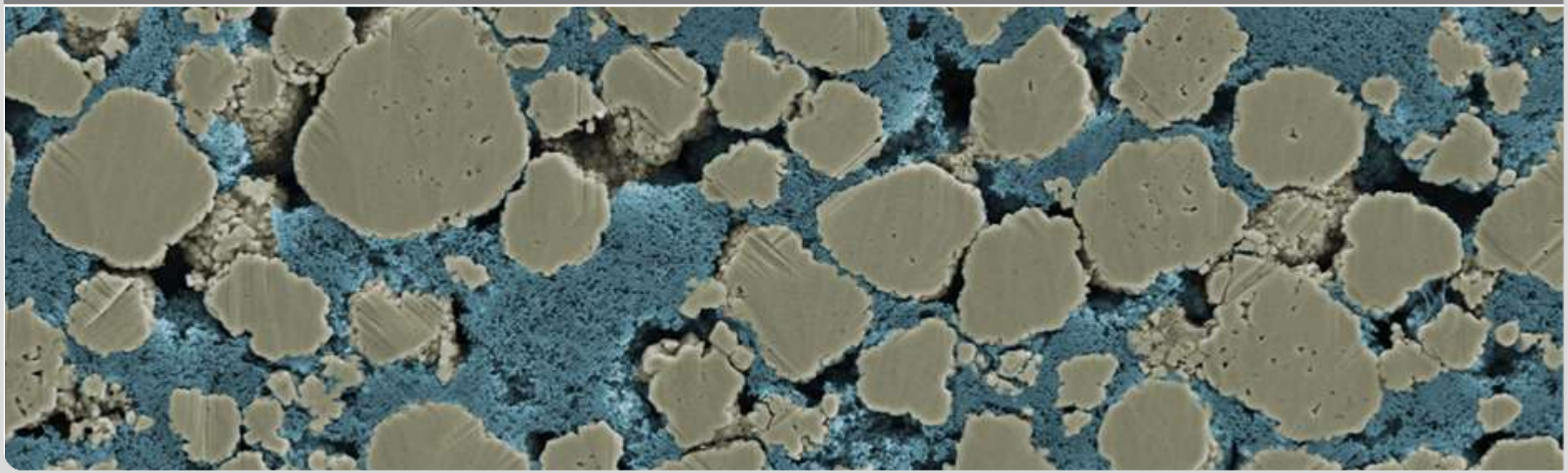
Karlsruhe Institute of Technology

IAM
Institute for Applied Materials

Investigation of the Additive Distribution in Electrodes for Lithium-Ion Batteries

Werner Bauer

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



With Contributions by

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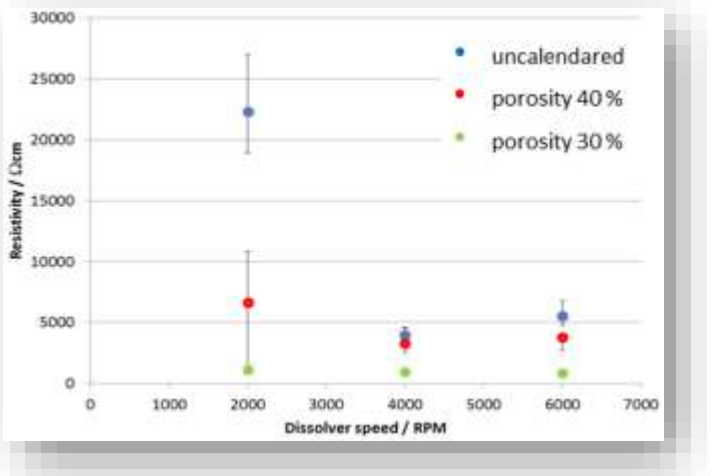
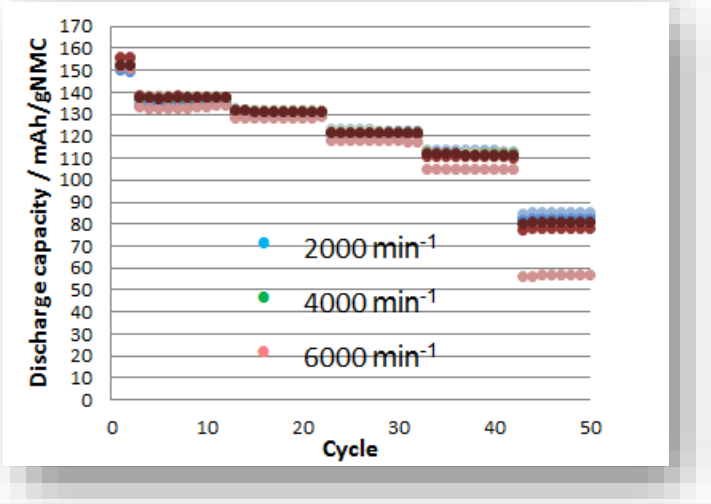
Jana Kumberg Philip Scharfer Ralf Diehm Stefan Jaiser	TVT-TFT

Structure – The Missing Link

- Processing – Structure – Property – Relationship

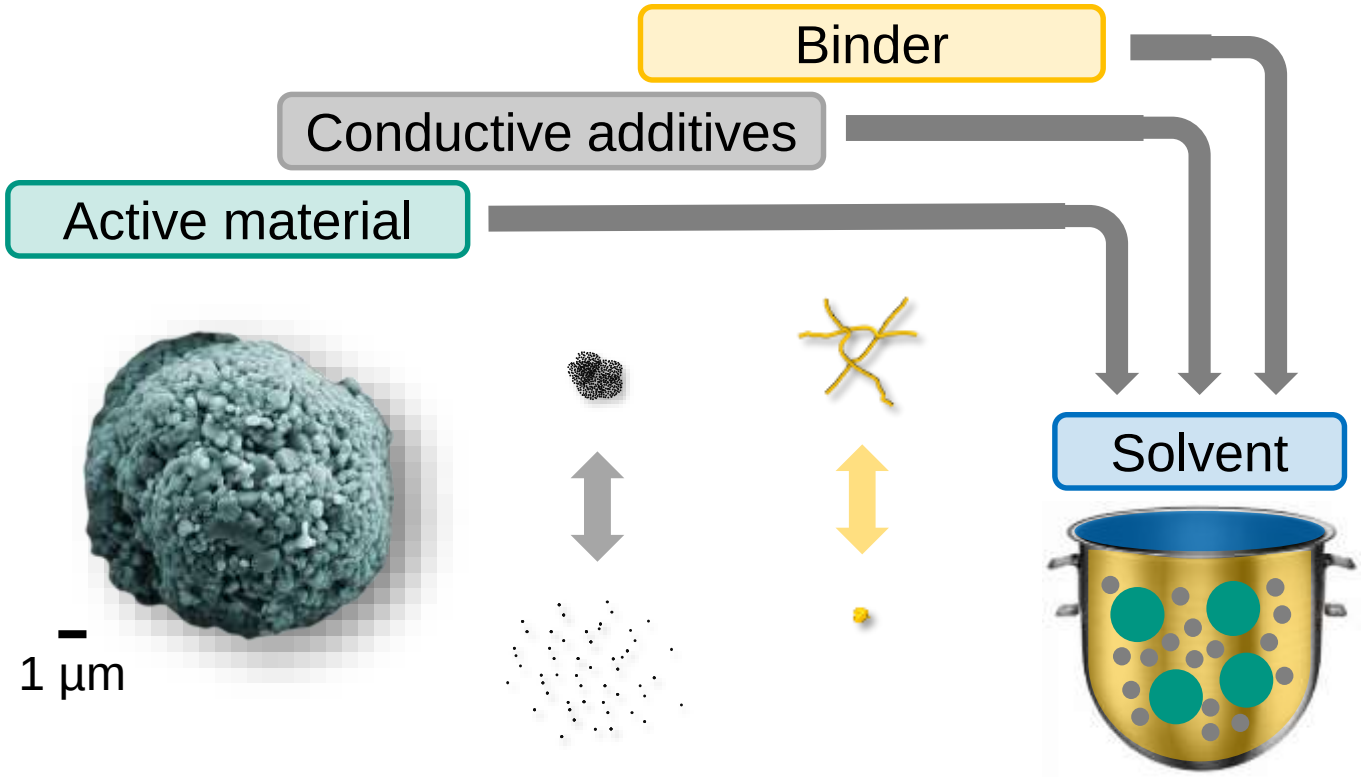
94 wt.% NMC
3 wt.% PVDF
3 wt.% carbon black





