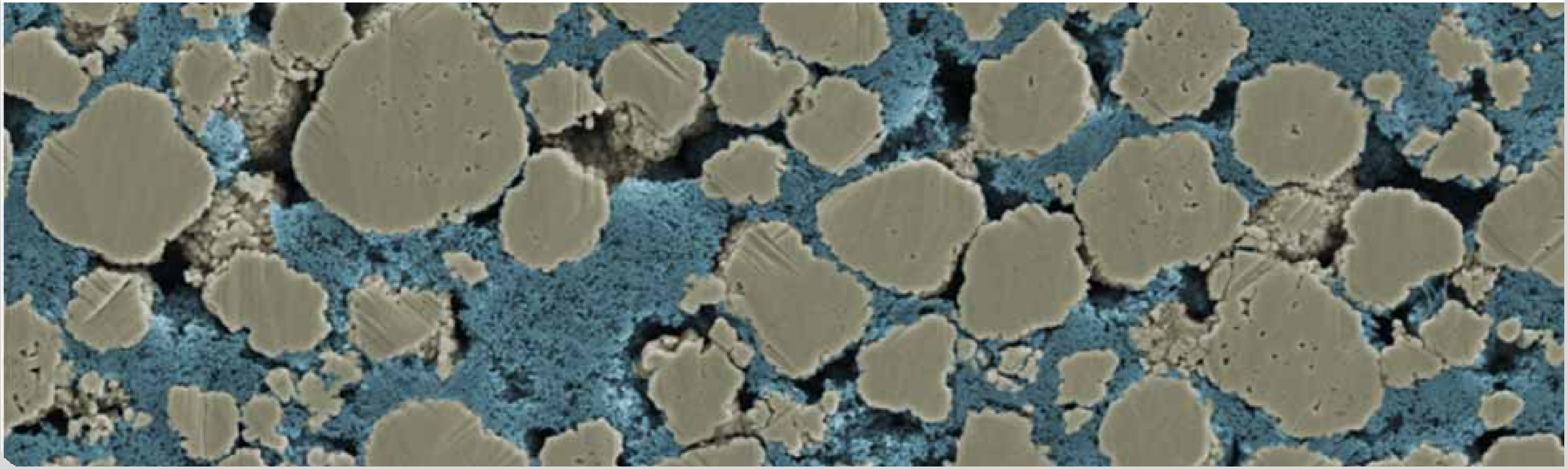
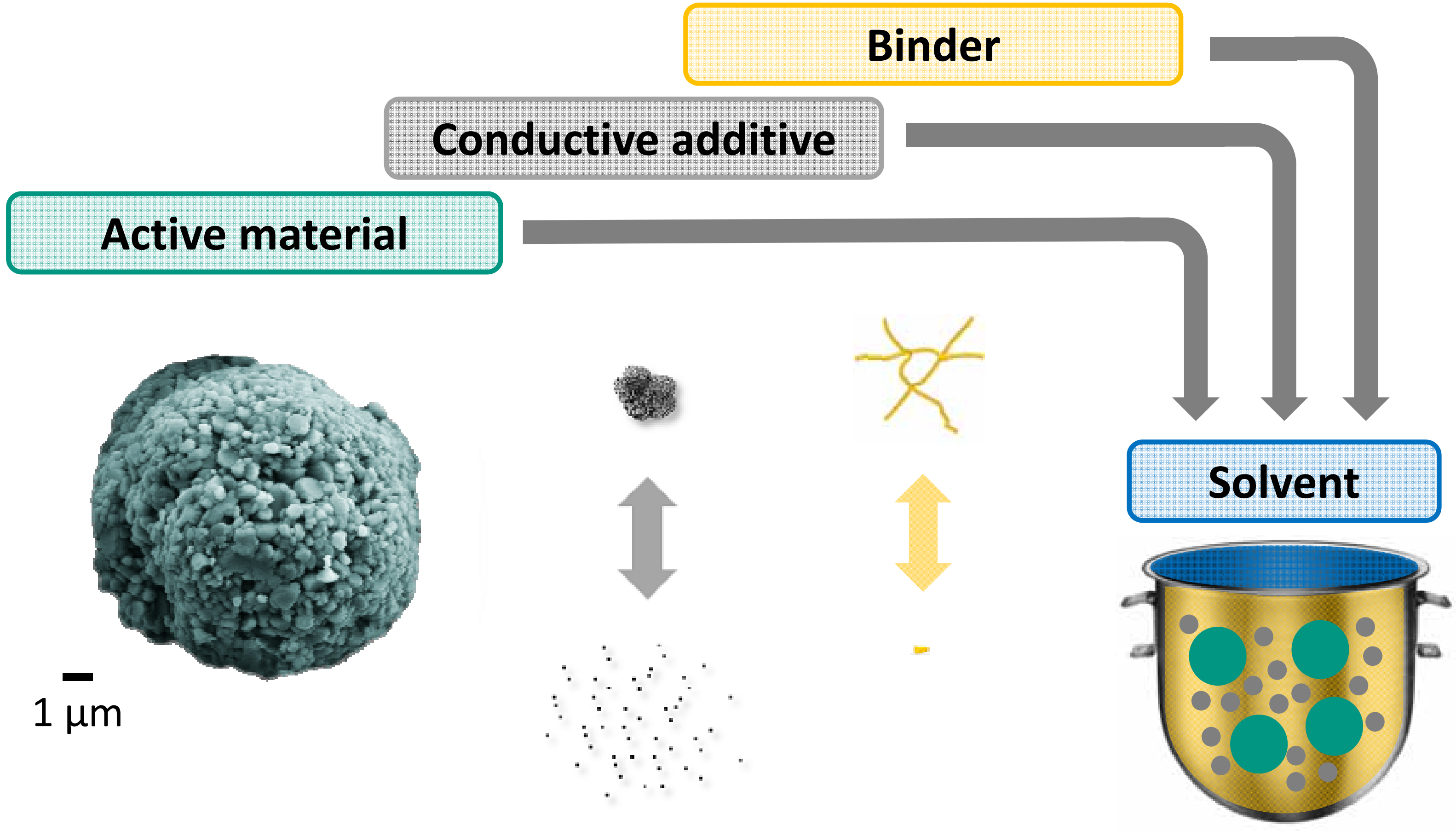
Inactive Electrode Materials and Slurry Preparation

Werner Bauer

INSTITUTE FOR APPLIED MATERIALS – CERAMIC MATERIALS AND PROCESSING (IAM-KWT)

