



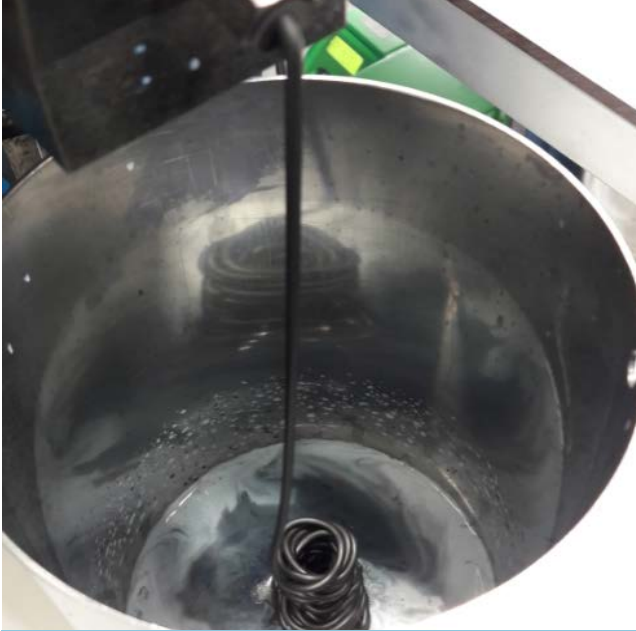
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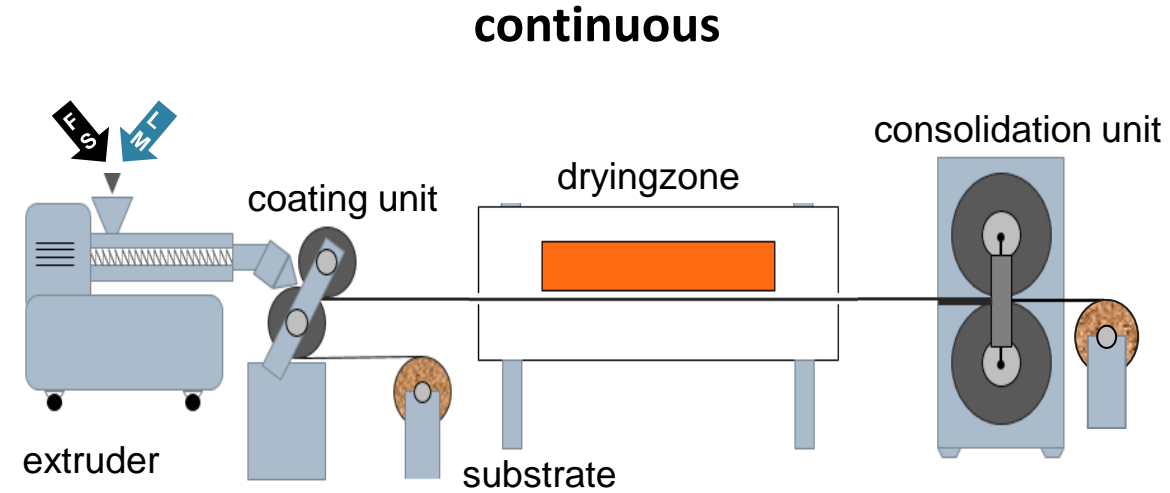
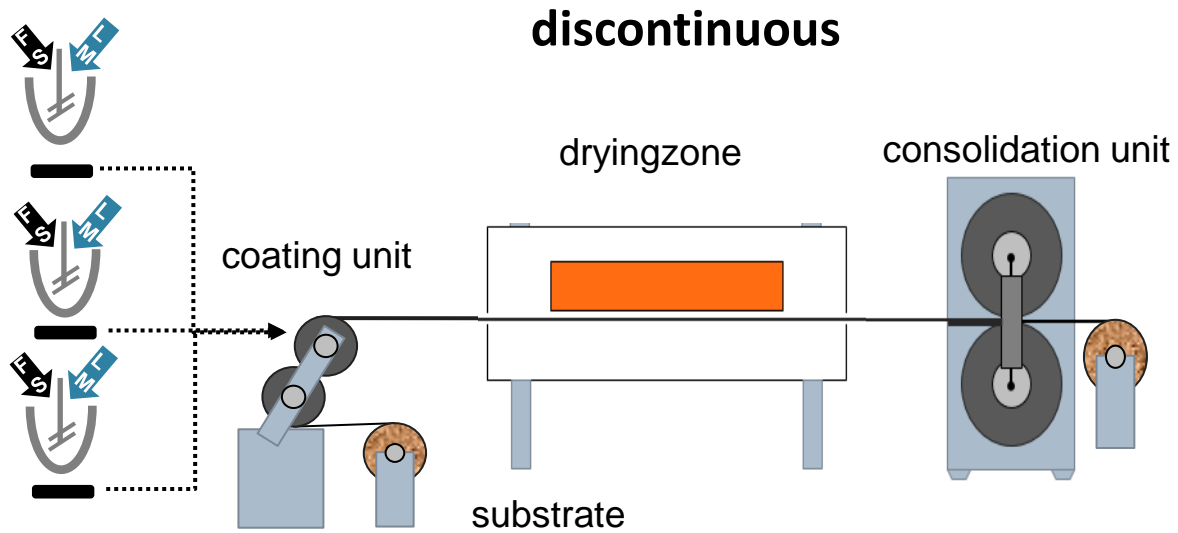