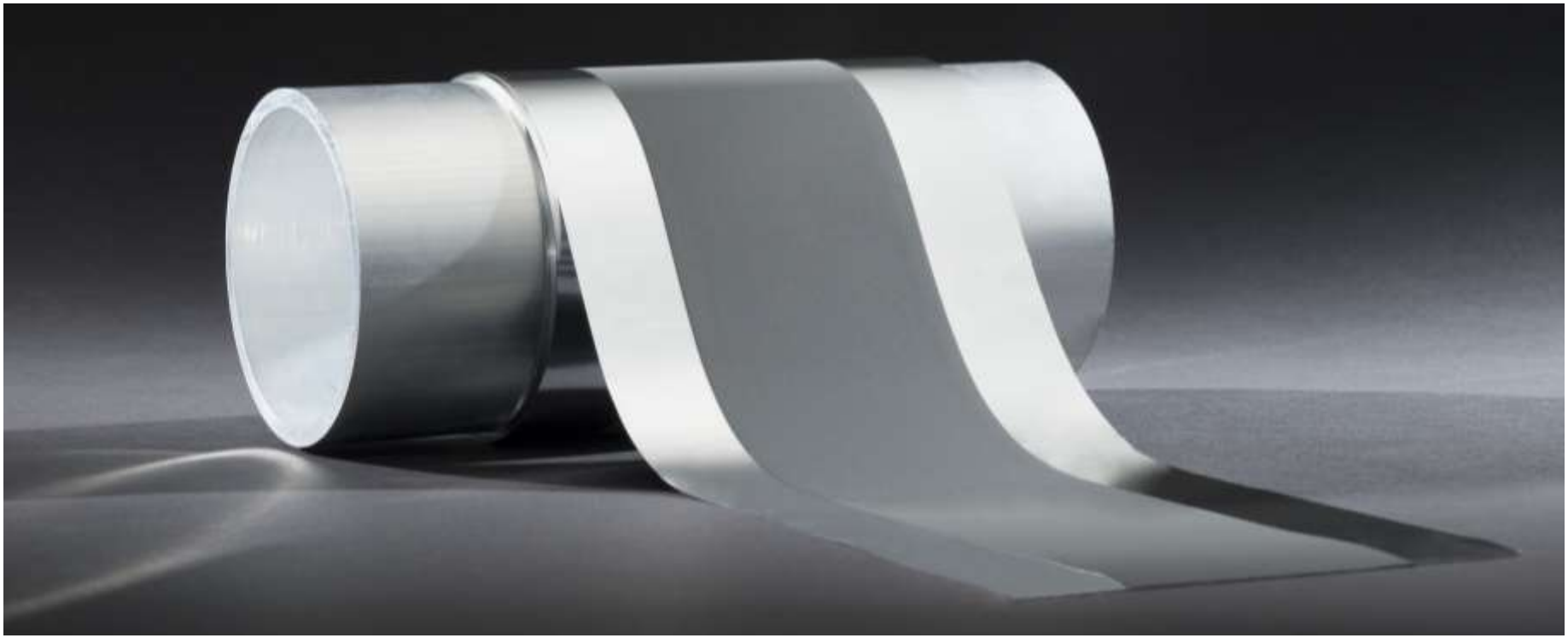
Homogeneity

- A material or image that is homogeneous is uniform in composition or character (Wikipedia).
- Homogeneity is the target of slurry mixing



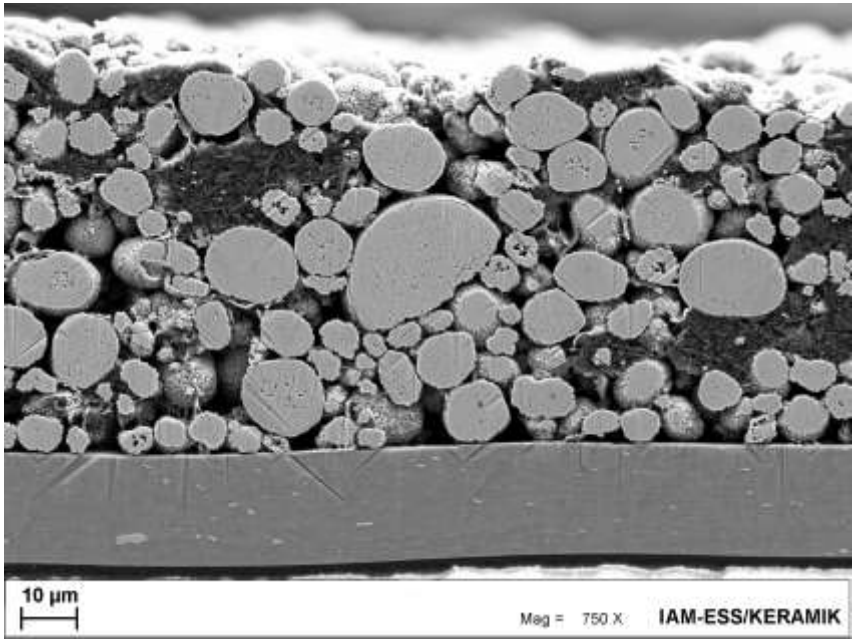
Macroscopic Level

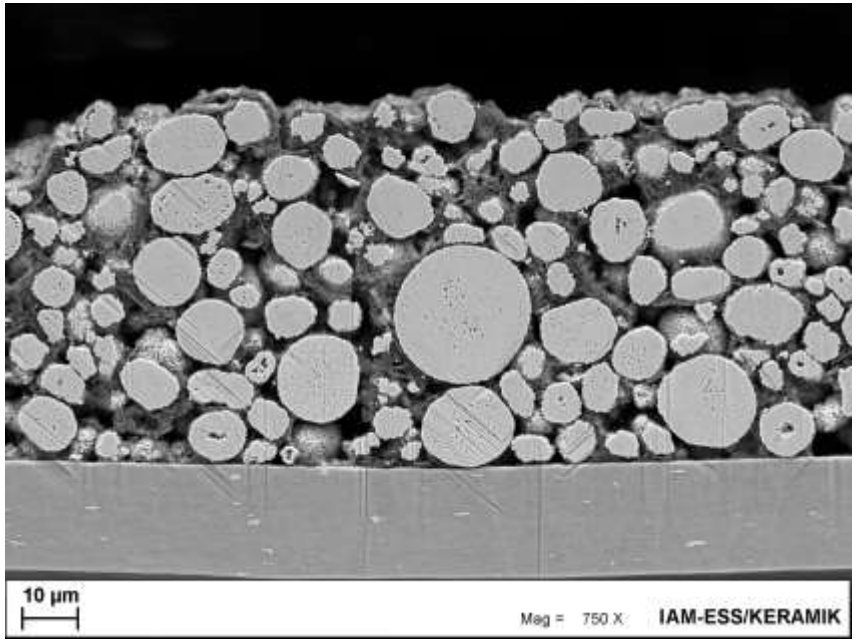
- Homogeneity: No visible agglomerates, pores, cracks, stripes …



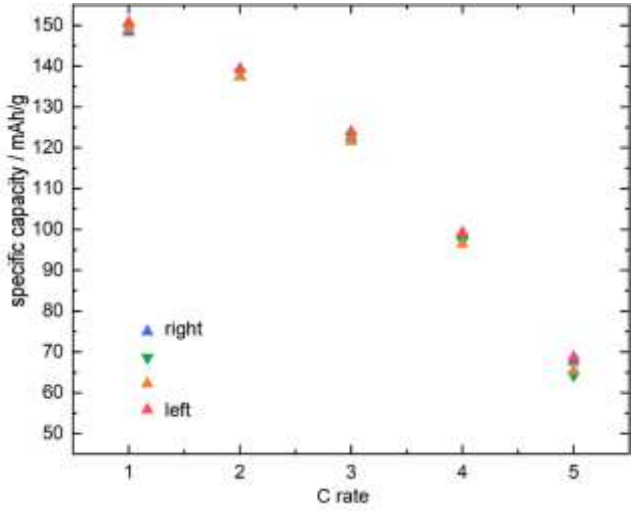
Mesoscopic Level

- Which microstructure is better?

