Advanced Energy Materials*, **2023**, *online*

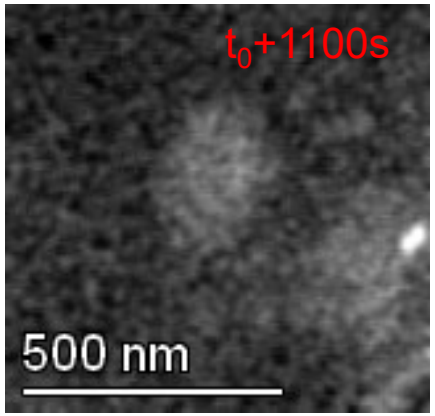
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

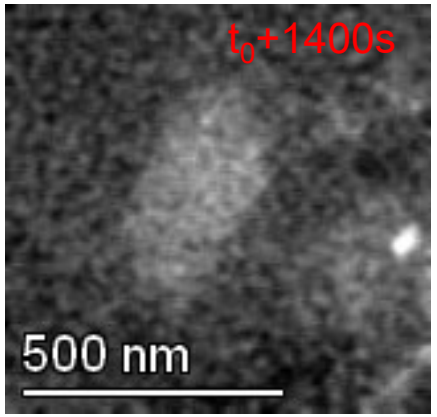
Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

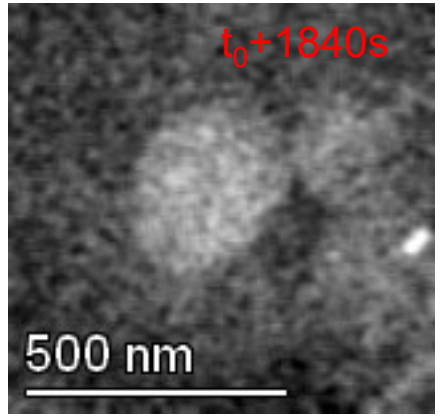
GB cracking and Na filament growth

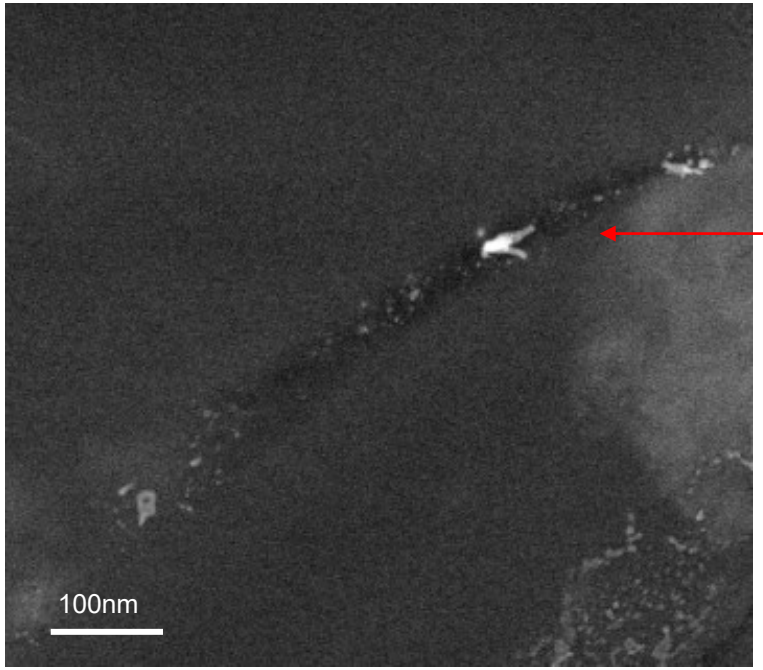
Z. Ding
Karlsruhe Institute of Technology











Na filaments grow along the whole GB gradually over time.

Crack at GB

Mechanical strength

Z. Ding et al., *Advanced Energy Materials*, **2023**, *online*

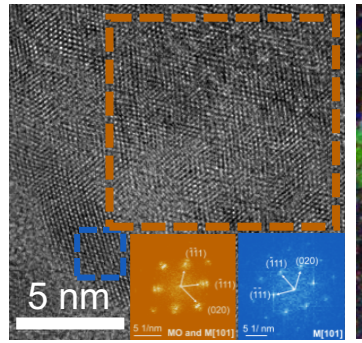
In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

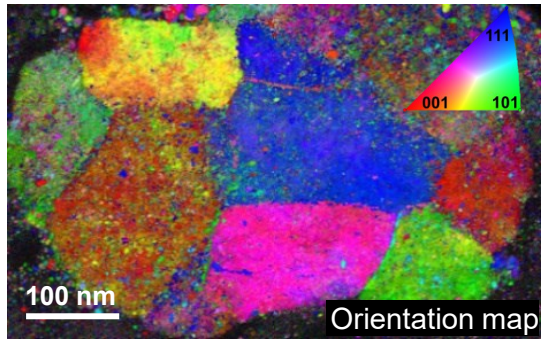
Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