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Improved Extrusion Technology for the Production of Batteries – Enhancing Performance and Reducing Costs. A Current and Future Perspective

Eike Wiegmann, Laura Helmers, Arno Kwade 13.11.2018

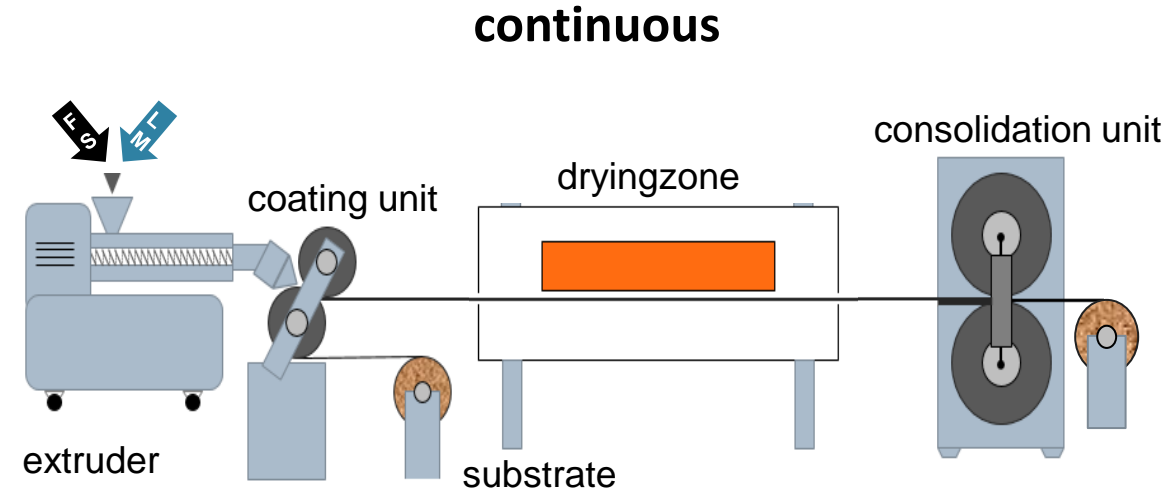
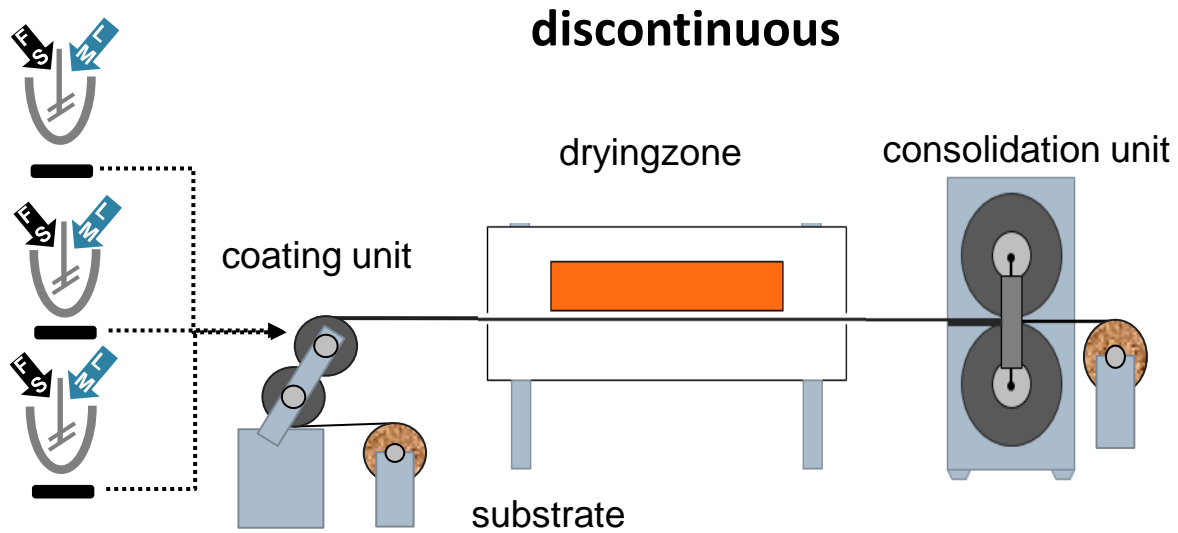


- Time and cleaning intensive, space blocking
- Low level of automation

- Integration of dispersion and coating

planetary mixer		extruder
3,81 €/kg _{suspension}	personnel costs	0,61 €/kg _{suspension} [1]
0,005 €/kg _{suspension}	energetic costs	0,002 €/kg _{suspension}

