Stability of Pastes for the Manufacturing of Lithium Ion Batteries

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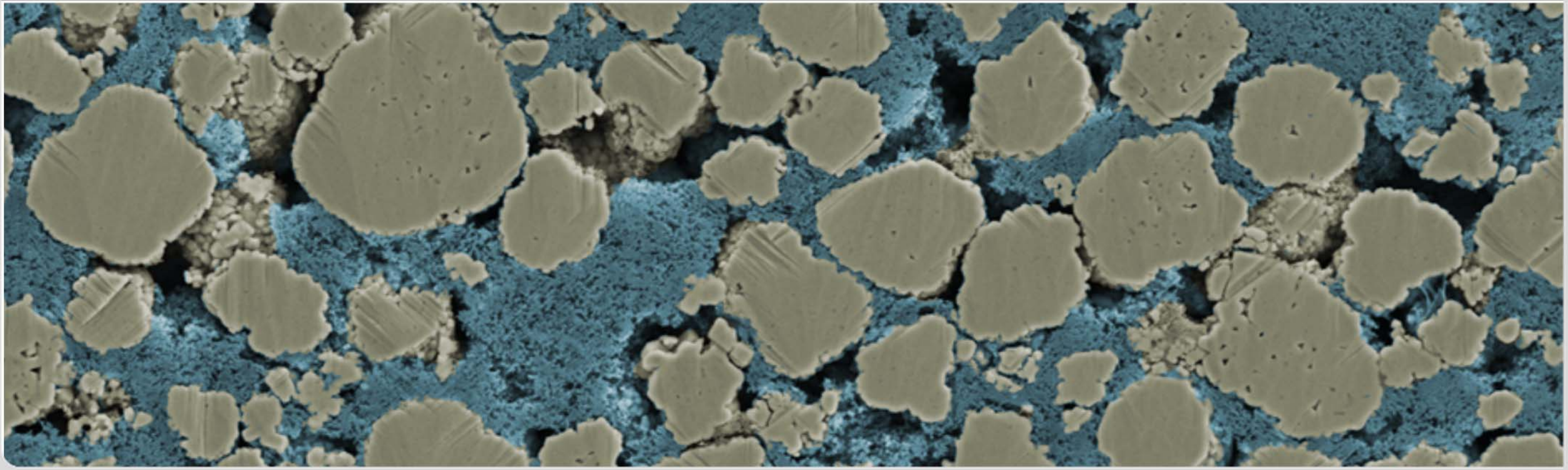
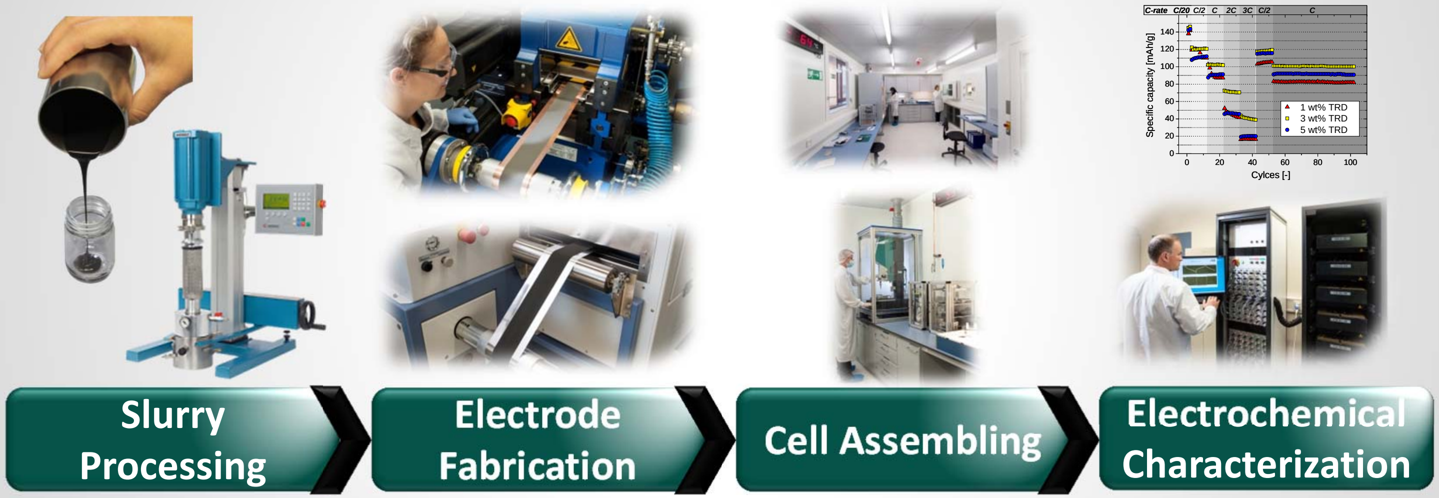