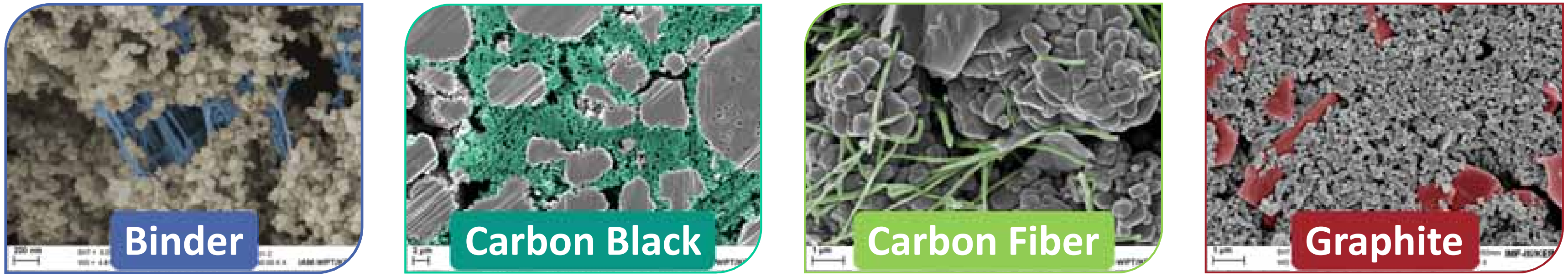


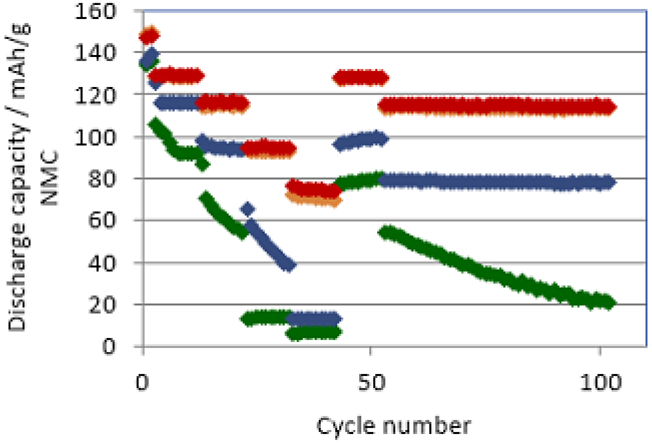
Battery Slurries – A Simple Story?



Inactive Materials

Which role play inactive materials for the manufacturing of electrodes and the application properties of cells?

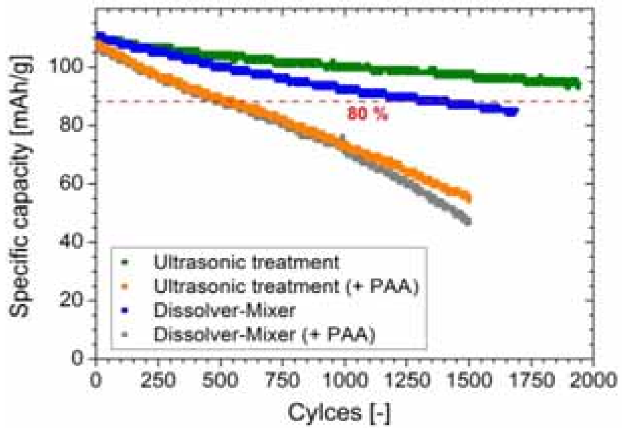




Capacity

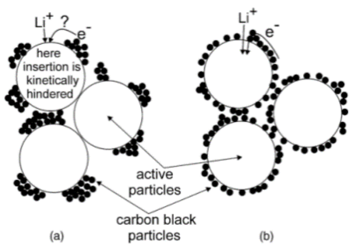
Rate Capability

Lifetime

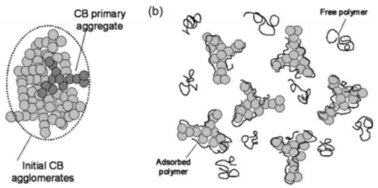


Selected Relevant Publications

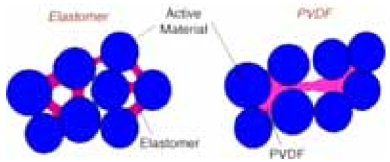
- No model comprises a complete description of the realistic distribution.
- Interaction of components is usually ignored.
- Prediction of complex electrode behavior is not feasible.



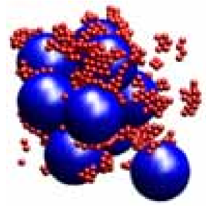
R. Dominko et al. / Journal of Power Sources 119–121 (2003) 770–773



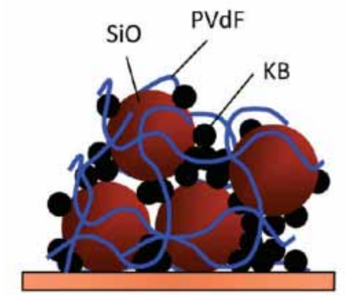
Guy et al., J. Electrochem. Soc.153 [4] (2006) A679-A688



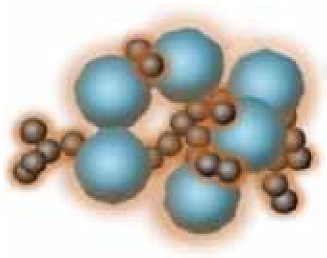
Guerfi et al, J. Power Sources 63 (2007) 1047–1052



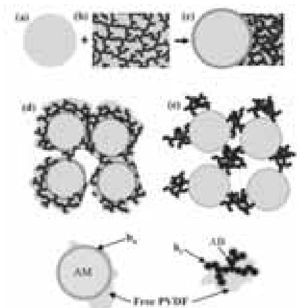
Zhu et al, J. Electrochem. Soc. 158 [10] (2011) A1155-A1159



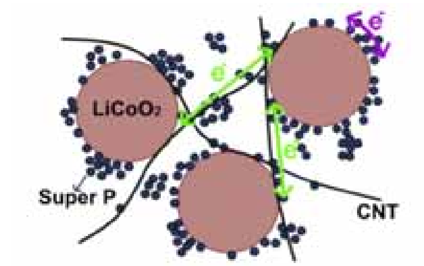
Komaba et al, J. Phys. Chem. C 115 (2011) 13487–1349



Liu et al, Adv. Mater. 23 (2011) 4679–4683

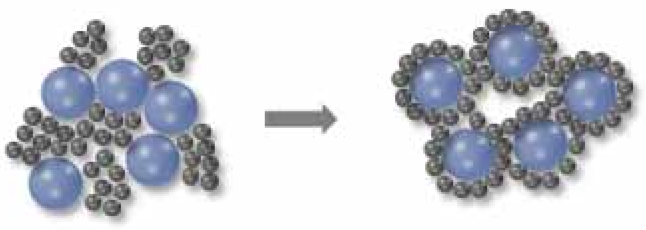


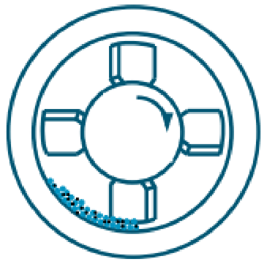
Liu et al, J. Electrochem. Soc. 159 [3] (2012) A214-A221