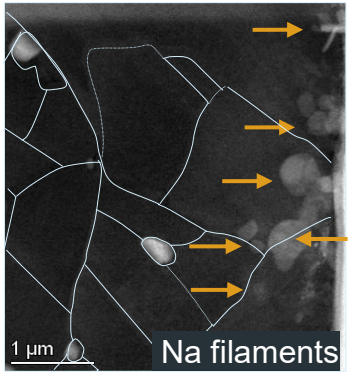
Summary

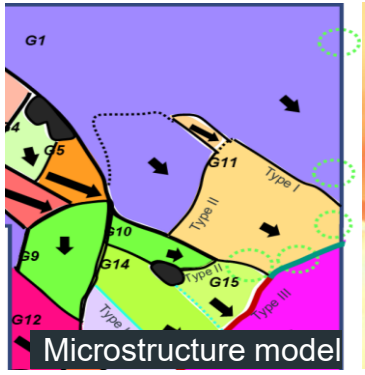
Advanced Electron Microscopy to Understand Processes in Batteries

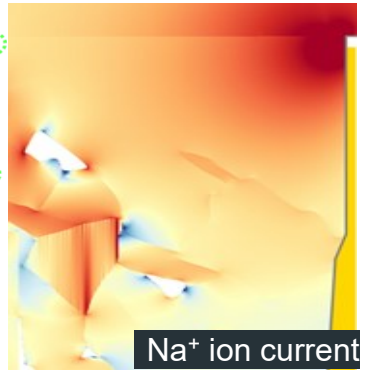
- Strength of combining imaging, spectroscopy and diffraction in hyperspectral analysis for *ex-situ* and *in-situ* TEM analysis
- Critical role of microstructure for electrochemical performance











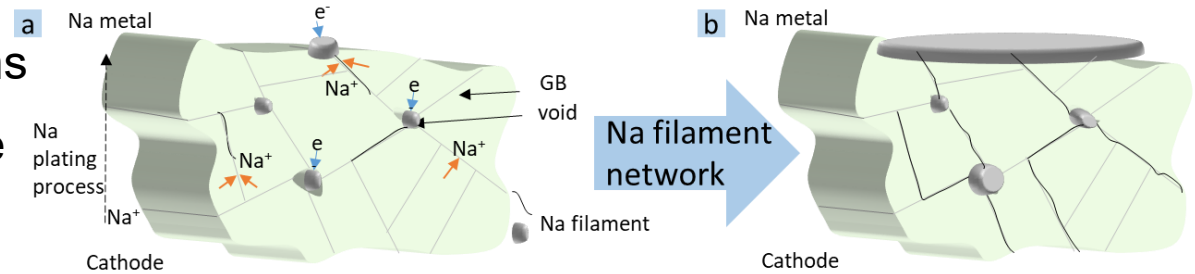
<u>Compositionally Complex Oxide Electrode</u>

- Cocktail effect in CCO electrode unraveled with defined role of all cations.

<u>Solid State Battery</u>

- Ion transport strongly affected by crystal orientation variations
- Filament formation at blocking boundaries in solid electrolyte with electrical contact to electrode.

→ GB engineering of SEs?



In-situ Electron Microscopy
Gemeinschaftslabor Nanomaterialien
Department of Materials & Earth Sciences

Institute of Nanotechnology
Karlsruhe Nano Micro Facility
Helmholtz Institute Ulm

Acknowledgement

Collaborators

Karlsruhe Institute of Technology
Abishek Sarkar, David Stenzel, Junbo Wang, Qingsong Wang, Yanyan Cui, Ben Breitung, Horst Hahn
Weibo Hua, Helmut Ehrenberg

Justus Liebig University Gießen
Till Ortmann, Marcus Rohnke, Jürgen Janek
Janis Kevin Eckhardt, Christian Heiliger

Staff Scientists / Postdocs

Alexey Boubnov
Ali Ahmadian
Andrei Mazilkin
Avnish Singh Pal
Carina Malikkal
Di Wang
Martin Velazquez-Rizo
Mehrdad Jalali
Torsten Scherer
Yemao Lu

Associated
Rafaela Debastiani
Sabine Schlabach
Svetlana Korneychuk
Vinga Szabo

PhD Students

Ajai Raj L
Lucas Brauch
Maximillian Töllner
Sangjun Kang
Vahid Tavakkoli
Yuting Dai
Ziming Ding

Associated
Ou Jin
Rui Xu

Technicians

Vanessa Wollersen

Former Group Members:

Xiaoke Mu now at Lanzhou University
Kai Wang now at CATL
Georgian Melinte now at KAUST
Yushu Tang now at HUAWEI
Xiaohui Huang now at HUWAI