Manufacturing of Lithium Ion Batteries

Laboratory **pouch cells are used** as a tool to investigate

- material properties
- processing aspects
- interaction of cell components



Ceramic Materials and Technologies (IAM-KWT)
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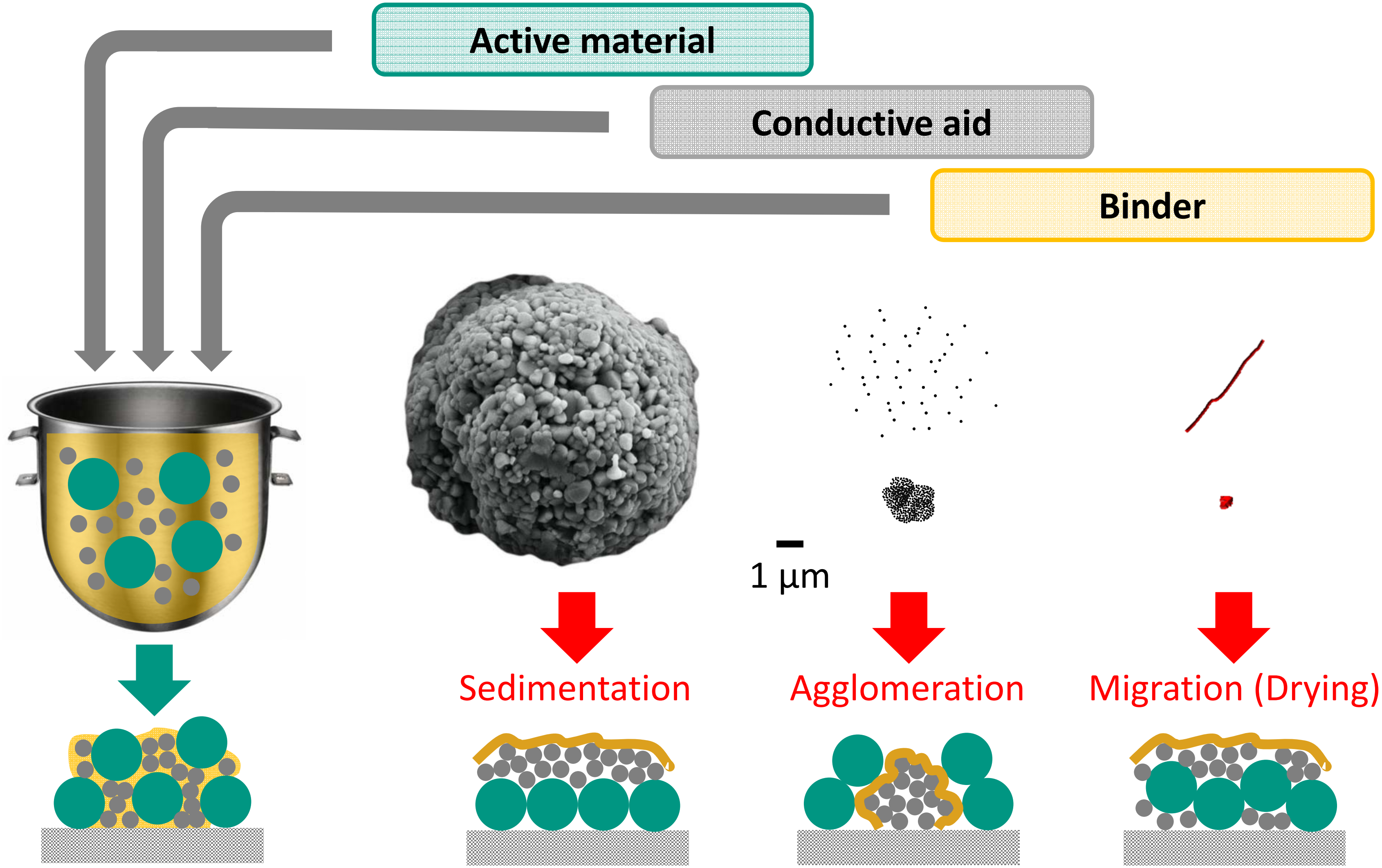
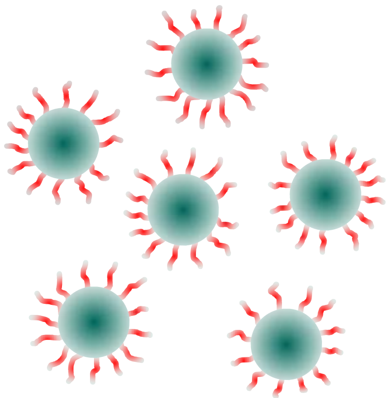
Segregation Effects in Battery Slurries



Stabilization of Battery Slurries

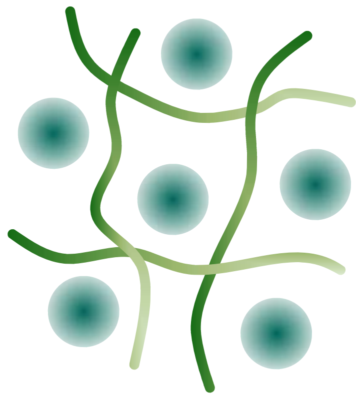
- Prevention of agglomeration or sedimentation is feasible by