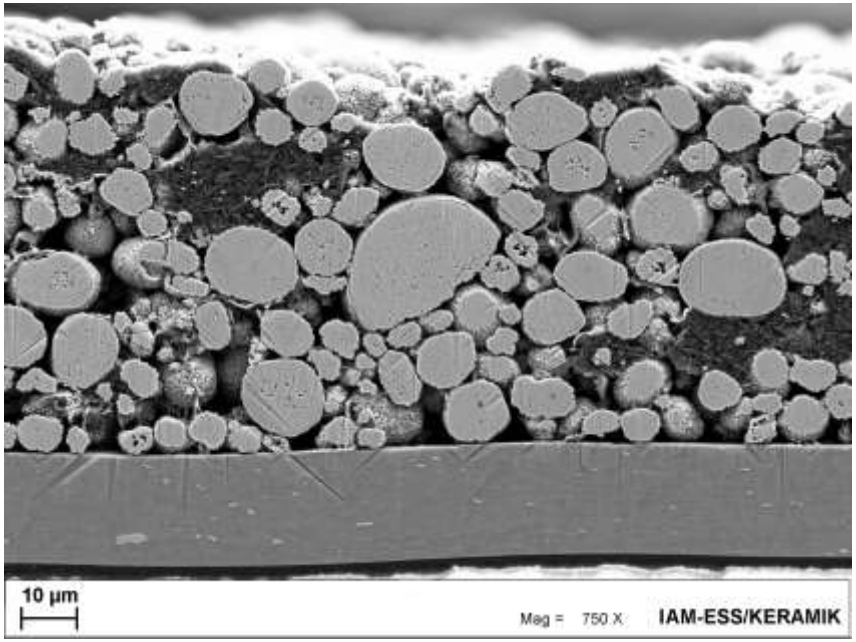


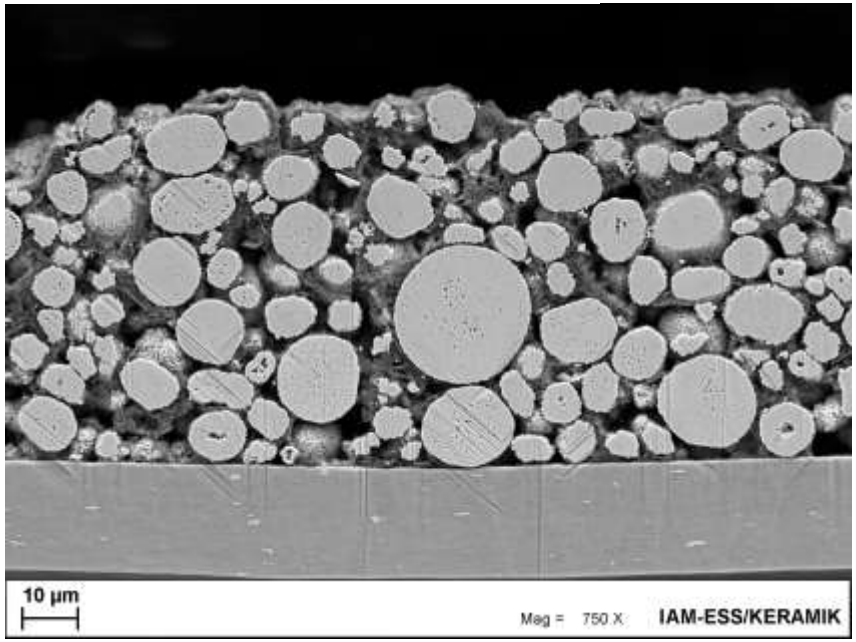


Mesoscopic Level



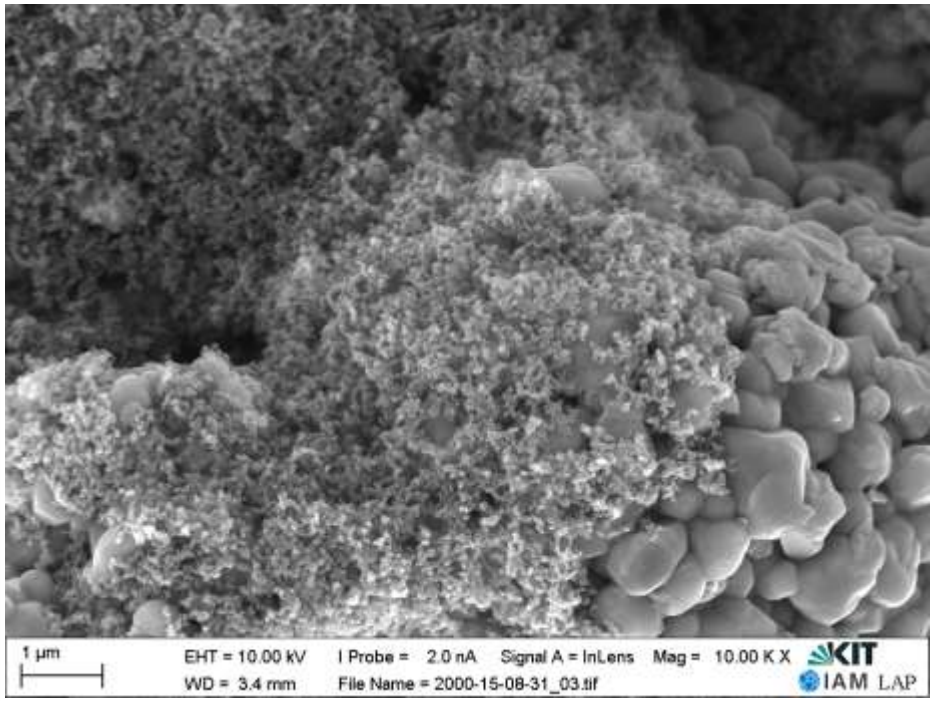
- Which microstructure is better?

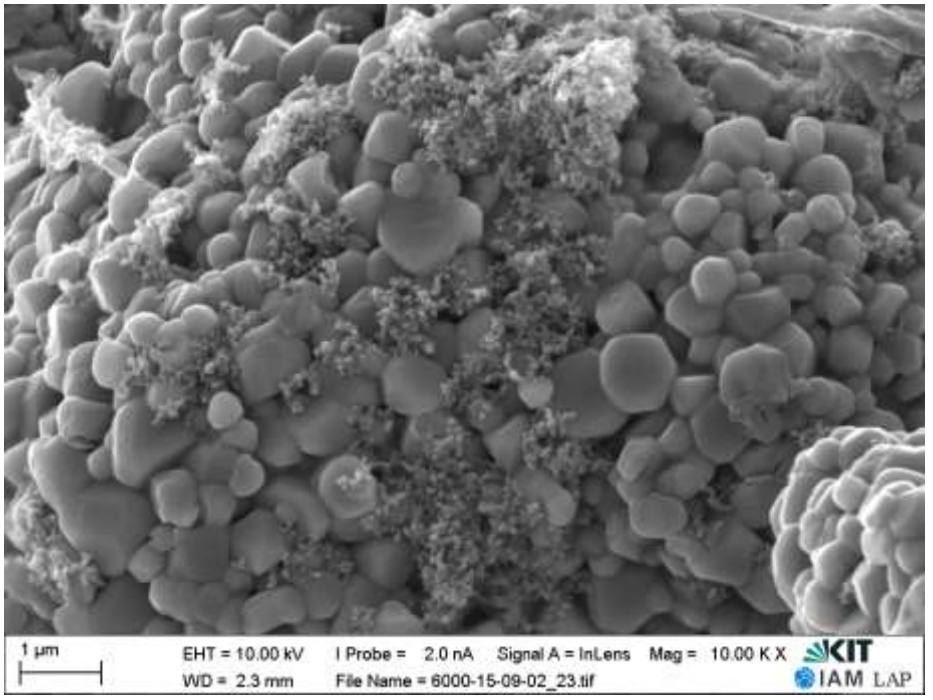




Microscopic Level

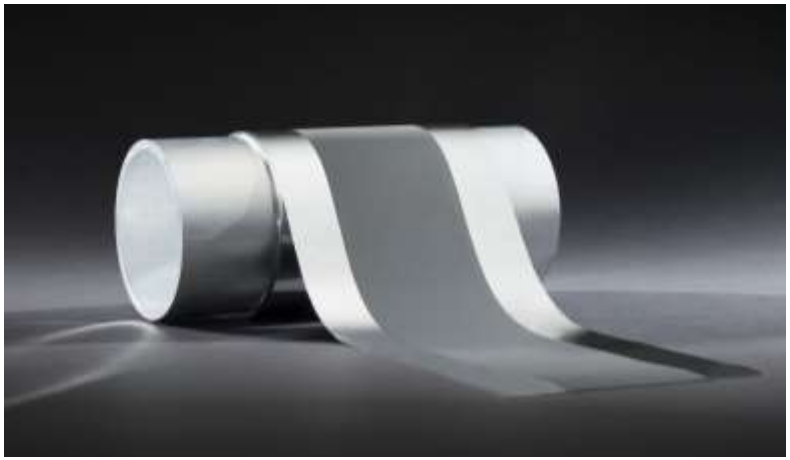
- Agglomeration is a must



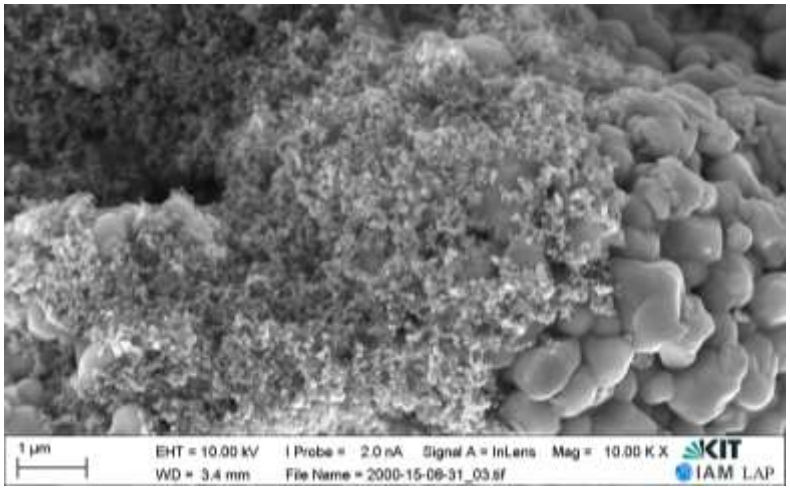


How much Homogeneity is Required?