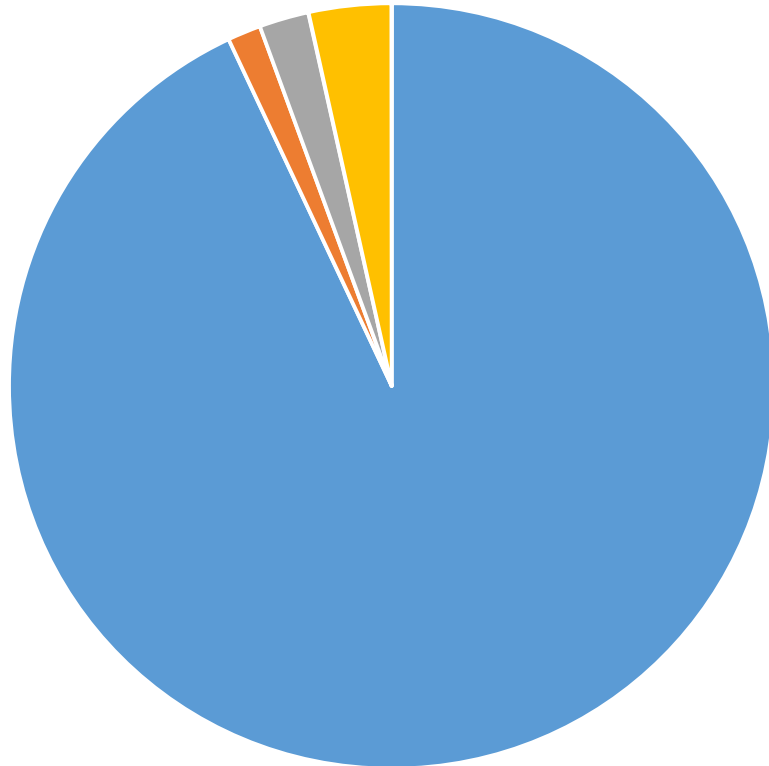
Extrusion in LIB-Production



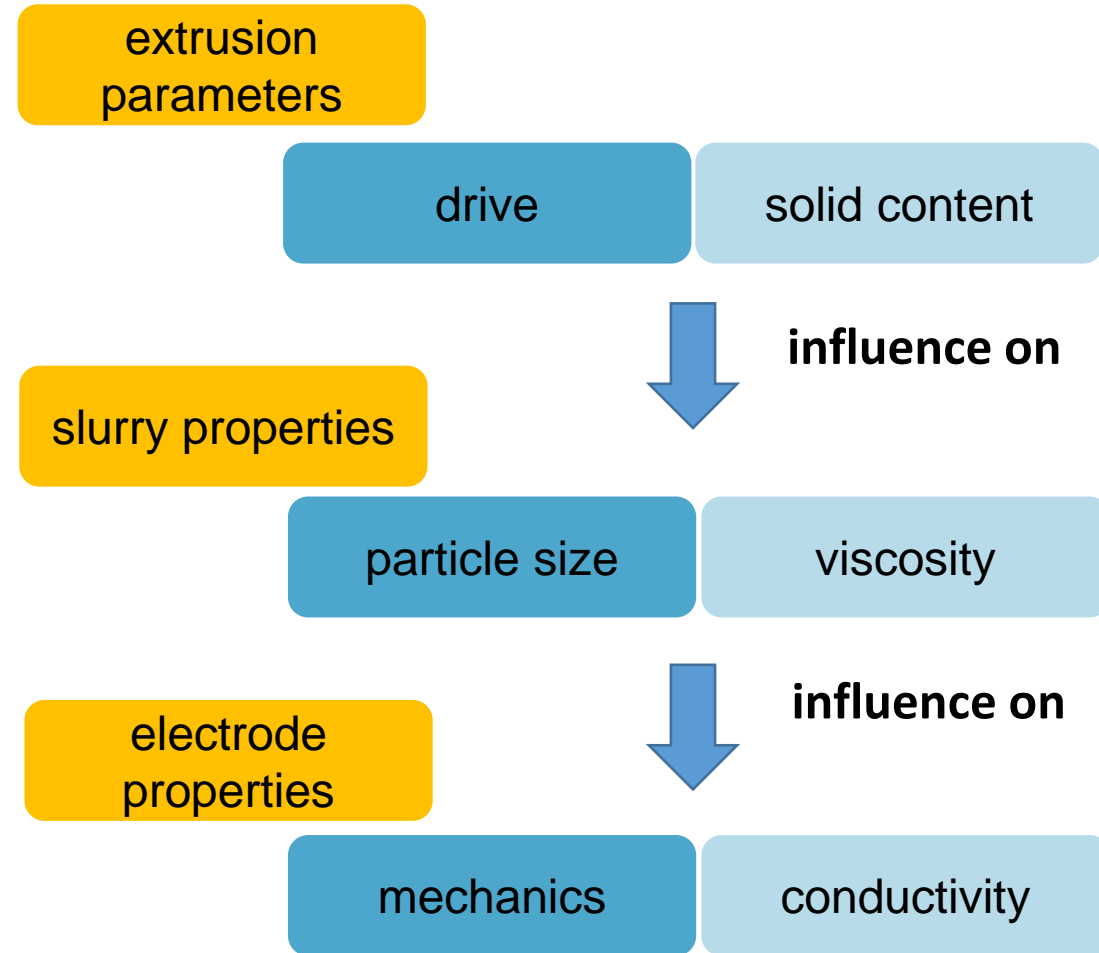
planetary mixer		extruder
3,81 €/kg _{suspension}	personnel costs	0,61 €/kg _{suspension} [1]
0,005 €/kg _{suspension}	energetic costs	0,002 €/kg _{suspension}