Steric Stabilization



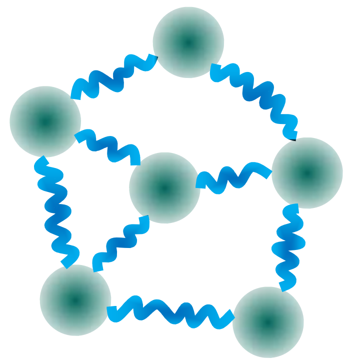
- Entropic repulsion
- Stabilization of Colloids
- No prevention of sedimentation for large particles
- Harmful to cell properties

Thickening



- Non associative thickener
- Kinetic restraint of particle movement
- Retardation of agglomeration or sedimentation

Gel Formation



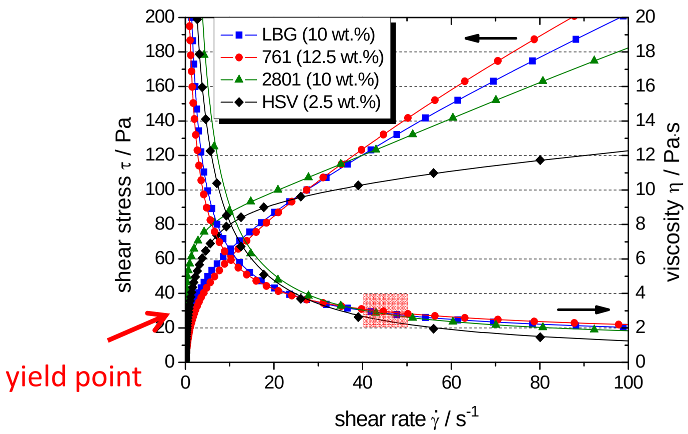
- Attractive interaction
- Particle immobilization
- Suppression of sedimentation **and** agglomeration