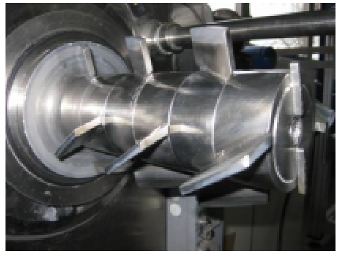


K. Wang et al, J.Power Sources 233 (2013) 209e215

Homogeneous Carbon Black Distribution by Dry Mixing

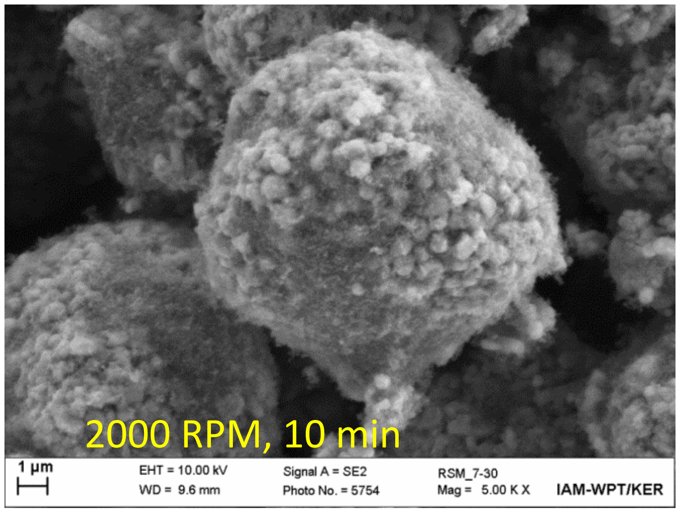


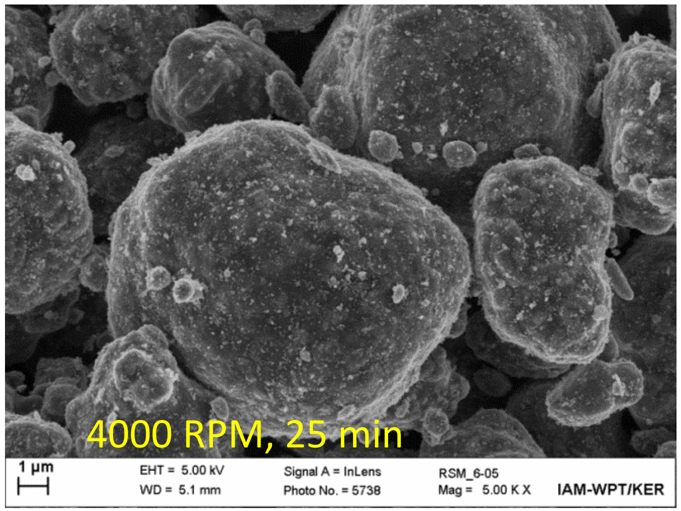




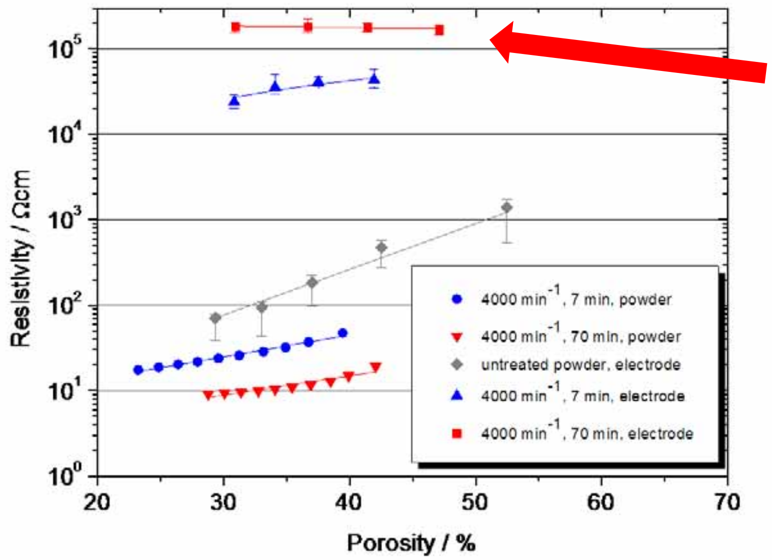
- Dry Mixing of NMC with carbon black
- Nobilta NOB-130 (Hosokawa Alpine)
- Agitation by fast rotating paddles

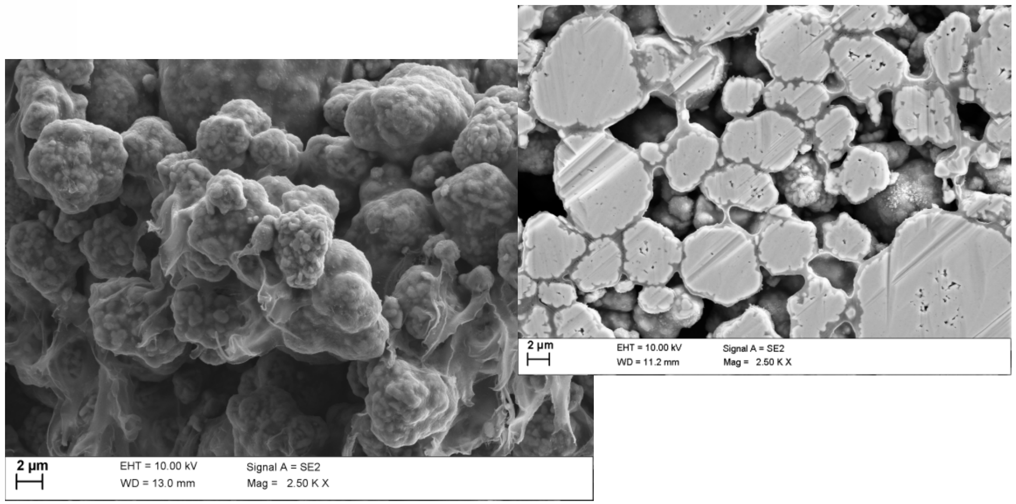
➡ Deposition of carbon black on the NMC surface