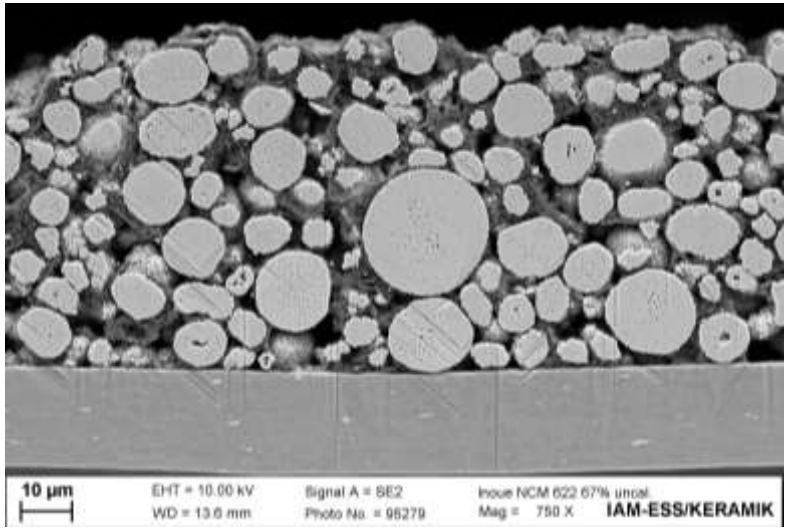
- Macroscopic level



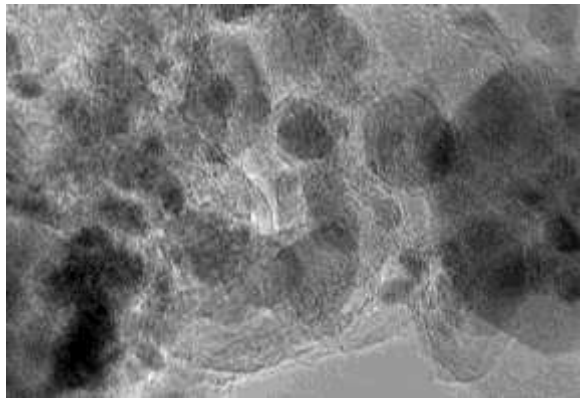
- Microscopic level



- Mesoscopic level



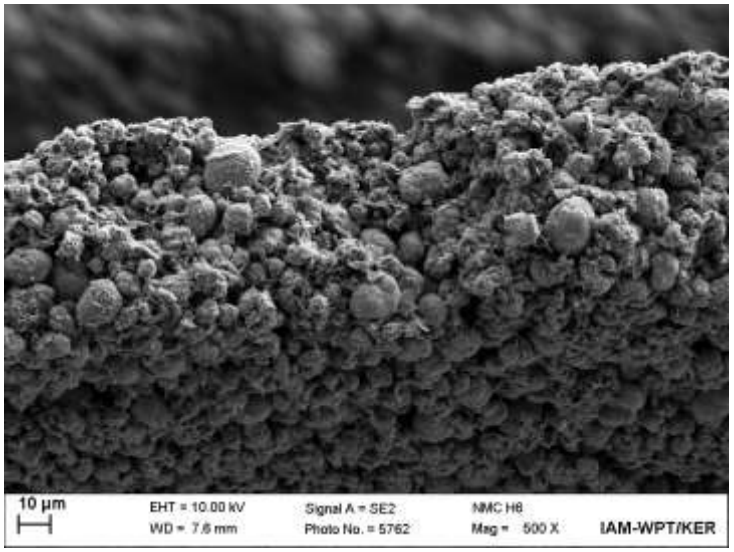
- Nanoscopic level

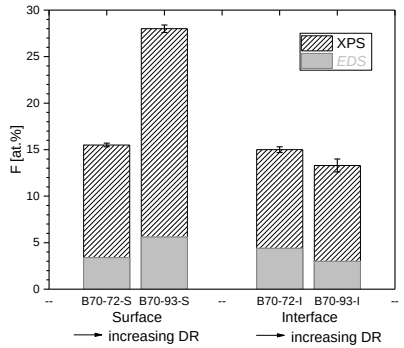


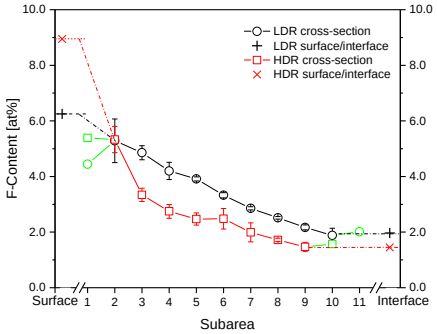
Investigation of Electrode Structure

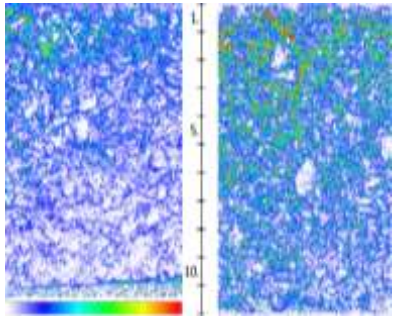
Distribution of

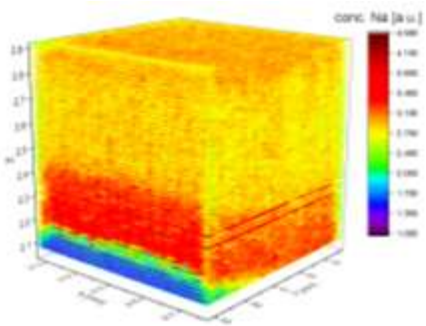
- Active materials
- Inactive components
  - Binder
  - Conductive additives
- Porosity







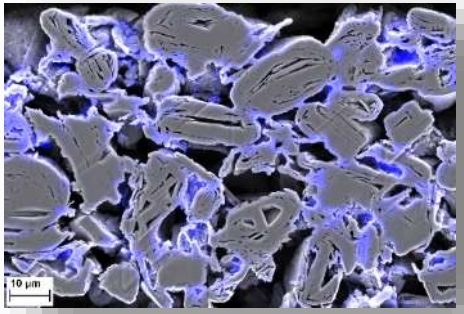




0D 1D 2D 3D

Evaluation of Additive Distributions

Styrene butadiene rubber (SBR) decoration by OsO_4

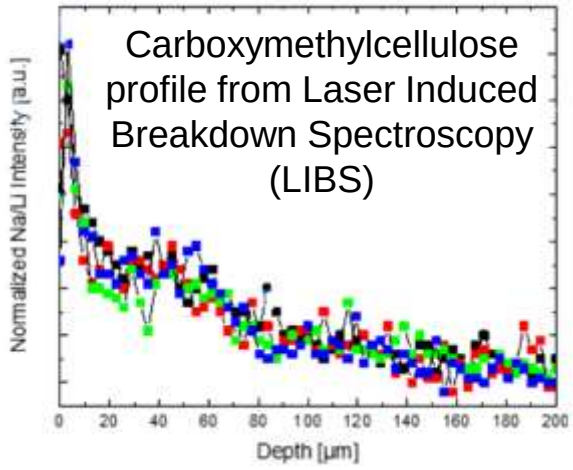


Sample preparation

Toolbox

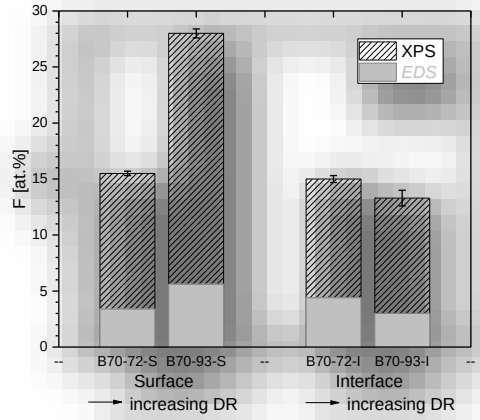
Binder

Carboxymethylcellulose profile from Laser Induced Breakdown Spectroscopy (LIBS)



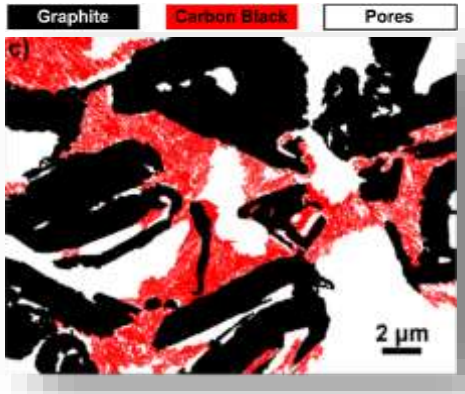
Conductive additives

Method screening



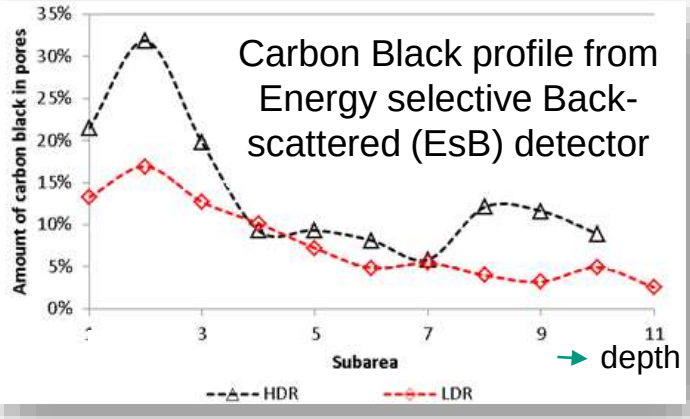
EDS / XPS

Detector adaption



Analyzed EsB

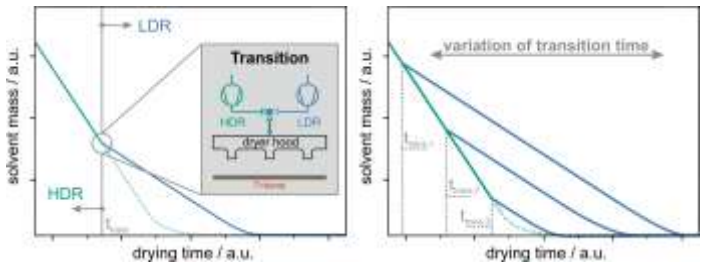
Carbon Black profile from Energy selective Back-scattered (EsB) detector

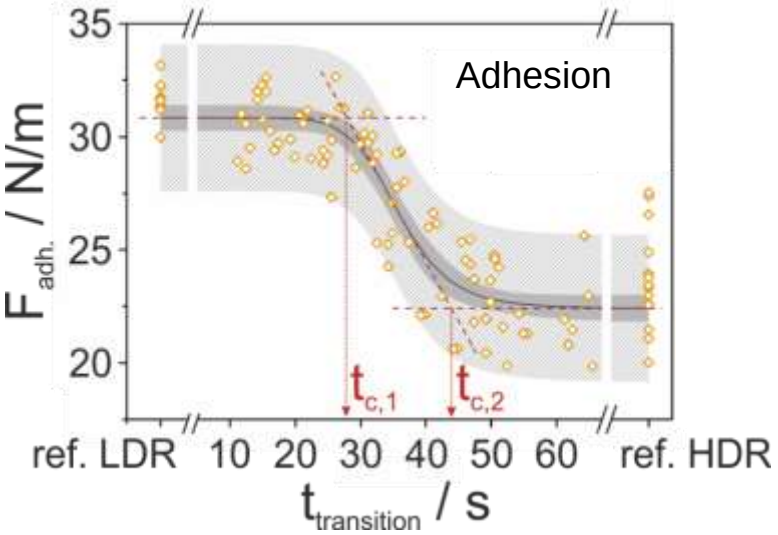


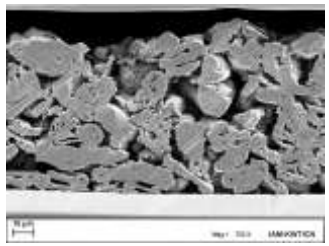
Investigation of the Electrode Drying Process

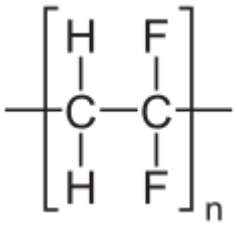
- Migration of binder

Setup



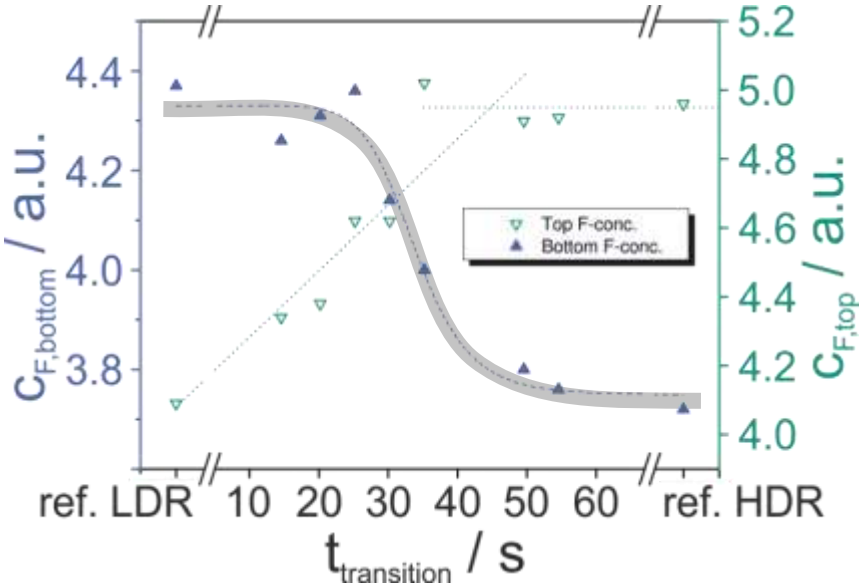






Graphite anode with PVDF binder →

Using the fluorine concentration as a marker for energy-dispersive x-ray spectroscopy (EDS)