Process Parameter Effects on LIB (Anodes)

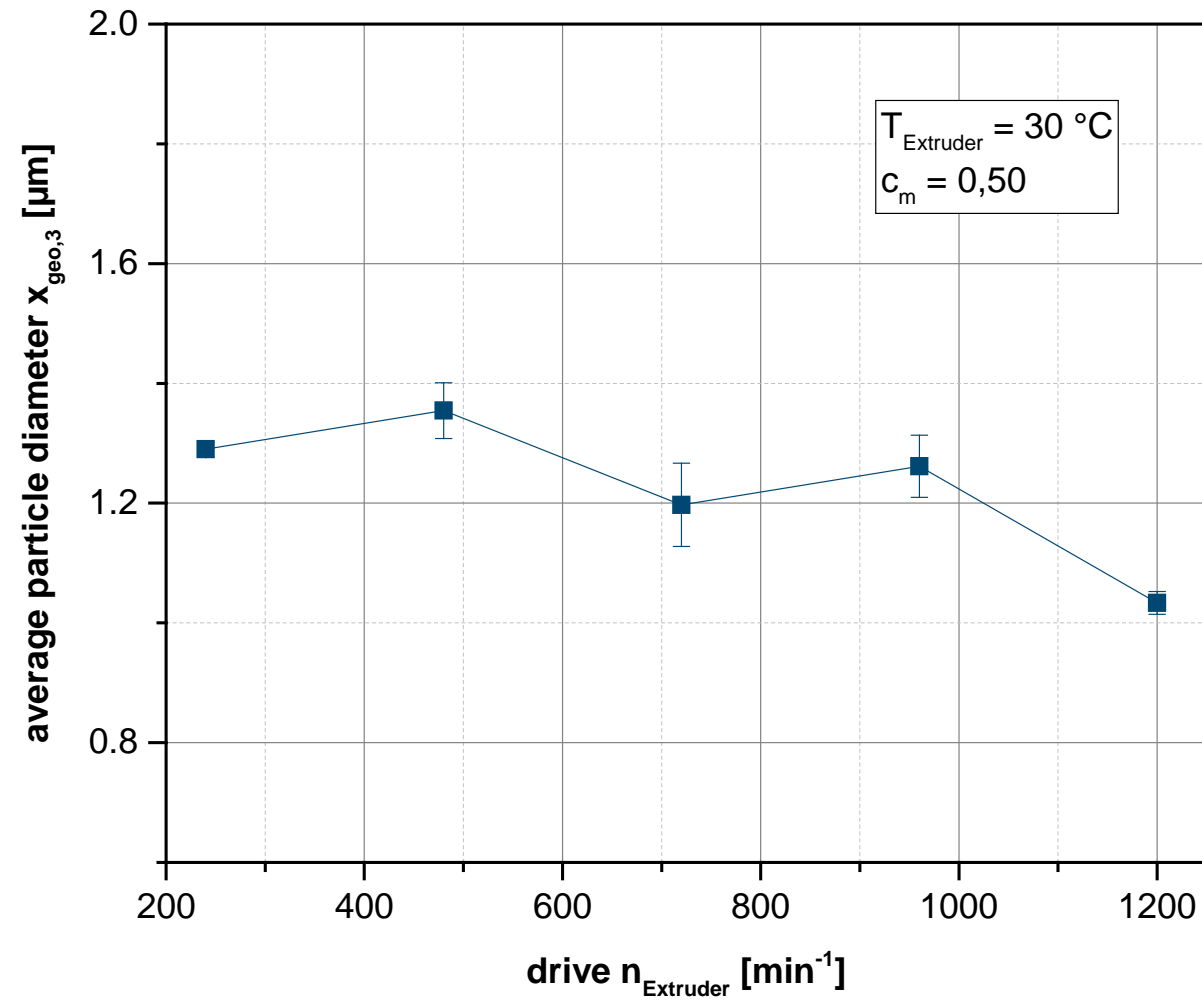
anode formulation

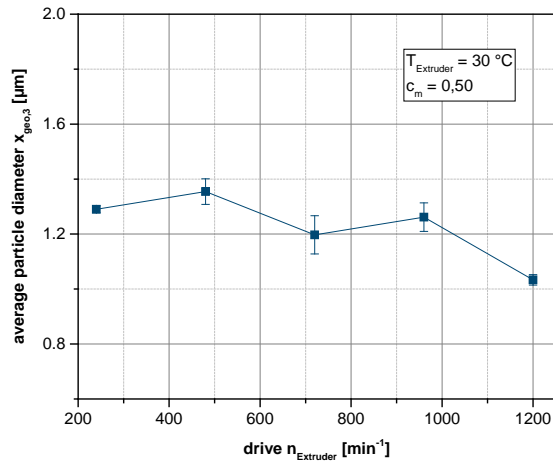


■ Graphite ■ Carbon Black ■ CMC ■ SBR



Influence of Drive - Slurry

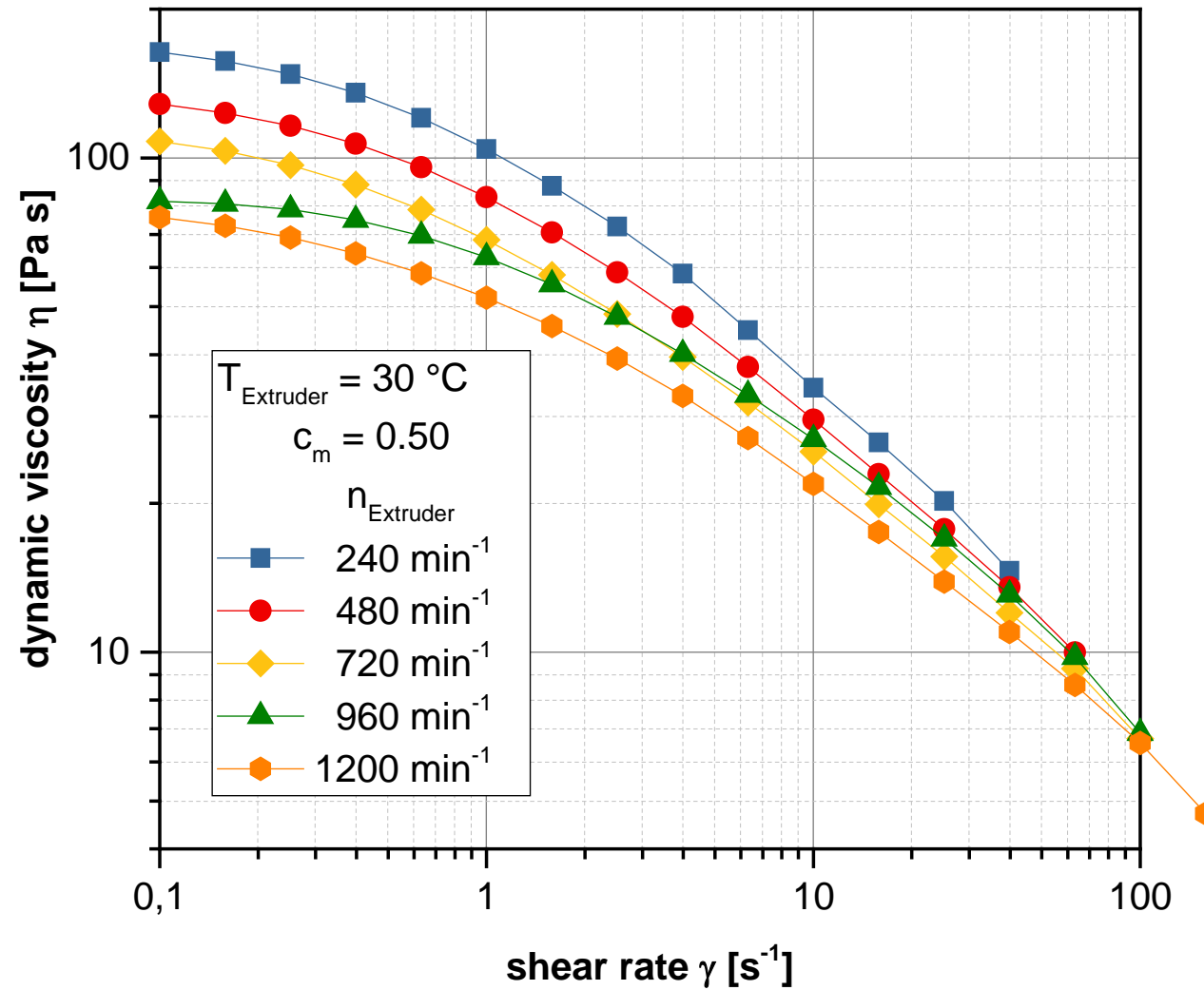