Significance of Binder-Carbon Black Distribution

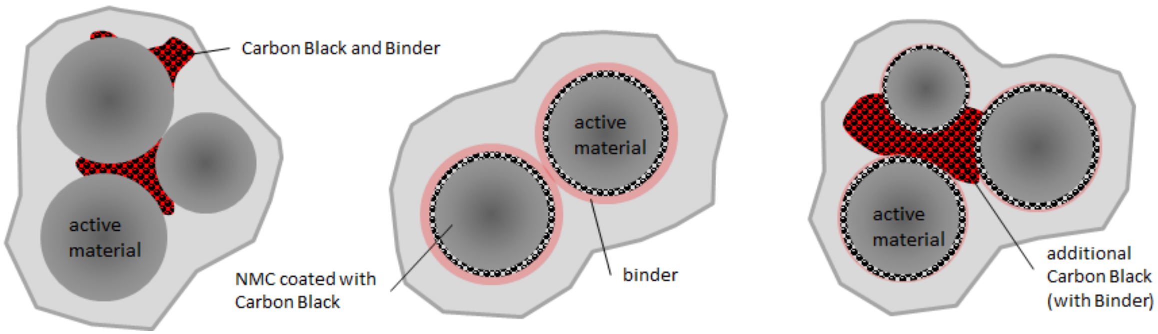




standard dispersing process

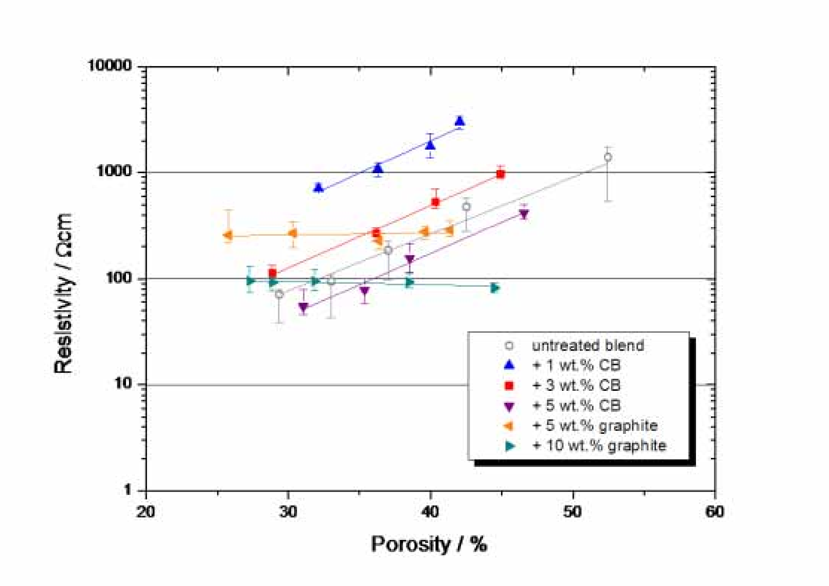
pre-treated material by a dry-mixing step

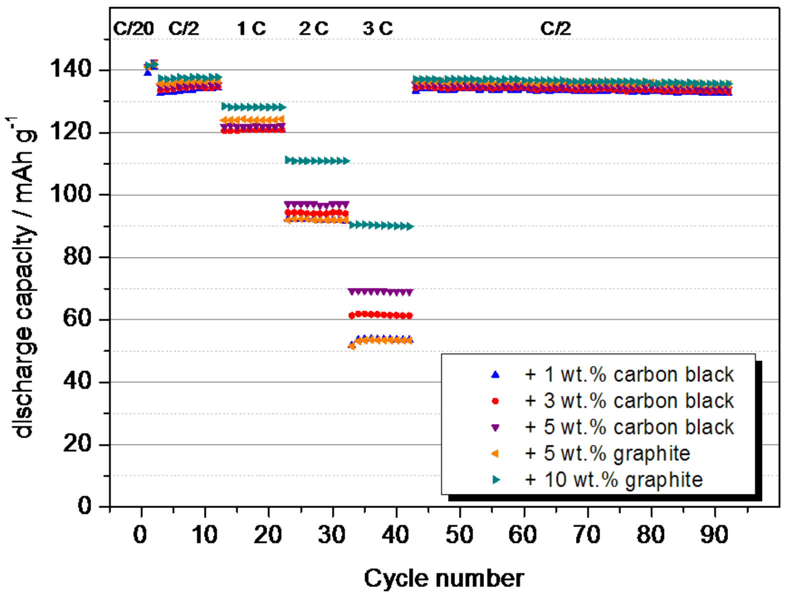
pre-treated material with additional CB

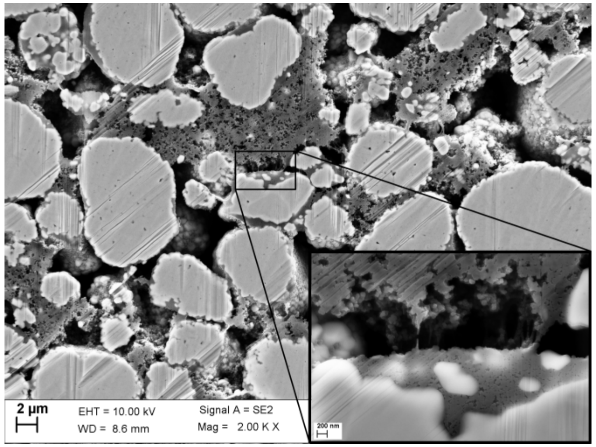


Source: Bauer et al., J. Power Sources, 288 (2015) 359-367

Effect of Additional Carbon Black or Graphite





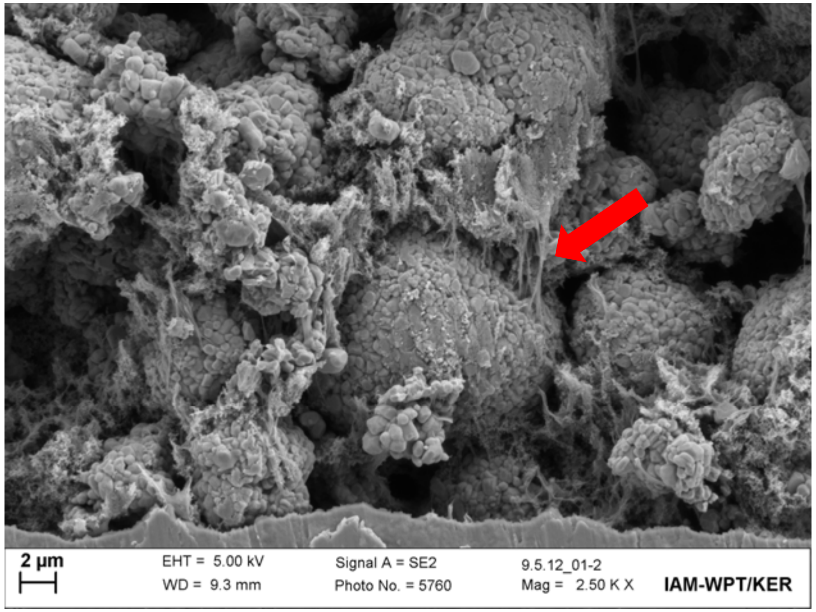


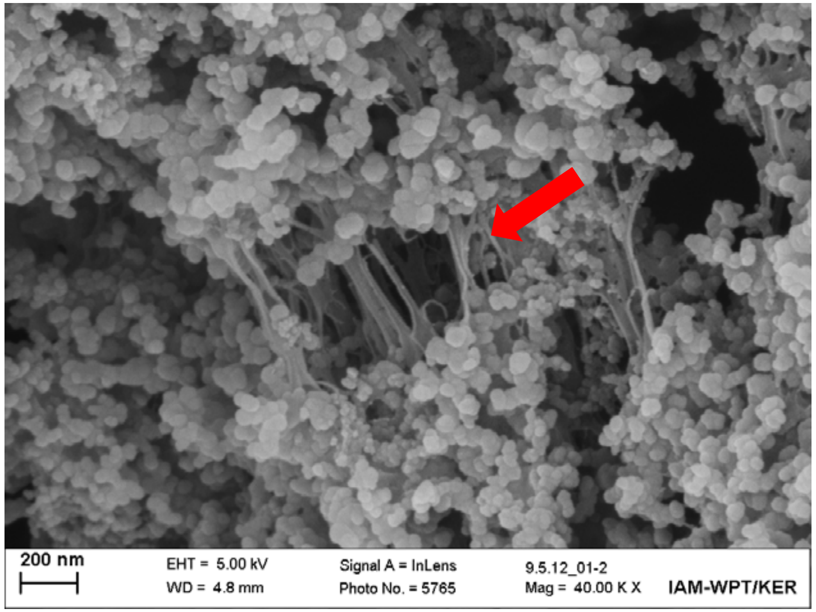
- Conductive additives are required to suppress the insulating effect of the binder.
- Immobilized carbon phase is insignificant to electrode conductivity.
- Electrode properties are determined by the interaction of binder **and** conductive aids.