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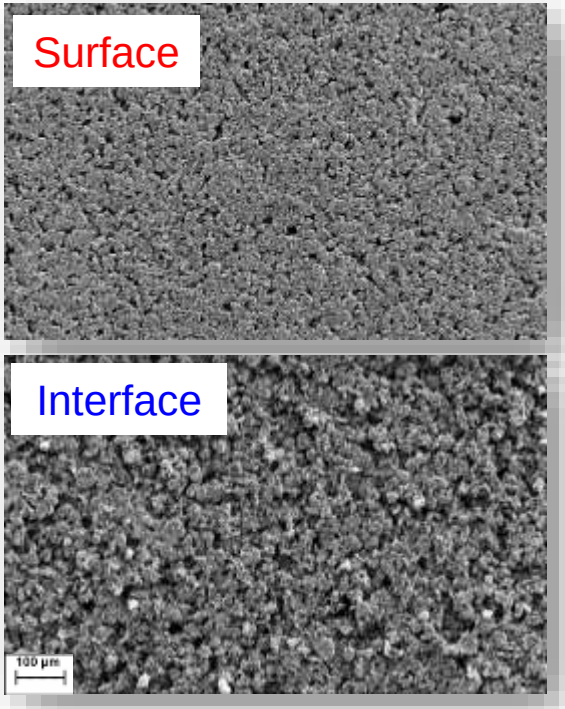
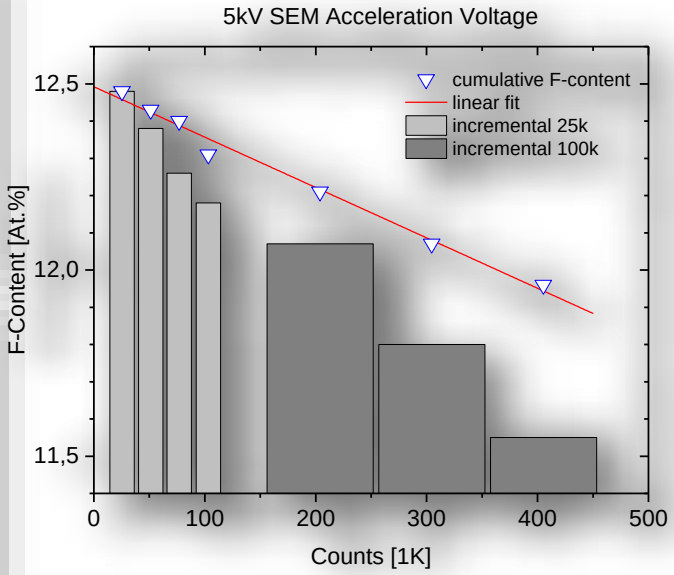
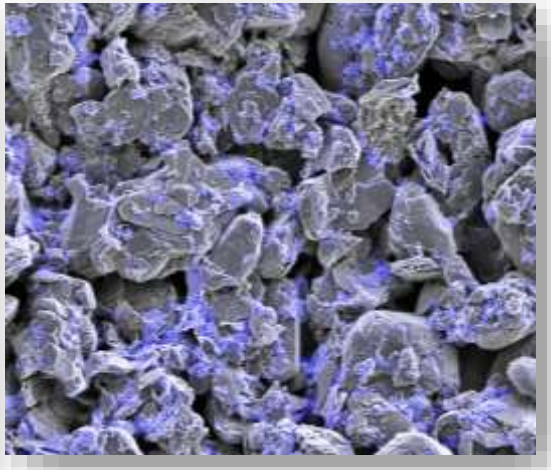
Quantitative Analysis with EDS

- Ideal sample
  - smooth surface
  - stable materials
  - homogeneous composition
- Electrode sample
  - rough surface
  - instable in the electron beam
  - inhomogeneous binder distribution







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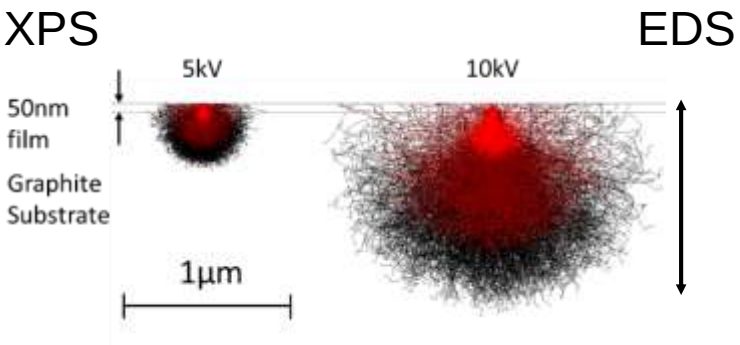
Other Characterization Methods

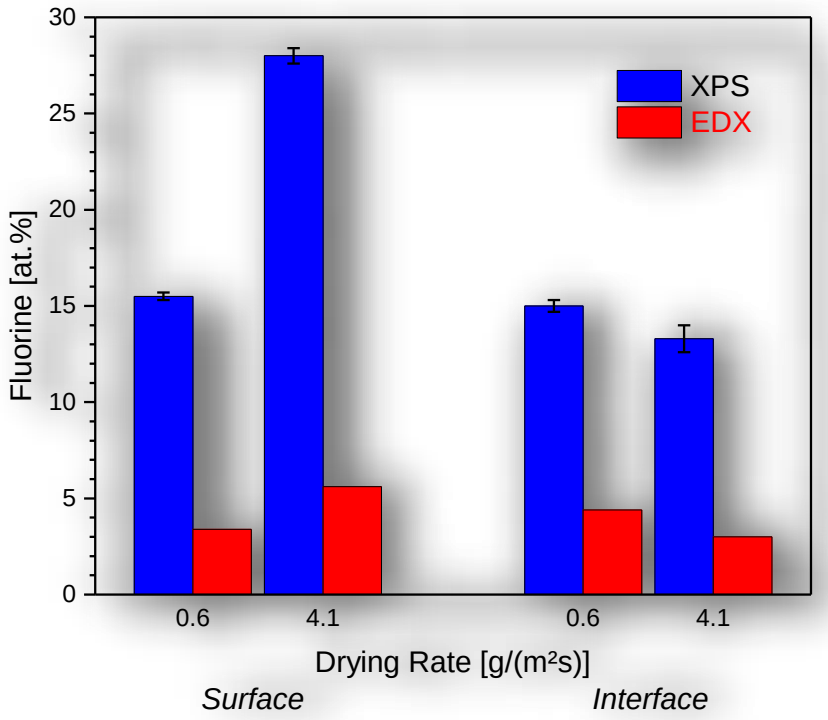
- Raman-Spectroscopy

  Insensitive to PVDF layers thinner than 1-2 µm → only large accumulations of PVDF are detected

- X-ray Photoelectron Spectroscopy (XPS)