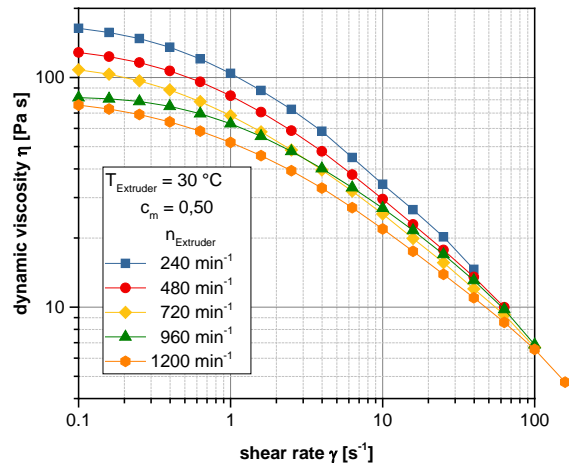
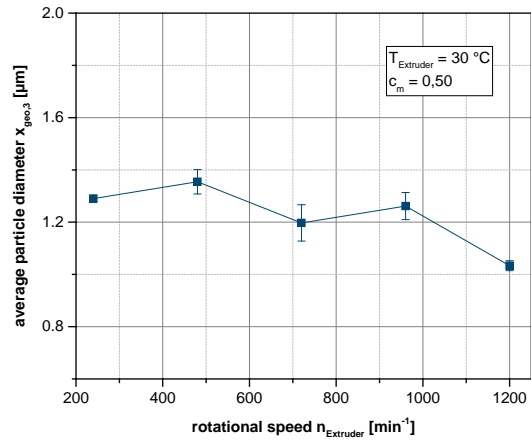


Particle size

- High rotational speed \rightarrow higher shear rates \rightarrow better dispersion
- High rotational speed \rightarrow shorter retention time \rightarrow worse dispersion