Ceramic Materials and Technologies (IAM-KWT)

The Role of the Binder - Fixation

- Adhesion of electrode layer on current collector
- Providing mechanical integrity by localization and fixation of the particles
  - Active materials
  - Conductive additives



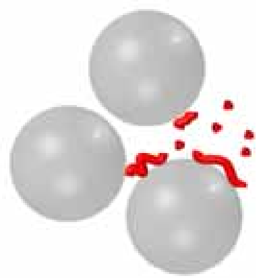


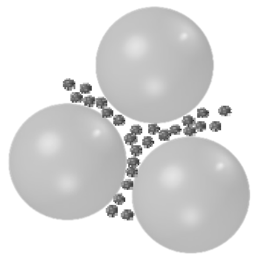
NMC, 4 wt.% carbon black, 3 wt.% PVDF

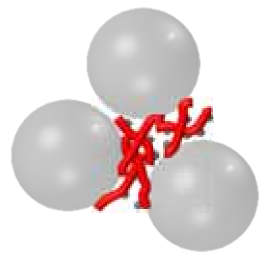
The Role of the Binder - Stabilization

- Stabilization Effects in NMP based slurries

Only PVDF	Only Carbon Black	With PVDF and Carbon Black



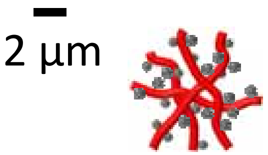




Only PVDF: Large particles → no gel formation

Only Carbon Black: Particulate gel → low gel strength

With PVDF and Carbon Black: Formation of binder/carbon black clusters

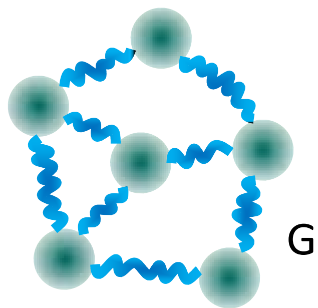


Nano sized particles
→ bridging flocculation

$$\text{Cohesive Energy } E_{coh} = \frac{1}{2} G' \cdot \gamma_{crit}^2$$

Binder	E_{coh} / 10^{-6} J/m³
No binder	198
5 wt.% 761	1975
5 wt.% HSV	1045

20 vol.% NMC + 4 wt.% carbon black



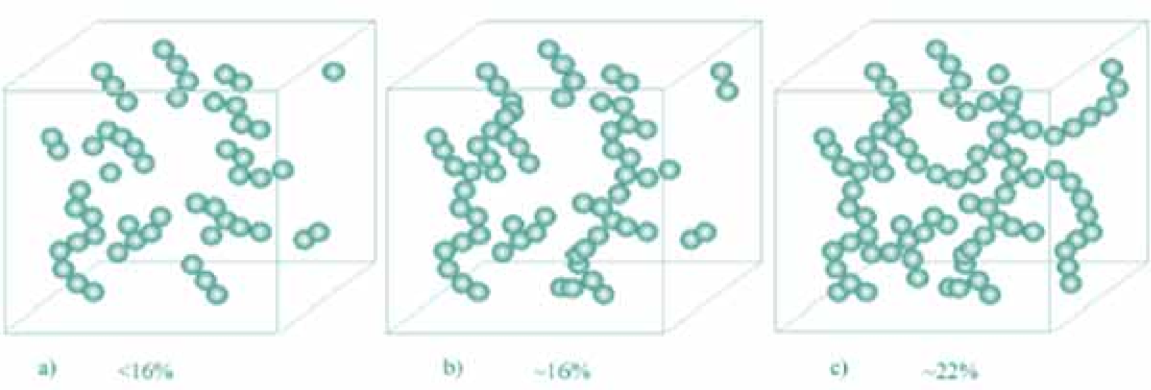
Gel structure

Source: Bauer & Nötzel, Ceram. Int., 40 (2014) 4591-4598

→ Immobilization of particles by attractive interaction → Suppression of sedimentation and agglomeration

The Role of Conductive Additives

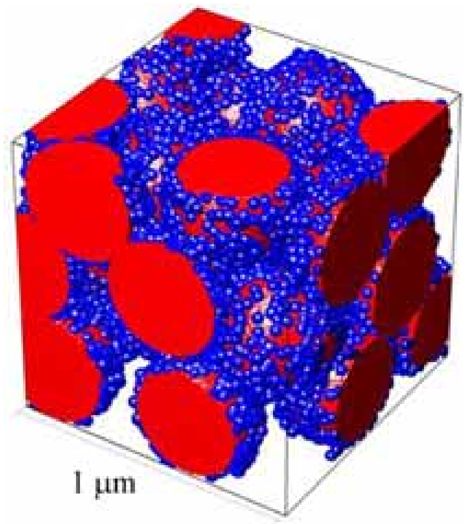
- Improvement of electronic conductivity
- Formation of conductive paths to current collector
- Set-up of a percolation structure connecting the entire active material



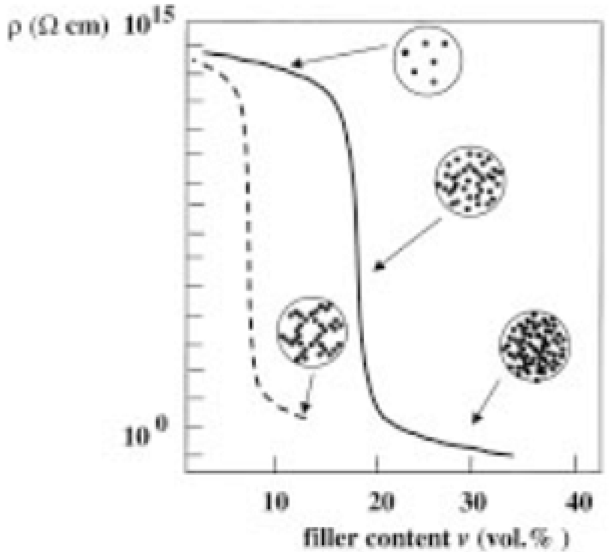
Source: Fortulan & Souza, Materials Research, Vol. 2, No. 3, 205-210, 1999

Conductivity Network

- Percolation threshold is lowered by geometrical constraint of active materials.
- Percolation structure also depends on fractal dimension of the conductive aid.
- For carbon black this corresponds with the level of deaglomeration.
- Higher percolation threshold is caused by an optimized carbon black deagglomeration.