  Surface sensitive method → higher concentrations are measured

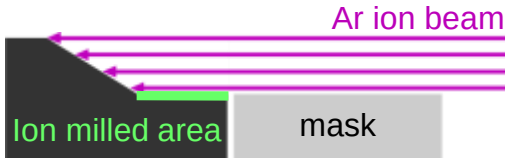




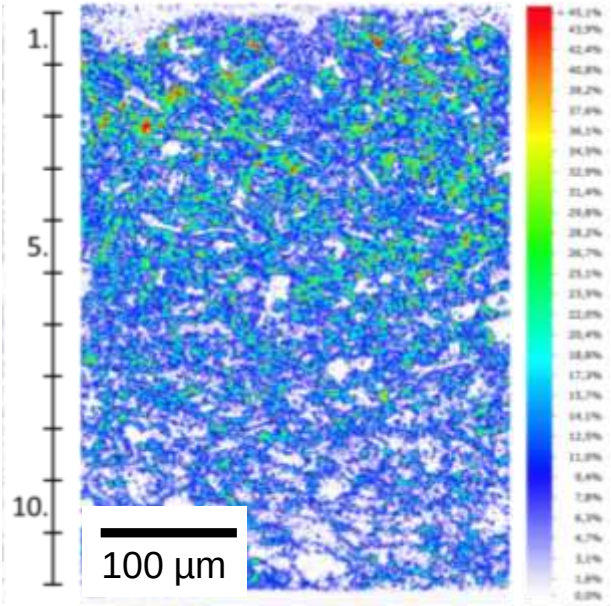
Investigation of Cross Sections by EDS

- Graphite/PVDF anode with 400 µm thickness

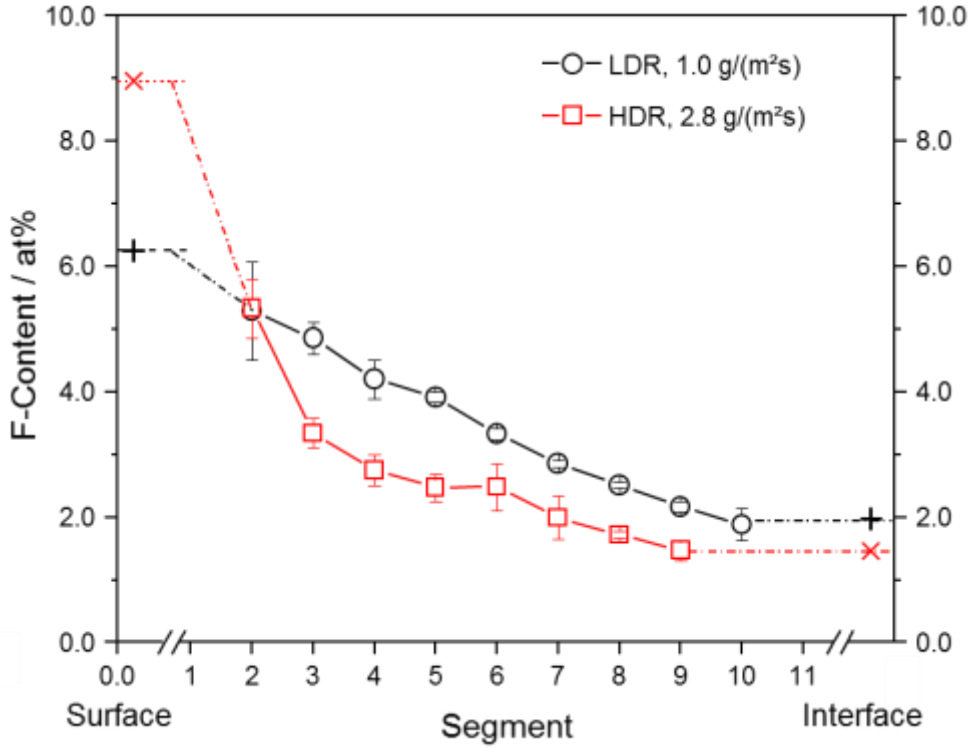
Ion Beam Milling System



Surface



Interface



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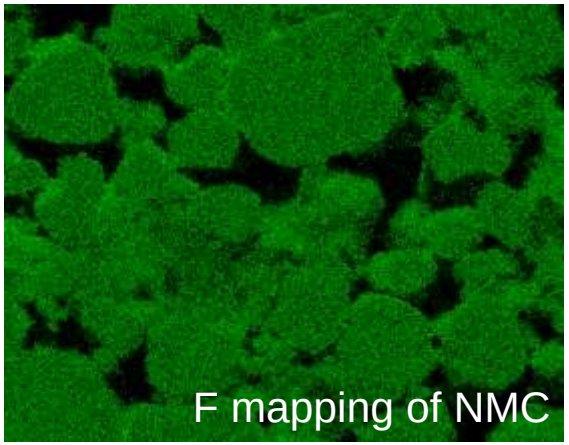
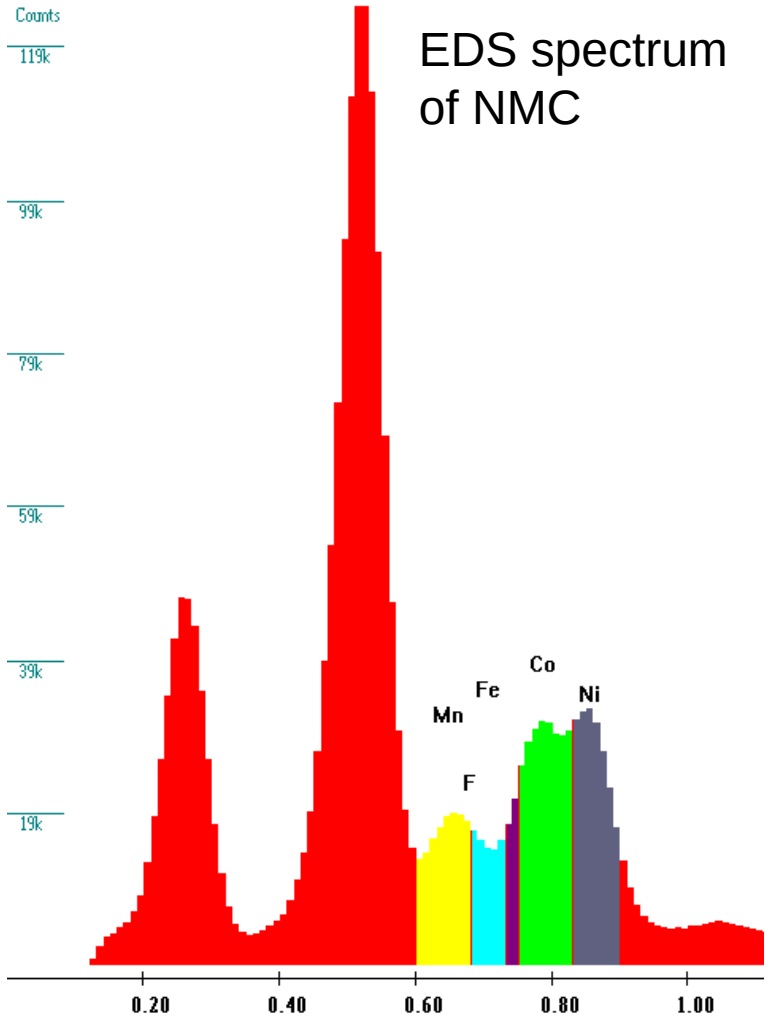
Investigation of Cathodes

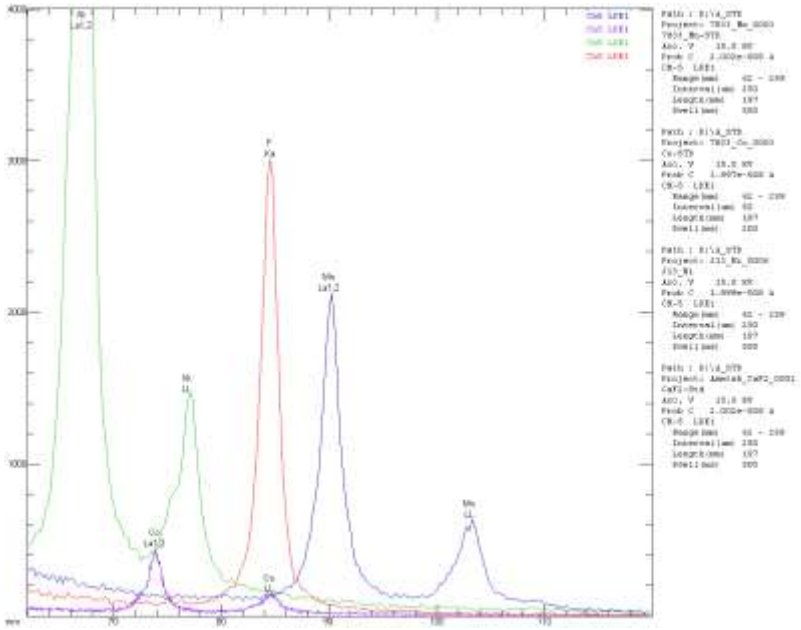
- Most prominent cathode materials
  - $Li(Ni_xMn_yCo_z)O_2$ (NMC)
  - $LiFePO_4$ (LFP)
- NMC or LFP Cathode with PVDF
  - Overlap of regions of interest for F with Mn or Fe
  - Feasibility depends on sensitivity of EDS





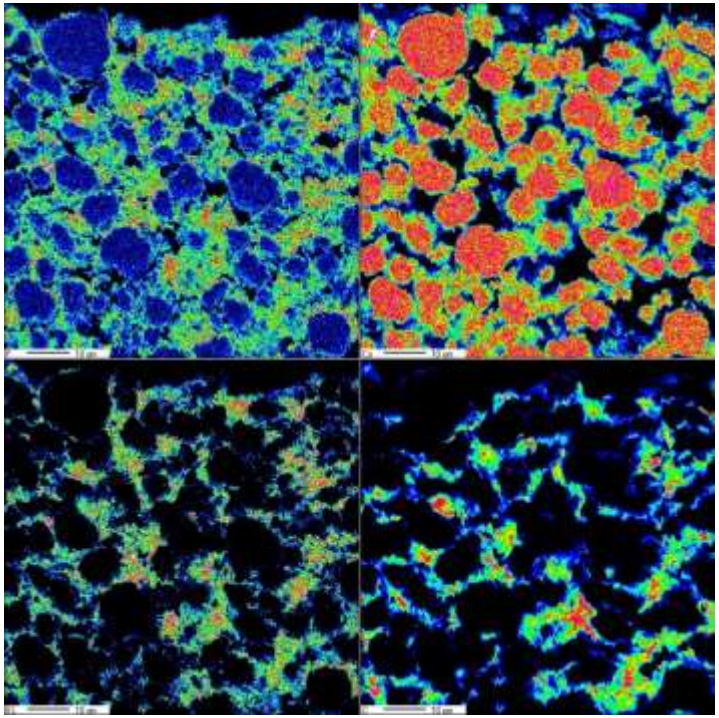
Wavelength Dispersive X-ray Spectroscopy (WDS)

- WDS has a higher energy resolution
- Separation of F and Mn possible
- Interference by a Cobalt side peak → Substraction of F and Co spectrum allows qualitative analysis