Influence of Drive - Slurry





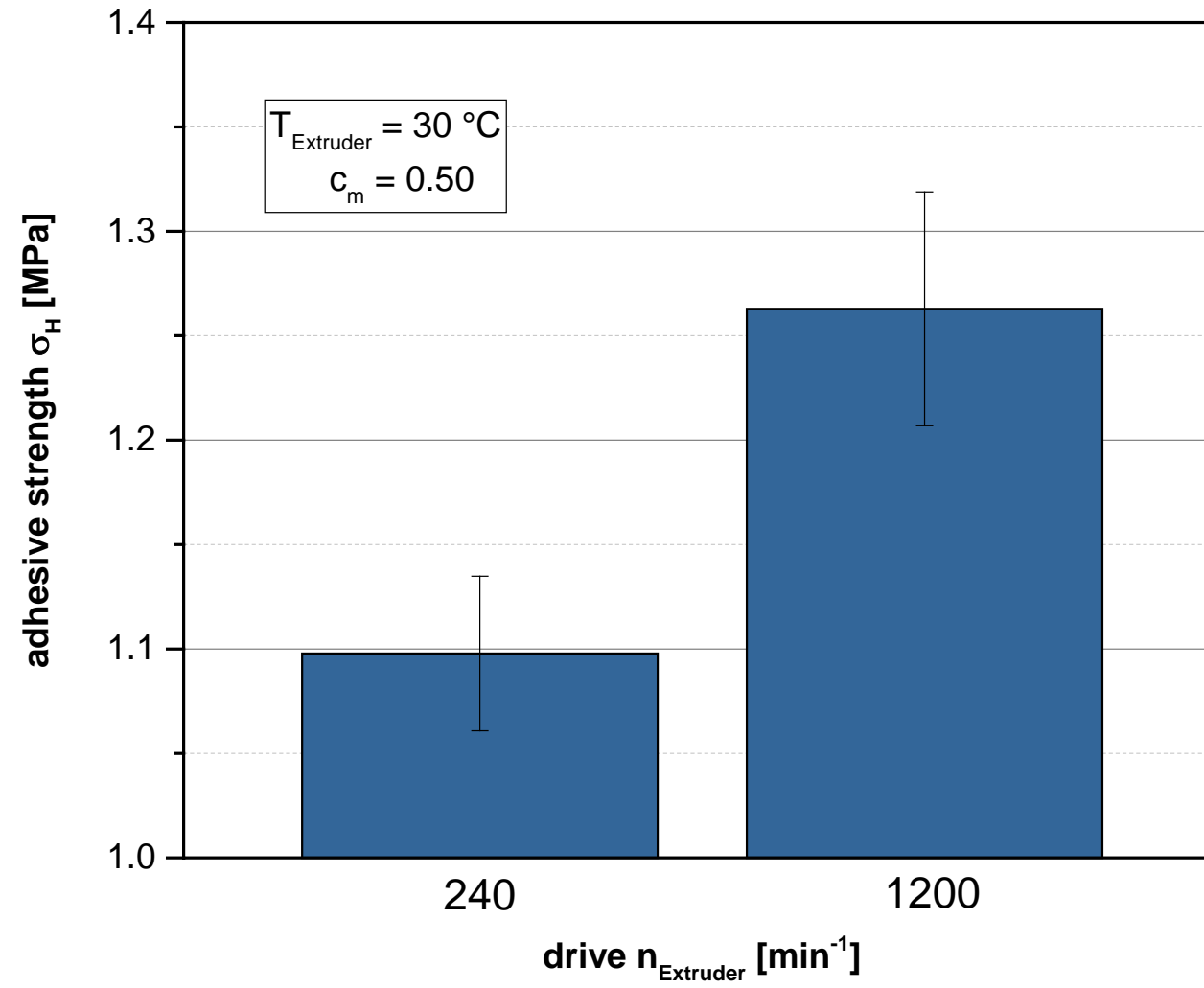
Particle size

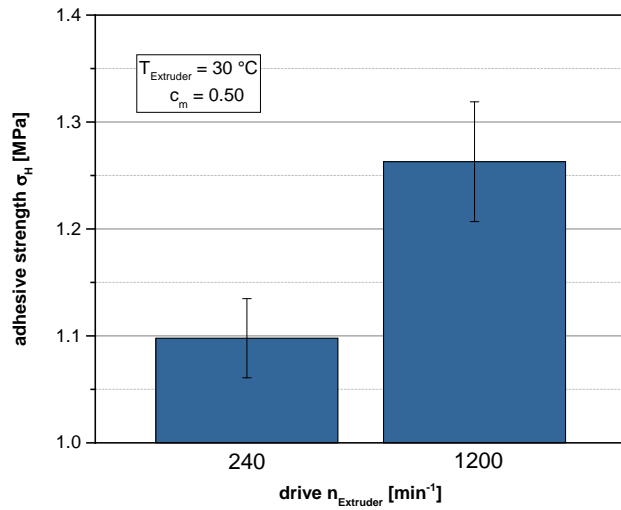
- High rotational speed \rightarrow higher shear rates \rightarrow better dispersion
- High rotational speed \rightarrow shorter retention time \rightarrow worse dispersion

Rheology

- Shear dilutive | viscoelastic liquid
- Higher shear stress \rightarrow less cross-linking + network weakening