➡ yield point is representative

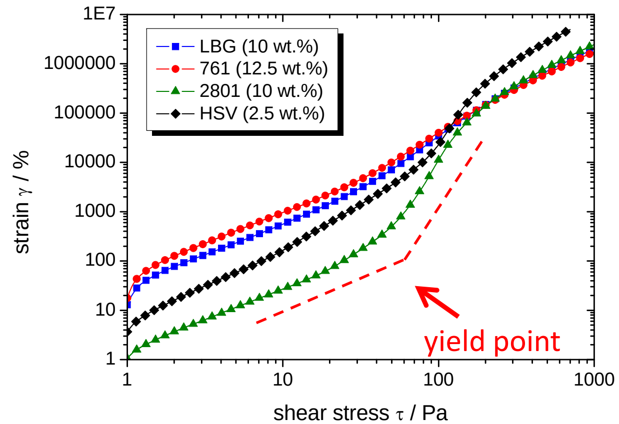
Rheological Characterization

Steady State Measurements

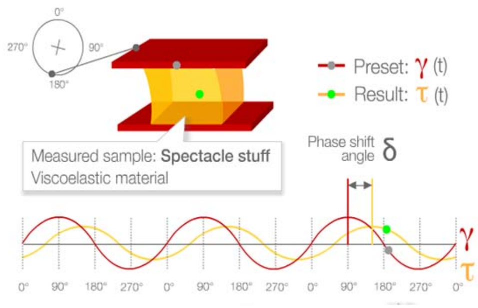
Flow and viscosity curve



Deformation curve



Oscillation Measurements



- Storage modulus

$$G' = \frac{\tau_0}{\gamma_0} \sin\delta$$

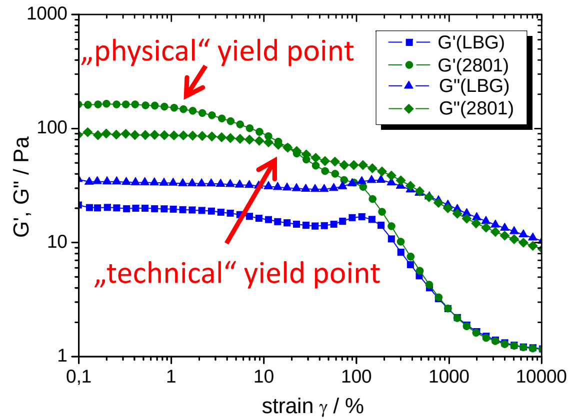
- Loss modulus

$$G'' = \frac{\tau_0}{\gamma_0} \cos\delta$$

- Loss factor

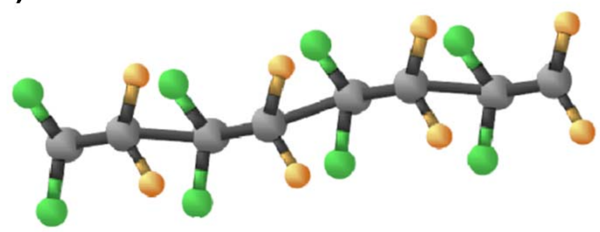
$$\tan(\delta) = \frac{G''}{G'}$$

Amplitude (and frequency) sweep

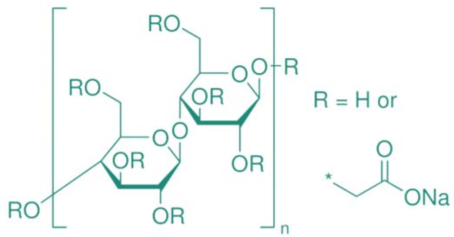


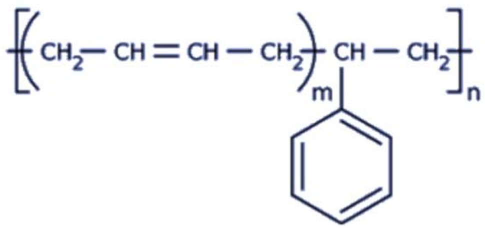
Organic vs Aqueous Processing

- Organic Processing
  - Solvent: N-Methyl-2-pyrrolidone (NMP)
  - Standard binder: Polyvinylidene fluoride (PVDF)



- Aqueous Processing
  - Solvent: Water
  - Standard binder: Carboxy Methyl Cellulose (CMC) | Styrene Butadiene Rubber (SBR)





Viscoelastic Behavior of PVDF Slurries

- Gel formation takes place only with small particles.
- Increasing tendency for gel formation at high molecular weight and high degree of functionalization.

PVDF		Active Material		
MW (g/mol)	Features	0.18 µm	1 – 3.7 µm	8.9 µm
410 000		fluid ↓	fluid ↓	fluid ↓
1 100 000		gel	fluid ↓	fluid ↓
>1 300 000		gel	gel	fluid ↓
450 000	HFP 6-8%	fluid	fluid ↓	fluid ↓
480 000	HFP 10-12%	gel	fluid ↓	fluid ↓
410 000	functionalized	gel	fluid ↓	fluid ↓
690 000		fluid ↓	fluid ↓	fluid ↓
1 100 000	functionalized	gel	fluid ↓	fluid ↓

(w/o carbon black or graphite)

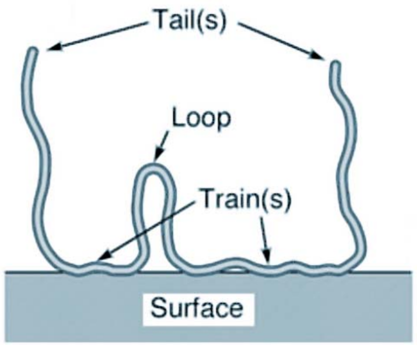
gel

fluid

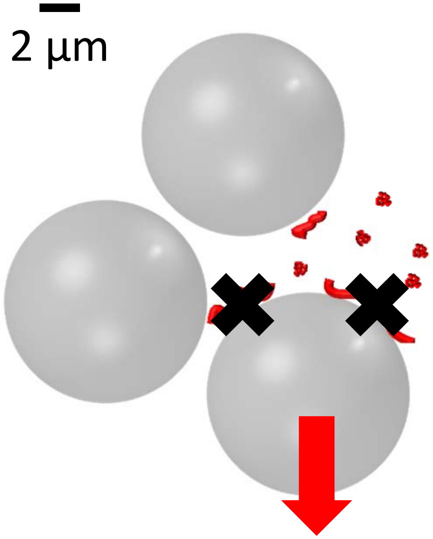
↓ Sedimentation

Interaction of PVDF with Large Particles

- PVDF properties, e.g. unbranched homopolymer MW = 700.000
  - Length of fully stretched configuration: 5.0 µm.
  - Radius of gyration for coiled configuration in NMP solution: 44 nm[1].
  - → small compared to NMC particles (size ≈ 10 µm)
- Weak interfacial adhesion → low unfolding tendency
- Binder enables only marginal interaction between particles