NMC/PVDF cathode

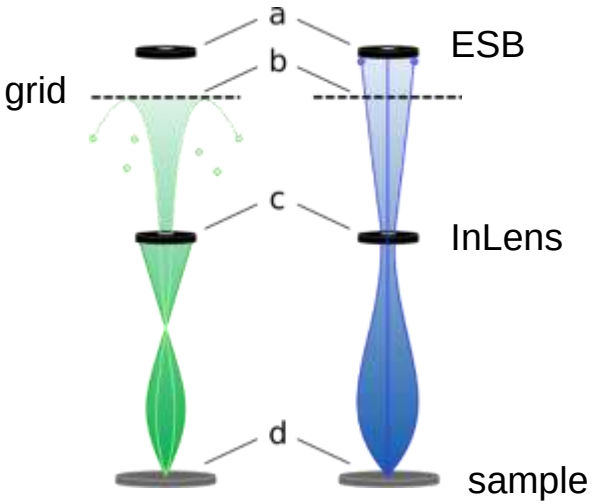
F Co

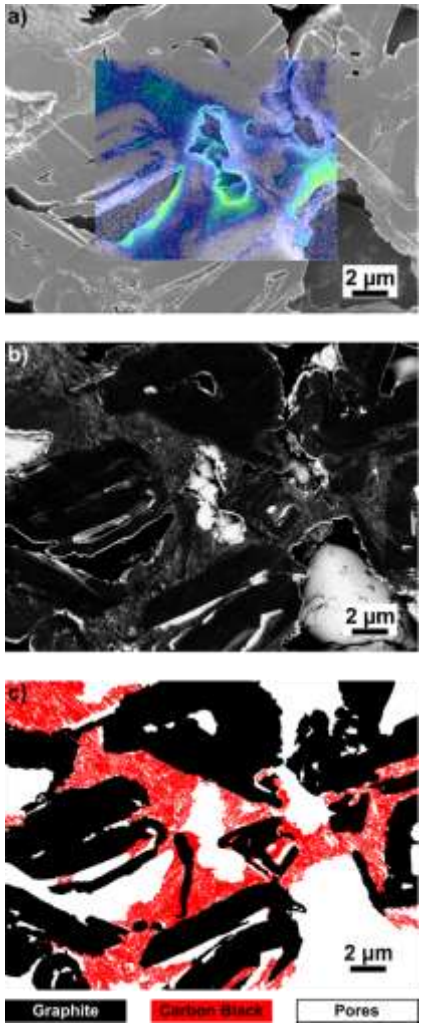


Modified F C

Investigation of Carbon Black Distribution

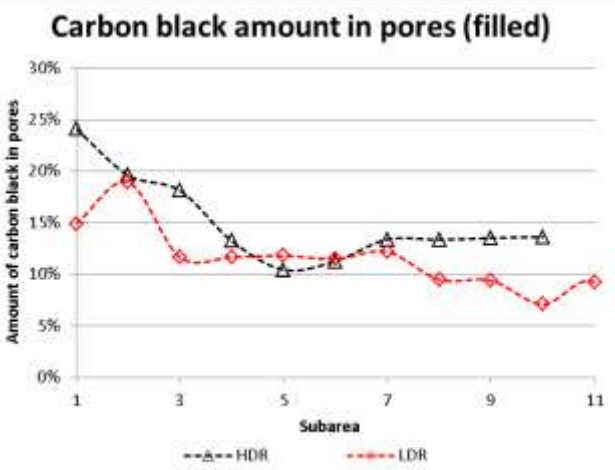
- Energy Selective Backscattered Electron Detector (ESB)
- Optimization of ESB grid voltage and the primary electron energy
- Contrast enhancement between C and F regions





Graphite/PVDF anode

- Imaging of PVDF – carbon black domain by silicone rubber filling of pores and grayscale analysis



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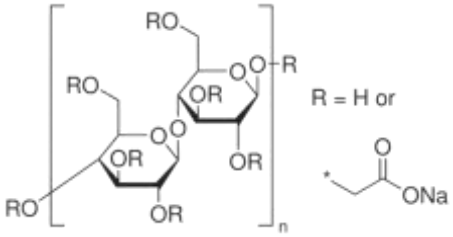
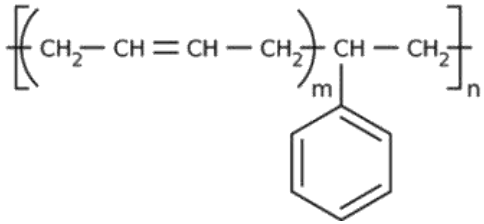
Binders for Aqueous Slurries

- Standard binders for aqueous slurries do not contain flourine

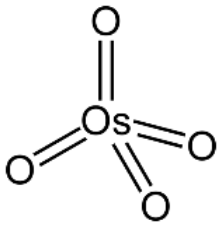


(Sodium salt of) Carboxy Methyl Cellulose (Na-CMC)

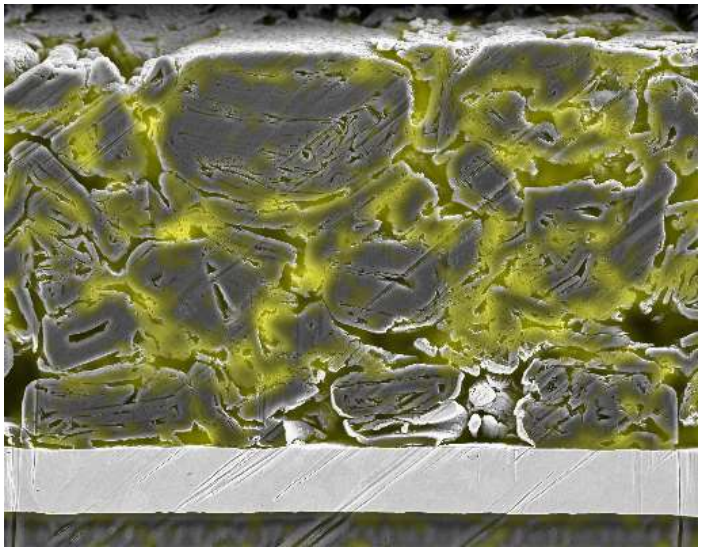


Styrene Butadiene Rubber (SBR)

- Osmium staining technique
  - Decoration of SBR binder with OsO_4
  - Sublimates at room temperature
  - Strong oxidant → reacts with double bonds in the SBR



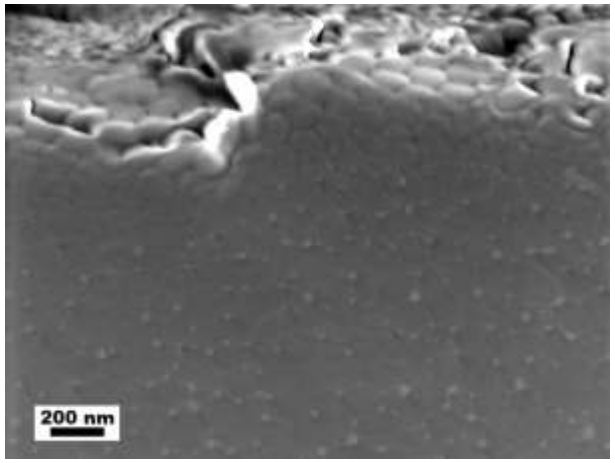
EDS mapping of Os decorated graphite with CMC/SBR binder



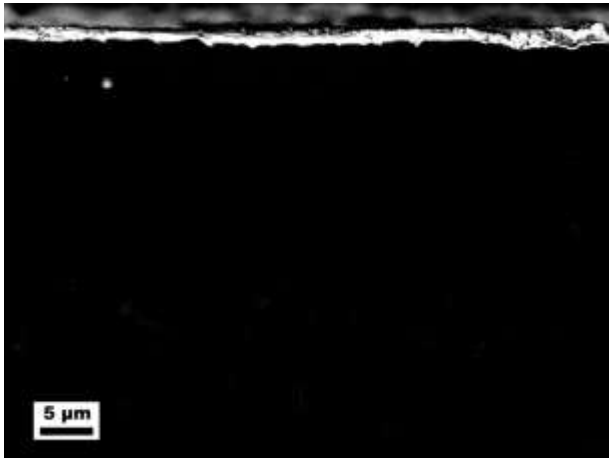
Structure of SBR Binder Films

- Binder films have low, but different porosity
- Blending with carbon black increases porosity of the film
  → with carbon black the binder layer becomes transparent for electrolyte and lithium

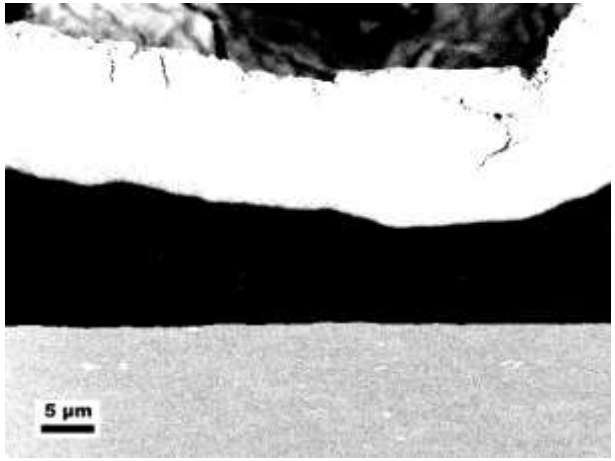
SBR binder film



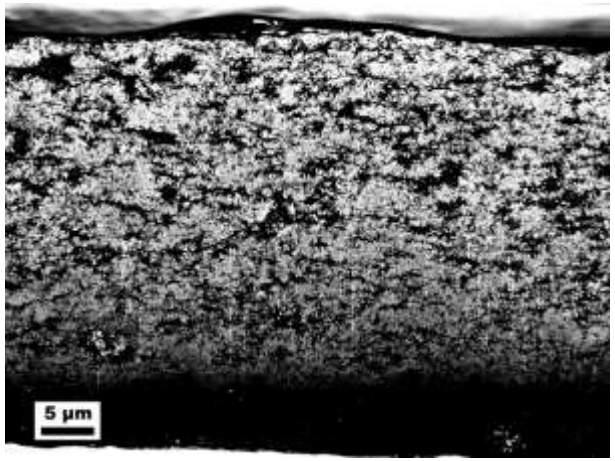
20 h OsO_4 exposure



SBR 1



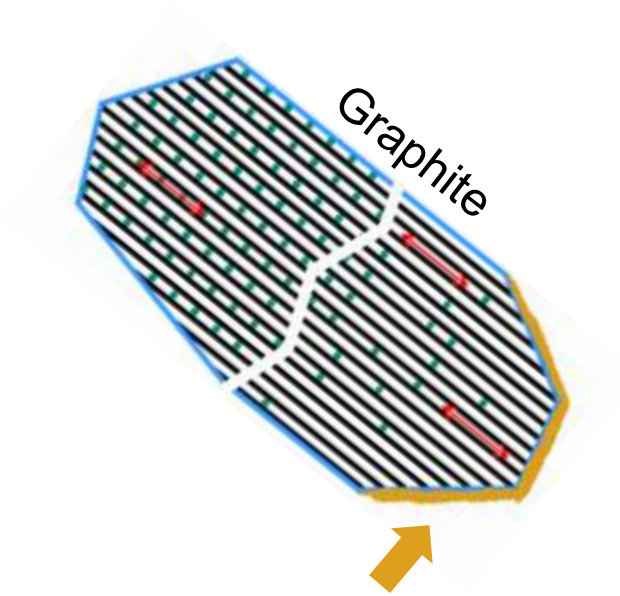
SBR 2



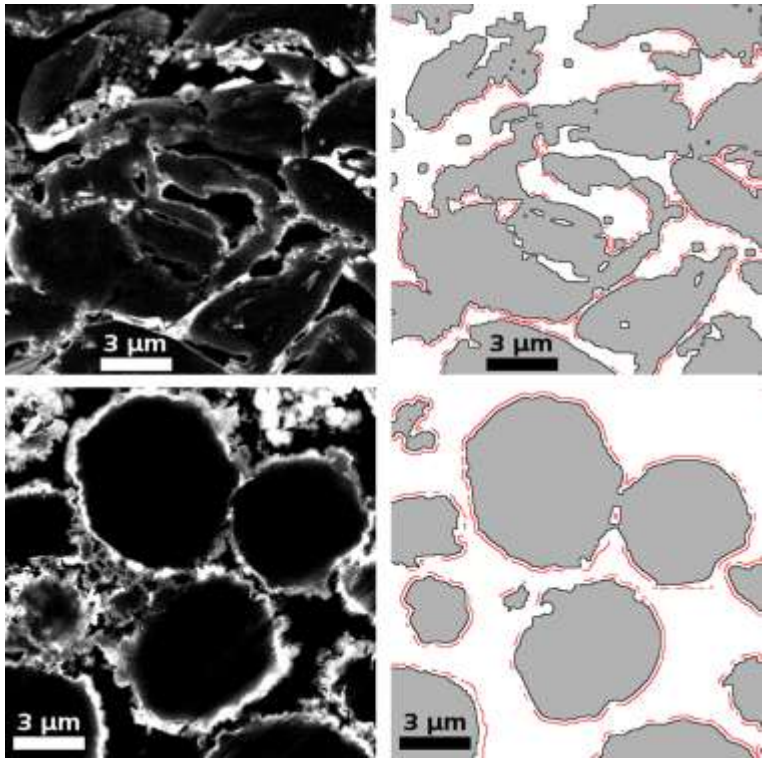
SBR + CMC + CB

Electrochemically Active Surface Area (EASA)