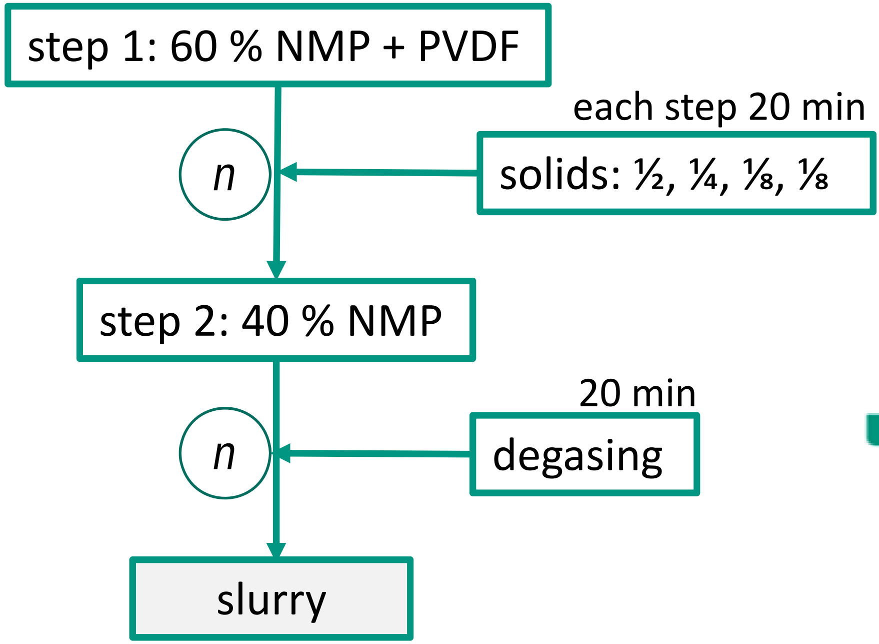
Source: http://www.bre.polyu.edu.hk/staff/bsmengni/



Source: Strümpler & Glatz-Reichenbach, J. Electroceramics 3:4 (1999) 329-346

Slurry Preparation

- Electrode components: 94 wt.% NMC, 3 wt.% carbon black, 3 wt.% PVDF
- Solid content of NMP based slurry: 25 vol.%
- Two stage mixing with dissolver

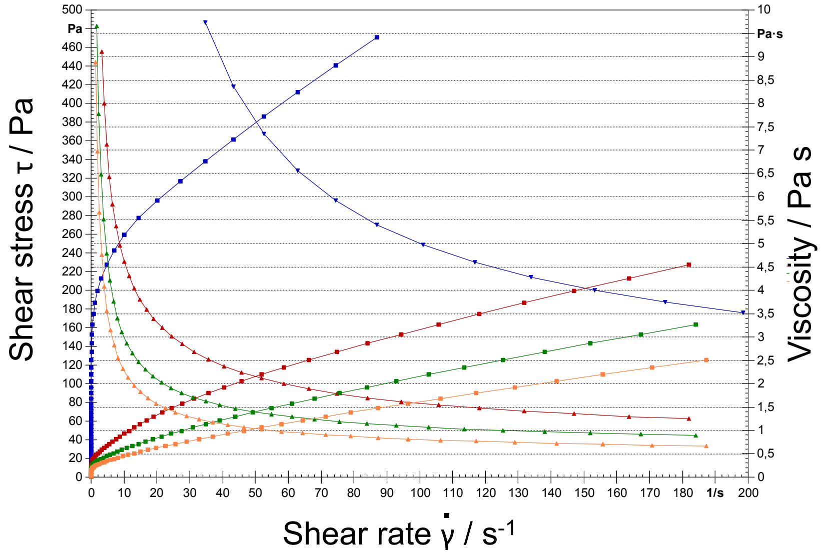


- Variation of rotation speed *n*
  - 2000 rpm
  - 4000 rpm
  - 6000 rpm

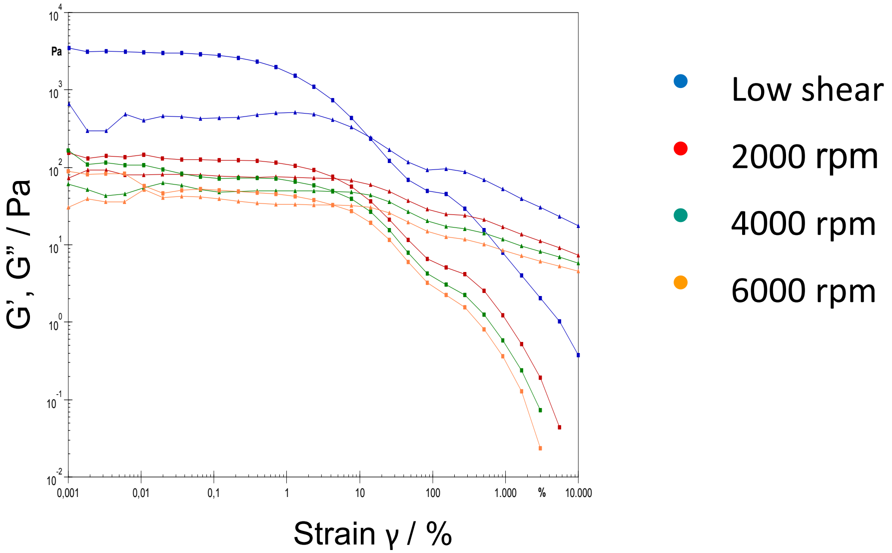
Slurry Rheology

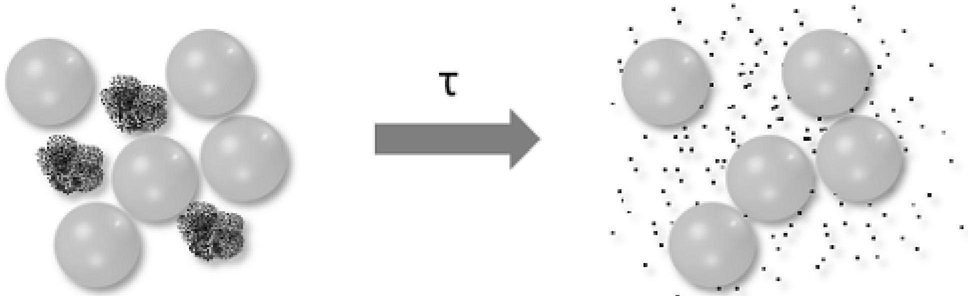
- Viscosity is reduced by intensive mixing
- All slurries keep a stabilizing gel structure