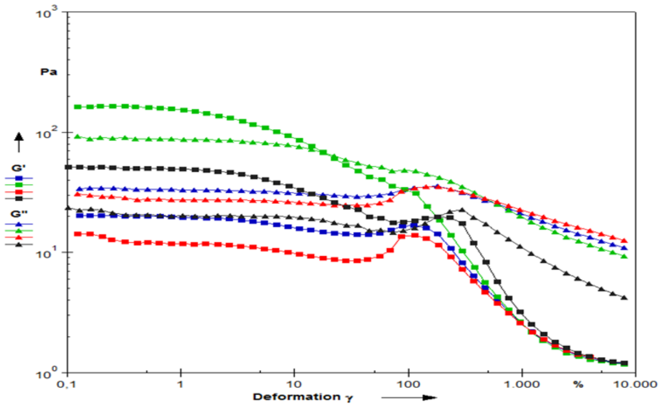
No stabilizing gel structure

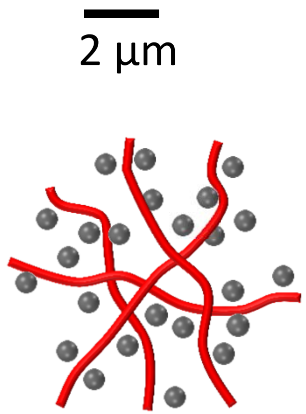


[1] Lutringer, Weill, Polymer 32 (1991) 877

Interaction of PVDF with Small Particles

- PVDF properties, e.g. unbranched homopolymer MW = 700.000
  - Length of fully stretched configuration: 5.0 µm.
  - Radius of gyration for coiled configuration in NMP solution: 44 nm[1].
  - → comparable to $LiFePO_4$ particles (size ≈ 0.2 µm)
- Formation of a pervasive polymer network.
- Bridging flocculation possible.





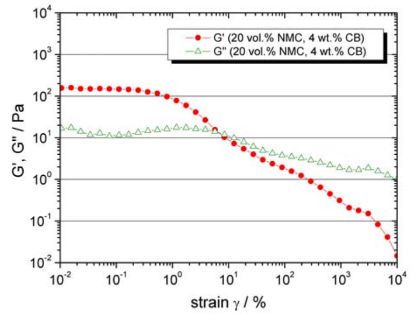
Stabilizing gel structure

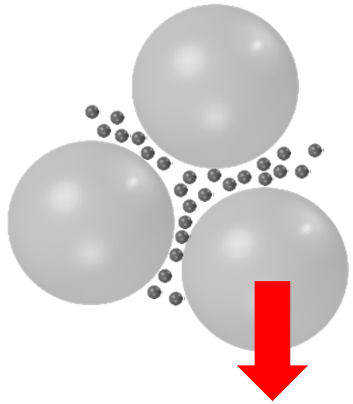
[1] Lutringer, Weill, Polymer 32 (1991) 877

Impact of Carbon Black

- NMP: polar solvent (relative permittivity 32.2, dipole moment 4.0930 D)
  → Carbon black forms a weak particulate gel in NMP

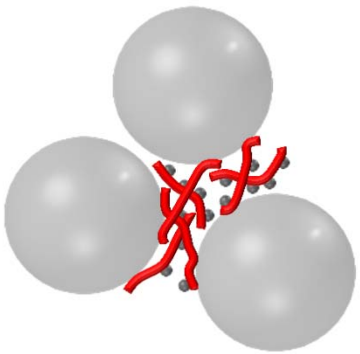
- Gel strength is to weak to enable the stabilization of large particles.





- Addition of PVDF binder allows the preparation of a stable slurry.

- Relevant is the interaction of binder with carbon black.
  → Formation of a percolating cluster structure



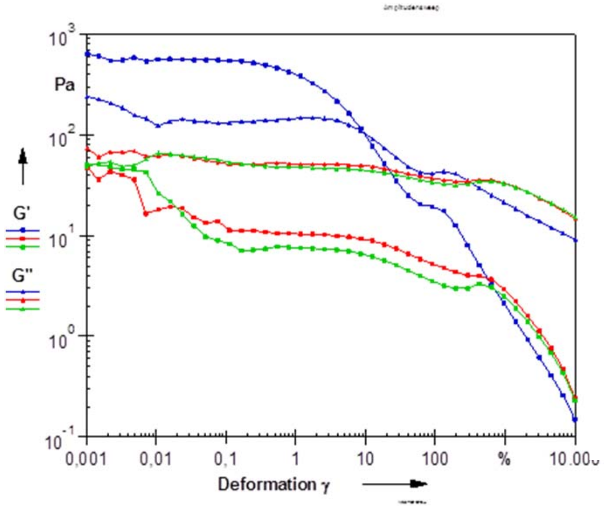
$$E_{coh} = \frac{1}{2} G' \cdot \gamma_{crit}^2$$