- OsO_4 intensively reacts with Lithium
- Visualization of the EASA by Osmium Staining



AsB detector | Image processing



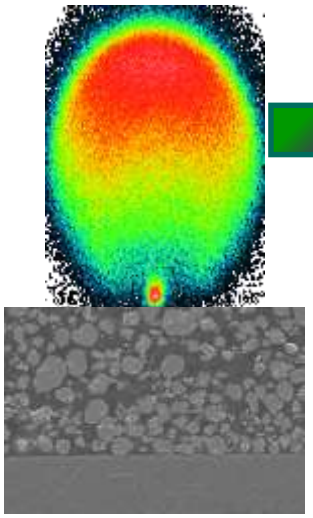
Graphite
EASA = 37%

Amorphous Carbon
EASA = 72%

L. Pfaffmann et al., J. Power Sources 307 (2016) 762-771

Laser-induced Breakdown Spectroscopy (LIBS)

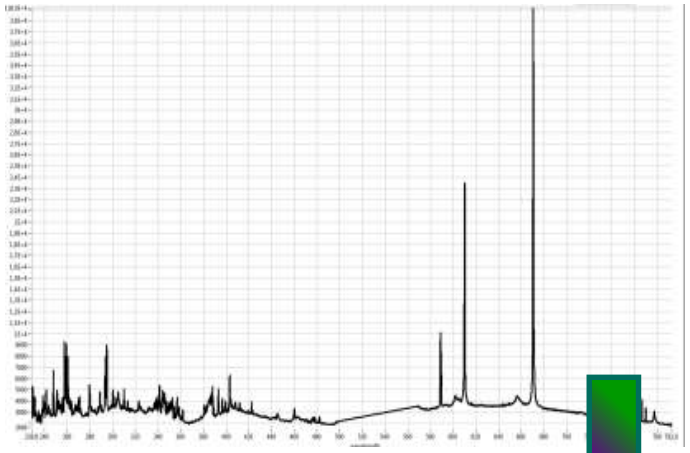
laser beam



Plasma light

spectrometer

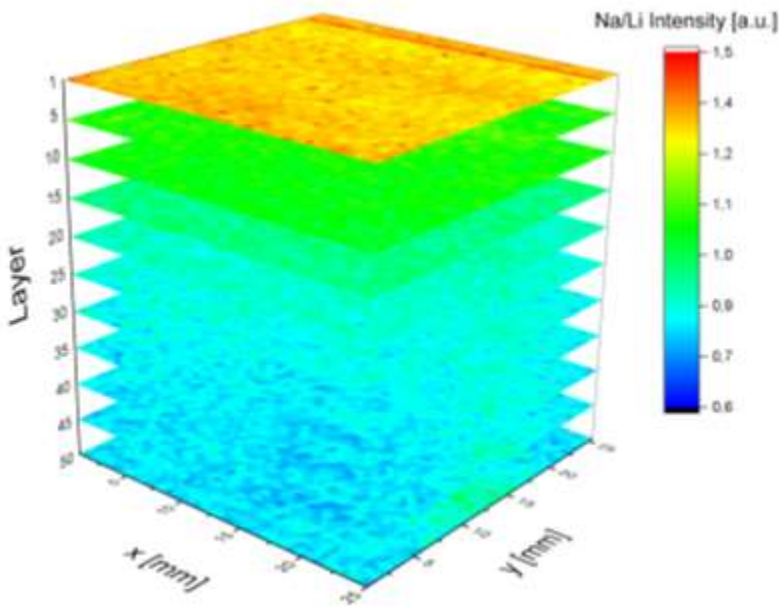
emission line intensity
as function of wavelength



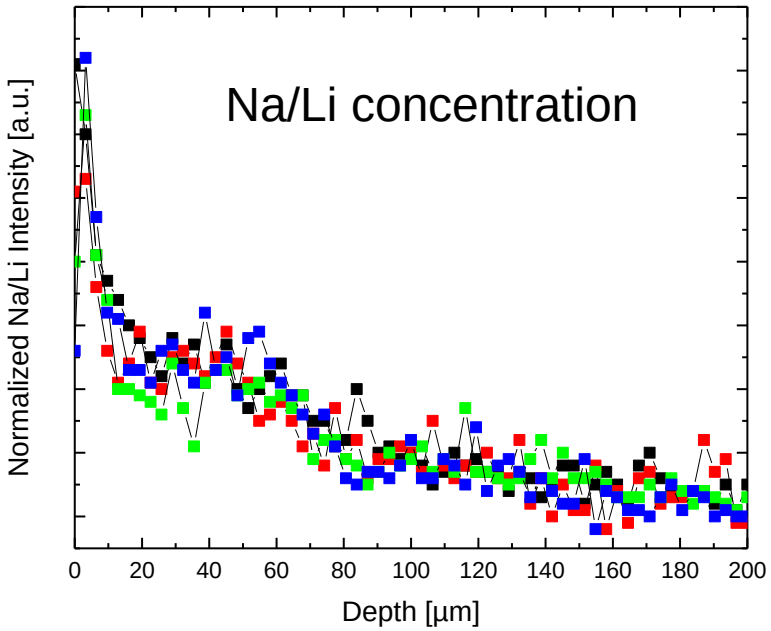
elemental
composition &
concentration

Binder Investigation by LIBS

- High sensitivity to alkaline elements
- Detection of Na residues in CMC binder possible



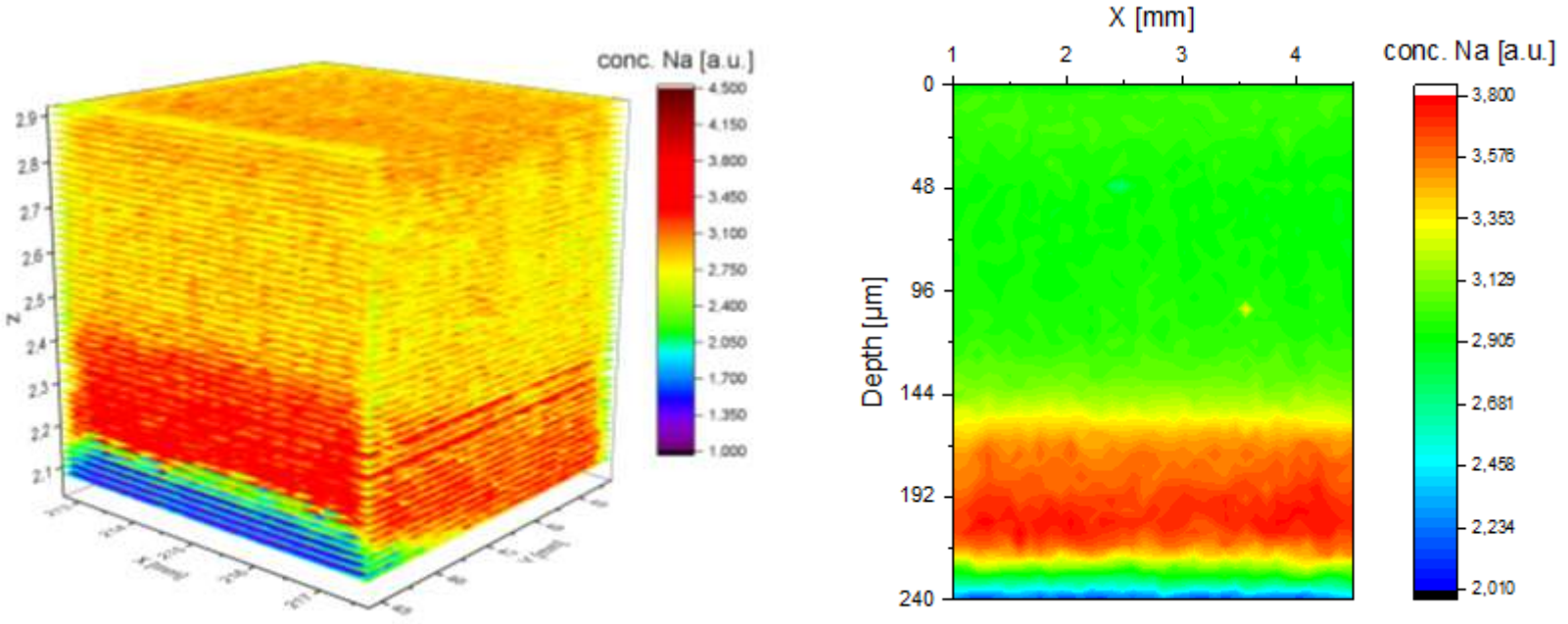
NMC with CMC/SBR binder



Investigation of Multilayer Electrodes

- Multilayer coating allows individual adjustment of binder amount
- Binder excess at current collector interface is beneficial
- Control of interdiffusion of CMC binder by LIBS

NMC with CMC/SBR binder



Thank you for your attention