Viscosity



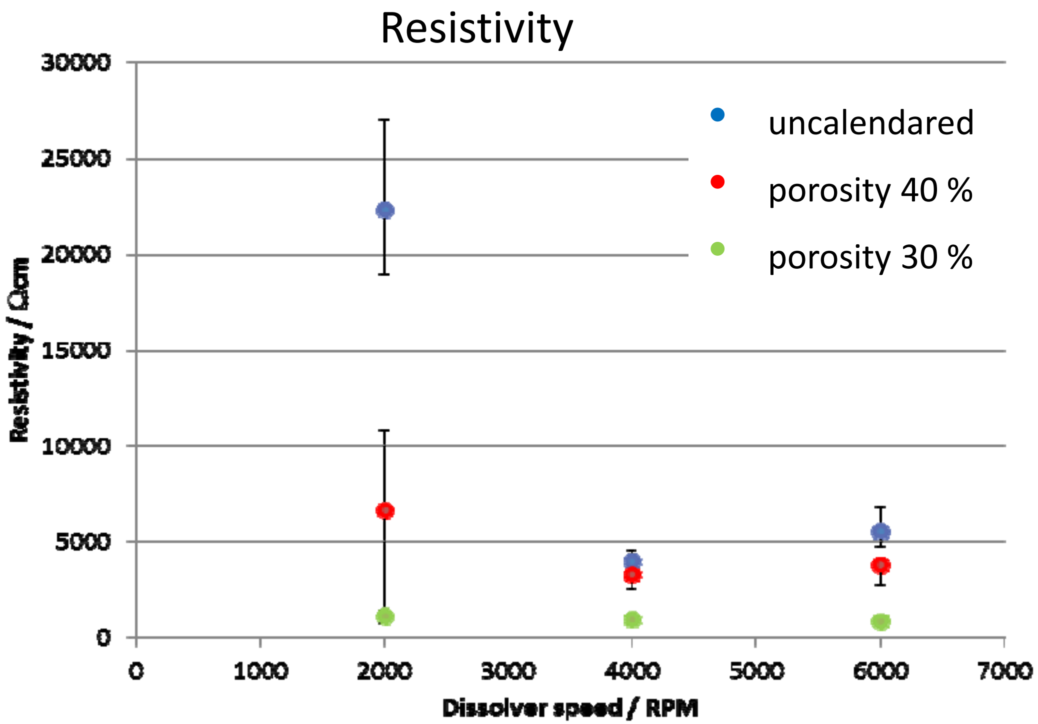
Amplitude sweep

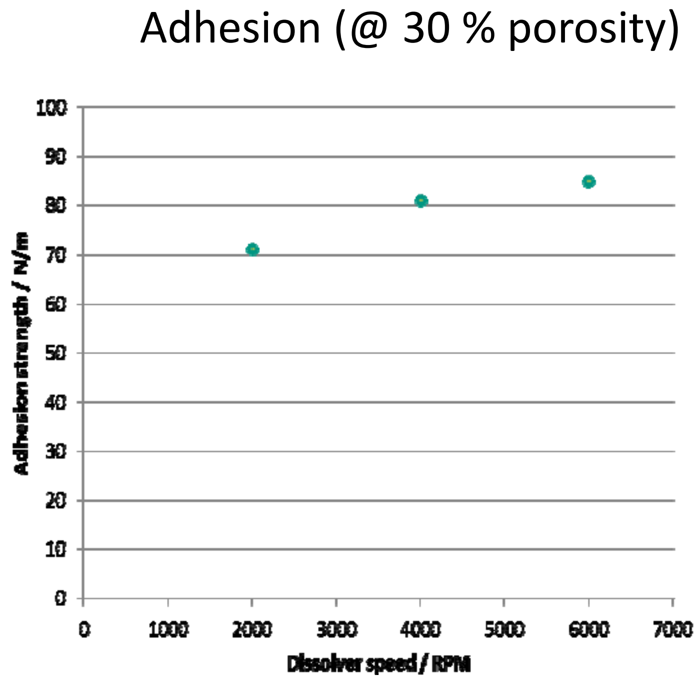




Electrode Properties

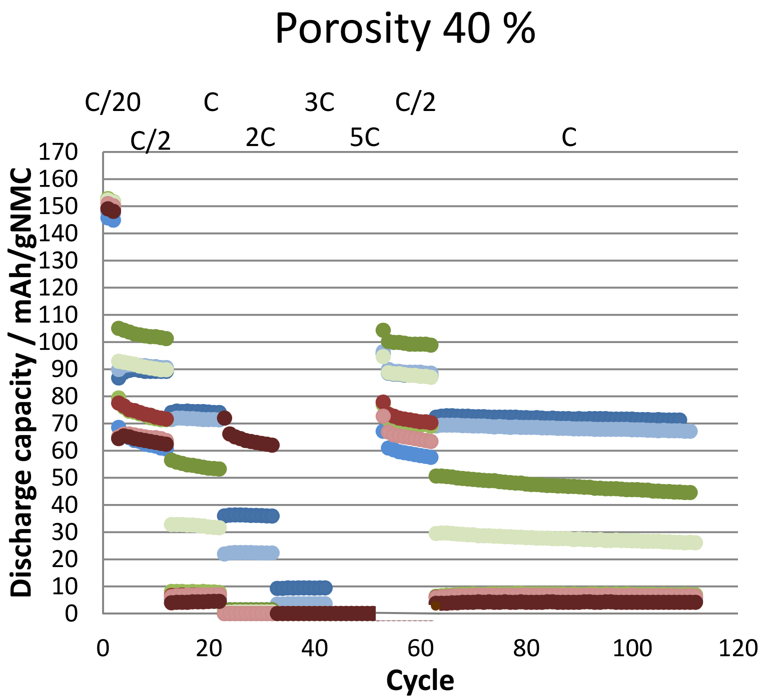
- Shear load reduces the (transition) resistance of the electrode.
- Intense mixing will involve an decrease of the conductivity once more.
- Effects are only detectable at moderate compression.

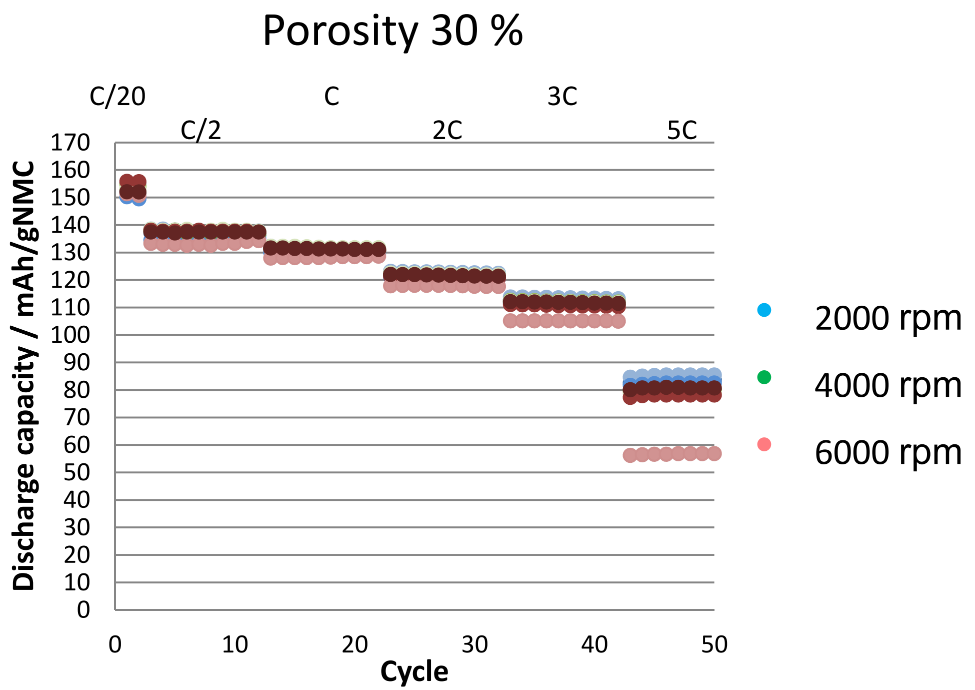




Electrochemical Properties

- Heavy scattering and decreased capacity at low electrode densification.
- Tendency of capacity reduction after intensive mixing.
- Moderate mixing seems to be more beneficial for electrode properties.