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

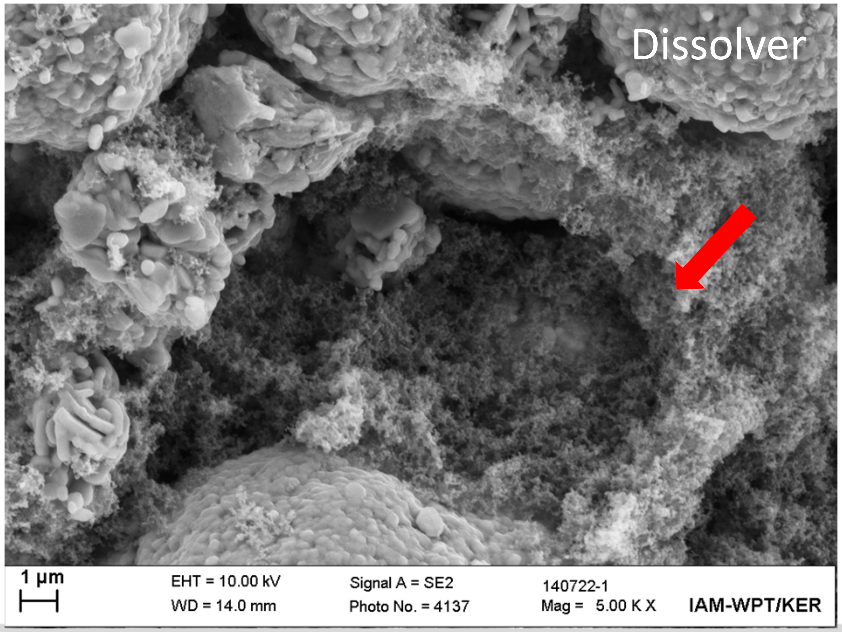
Relevance of Cluster Structure

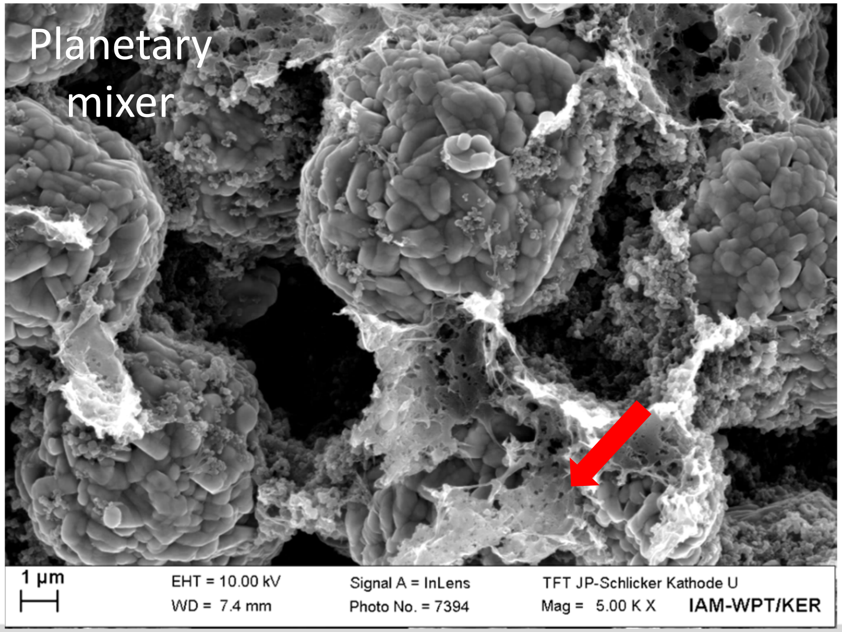
- Intensive mixing leads to fluidic behavior.
- Deviating carbon black and binder distribution compared to moderate mixing by dissolver.



Dissolver (30 min)

Planetary mixer (8 h)

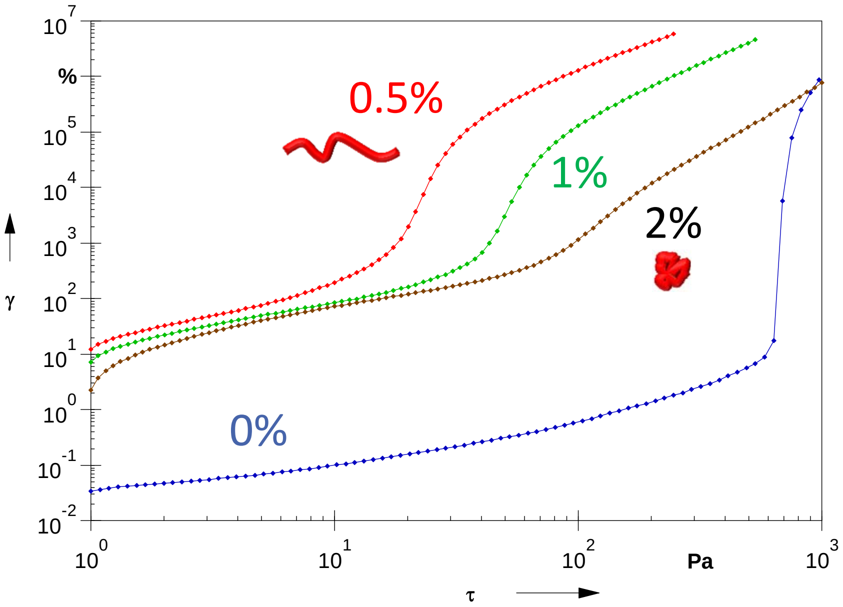




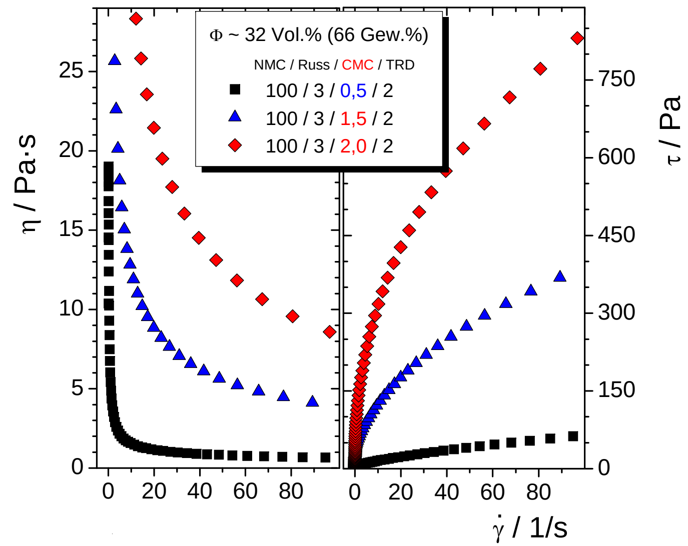
Aqueous Processing: Carboxy Methyl Cellulose