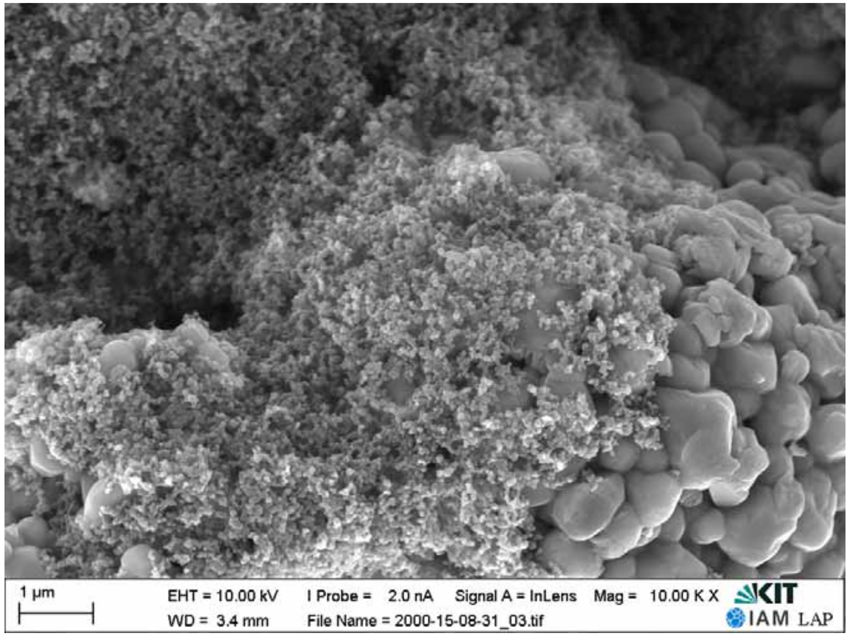




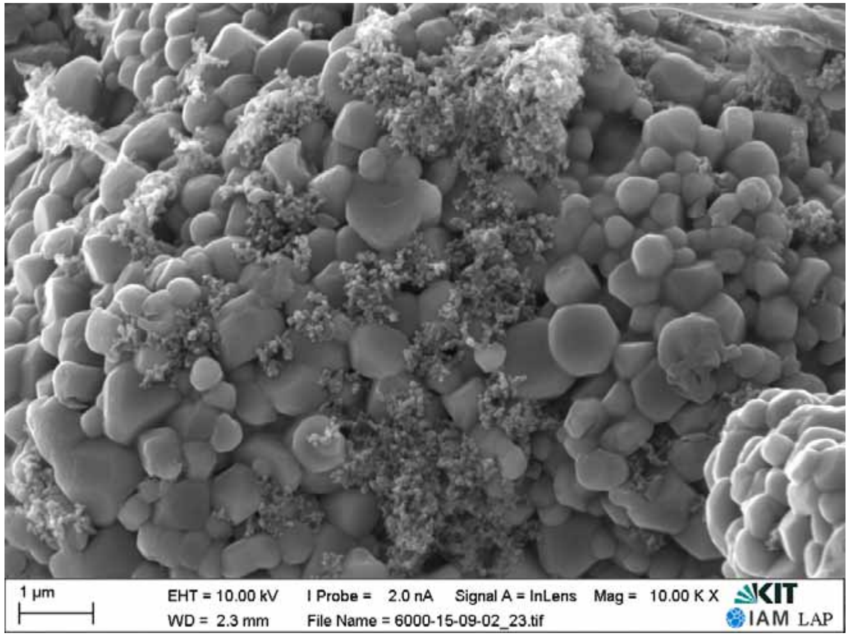
Electrode Structure

- No significant differences detectable in SEM micrographs.
- Indication on enhanced occurrence of isolated carbon black fragments.

2000 rpm

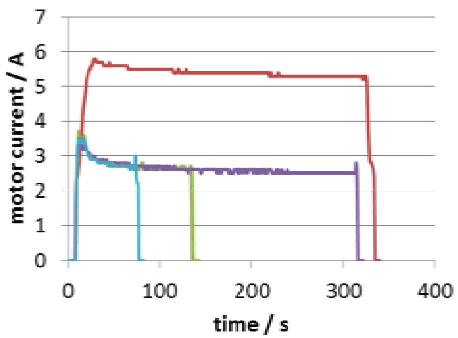


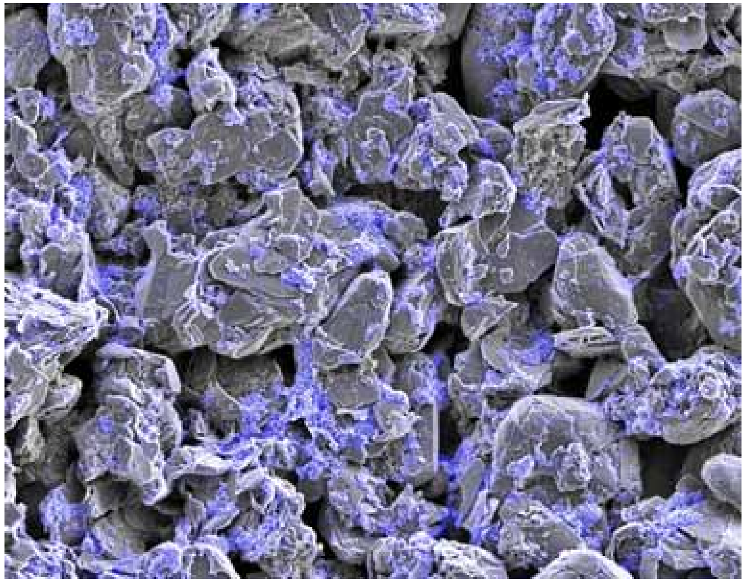
6000 rpm



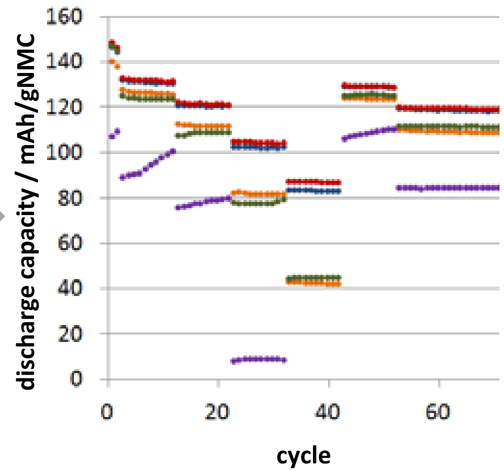
Outlook

- Investigation of process-structure-property – relationship
- Determination of the spatial distribution of additives
- Development of process and structure models





EDX mapping of PVDF on graphite anode



Thank you for your attention.