- Carboxy Methyl Cellulose (CMC) is a polyelectrolyte
  → Primary function: Dispersant for carbon black
- Strong viscosity rise by CMC addition
  → limited contribution as a binder

CMC addition to carbon black dispersion (5%)



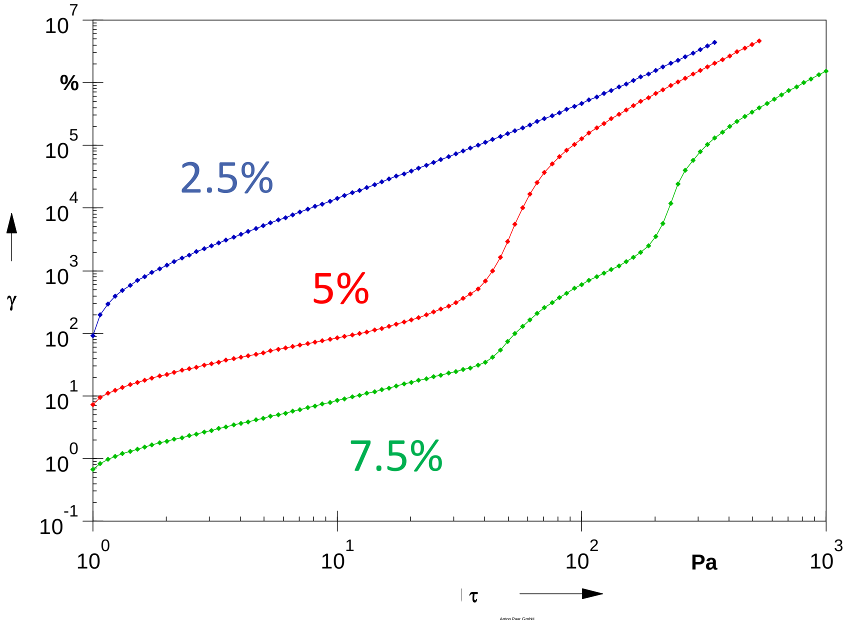
NMC slurry with CB and CMC

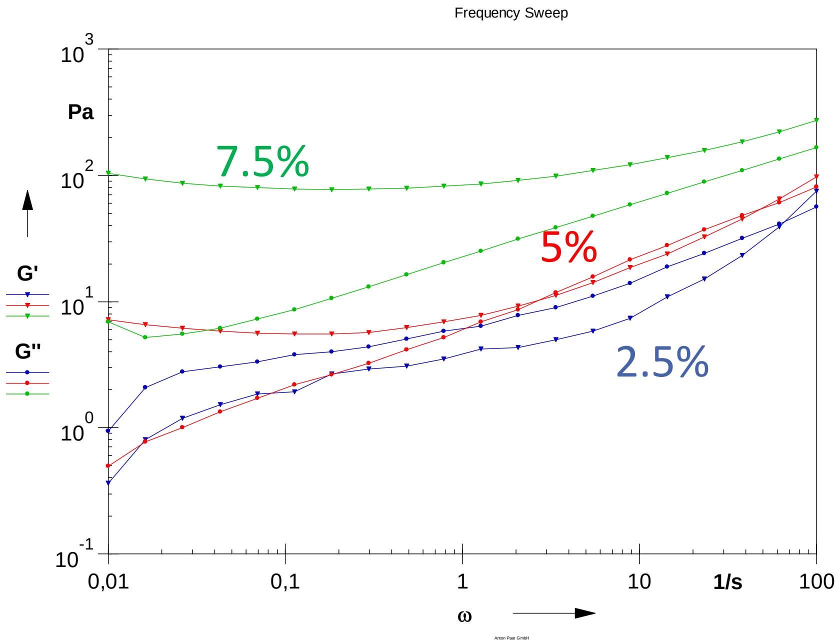


Aqueous Processing: Carbon Black

- Stabilizing potential of carbon black depends on slurry processing.
- Formation of stabilizing network above critical addition of carbon black.

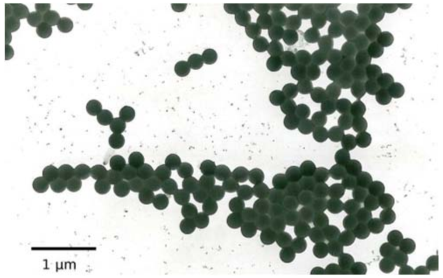
CB addition to CMC solution (1%)



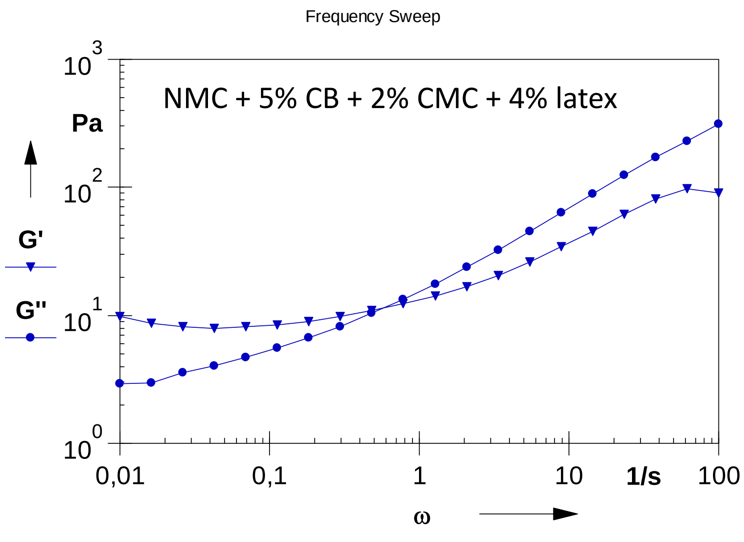


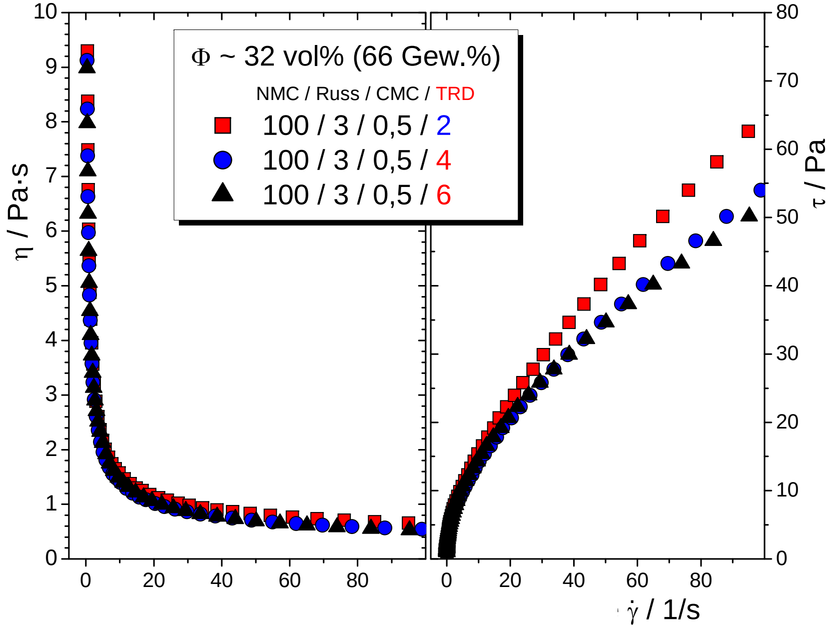
Aqueous Processing: Latex Binder

- Particle dispersion (d = 0.1 – 0.2 µm)
- Provides high adhesion strength
- Low impact on slurry rheology (at moderate solid content)
- Minor stabilization effects
- Additional binder required



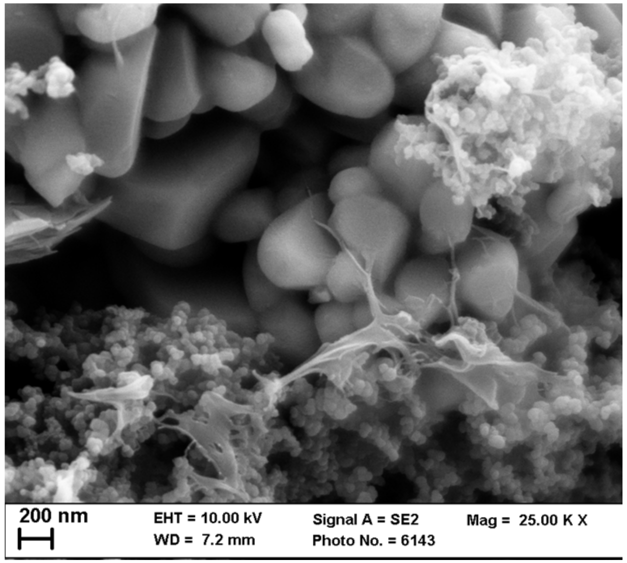
Source: Wikipedia





Summary

- Stabilization of the slurry prevents cell degradation by segregation effects.
- Slurry stabilization should be attained with essential electrode components.
- Interaction of polymer binder and carbon black is most significant.
- Clusters are also vital for the formation of a percolation structure.



Thank you for your attention.