Influence of Drive - Electrodes

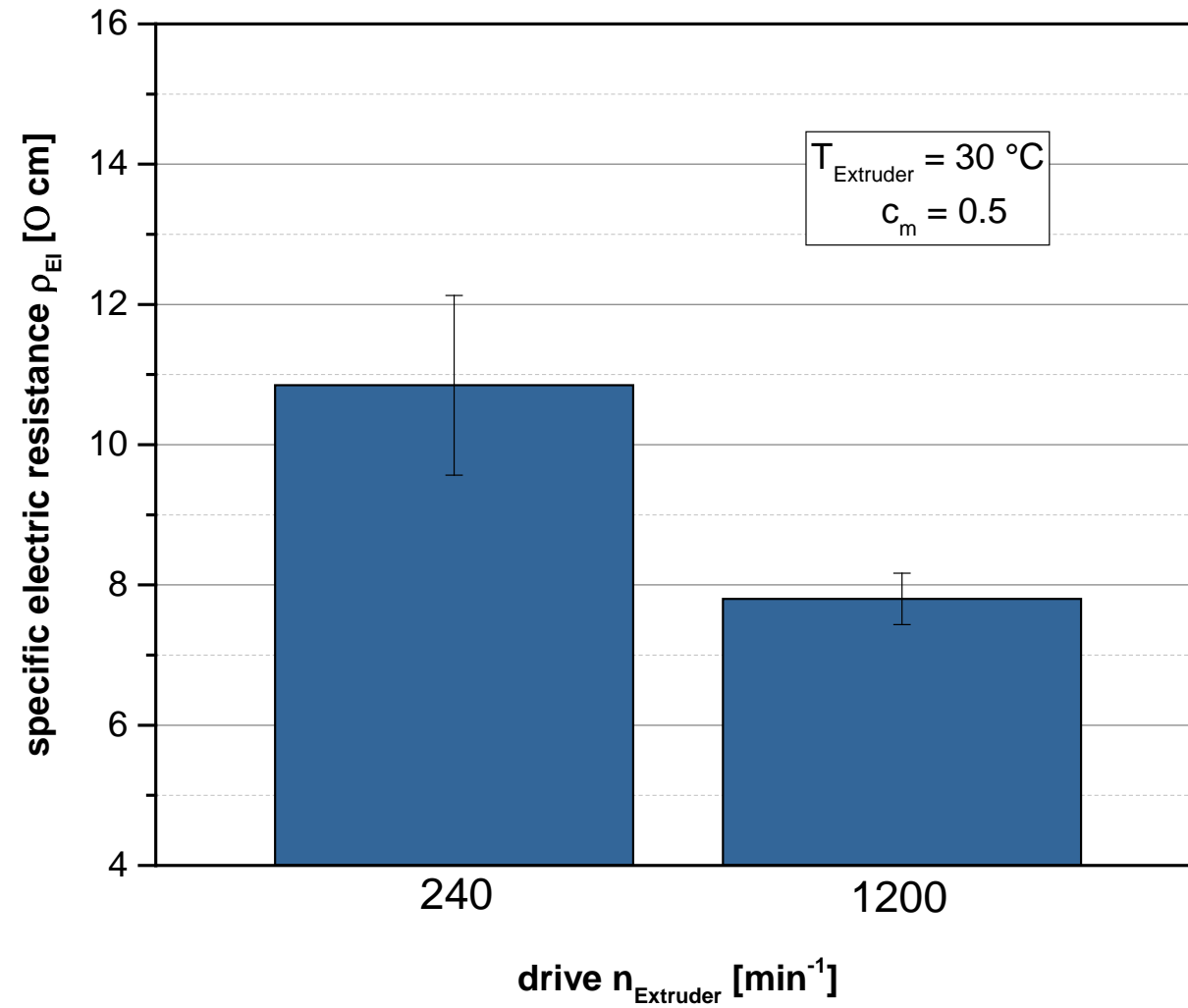


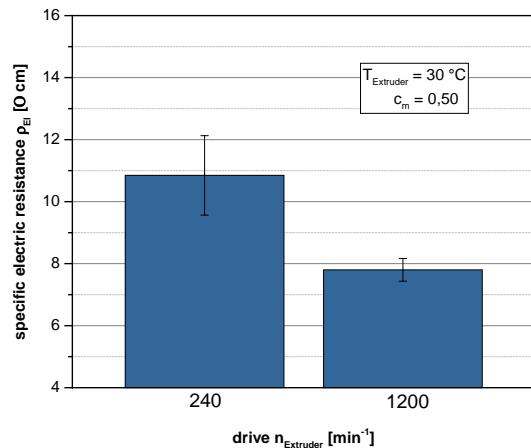
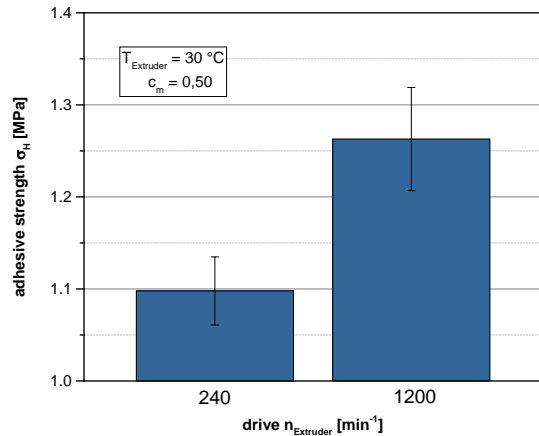


Adhesive strength

- Adhesive caused collapse \rightarrow agglutination of SBR
- Smaller particles \rightarrow higher specific surface + more contact points \rightarrow improved adhesive strength

Influence of Drive - Electrodes



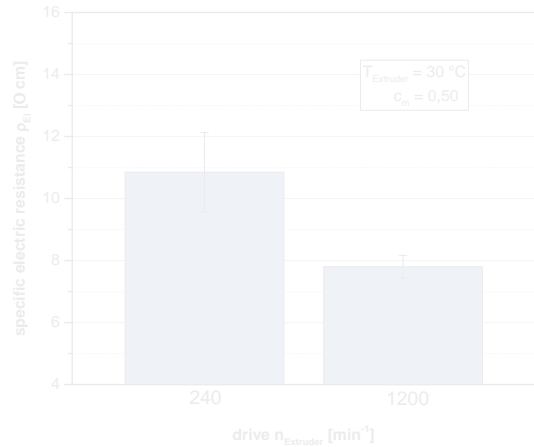
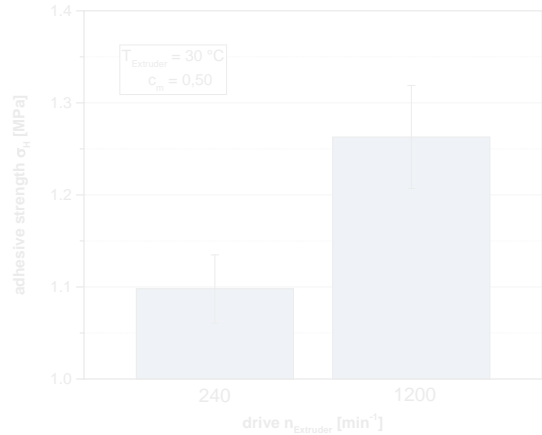


Adhesive strength

- Adhesive caused collapse \rightarrow agglutination of SBR
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Electric conductivity

- Correlation with particle size
- Improved dispersion \rightarrow homogenous allocation of carbon black



Influence of rotational high rotational speed

+ Processability

+ Adhesive strength

+ Conductivity

adhesive strength

- Adhesive caused collapse → agglutination of SBR

- Smaller particles → higher specific surface + more contact points →

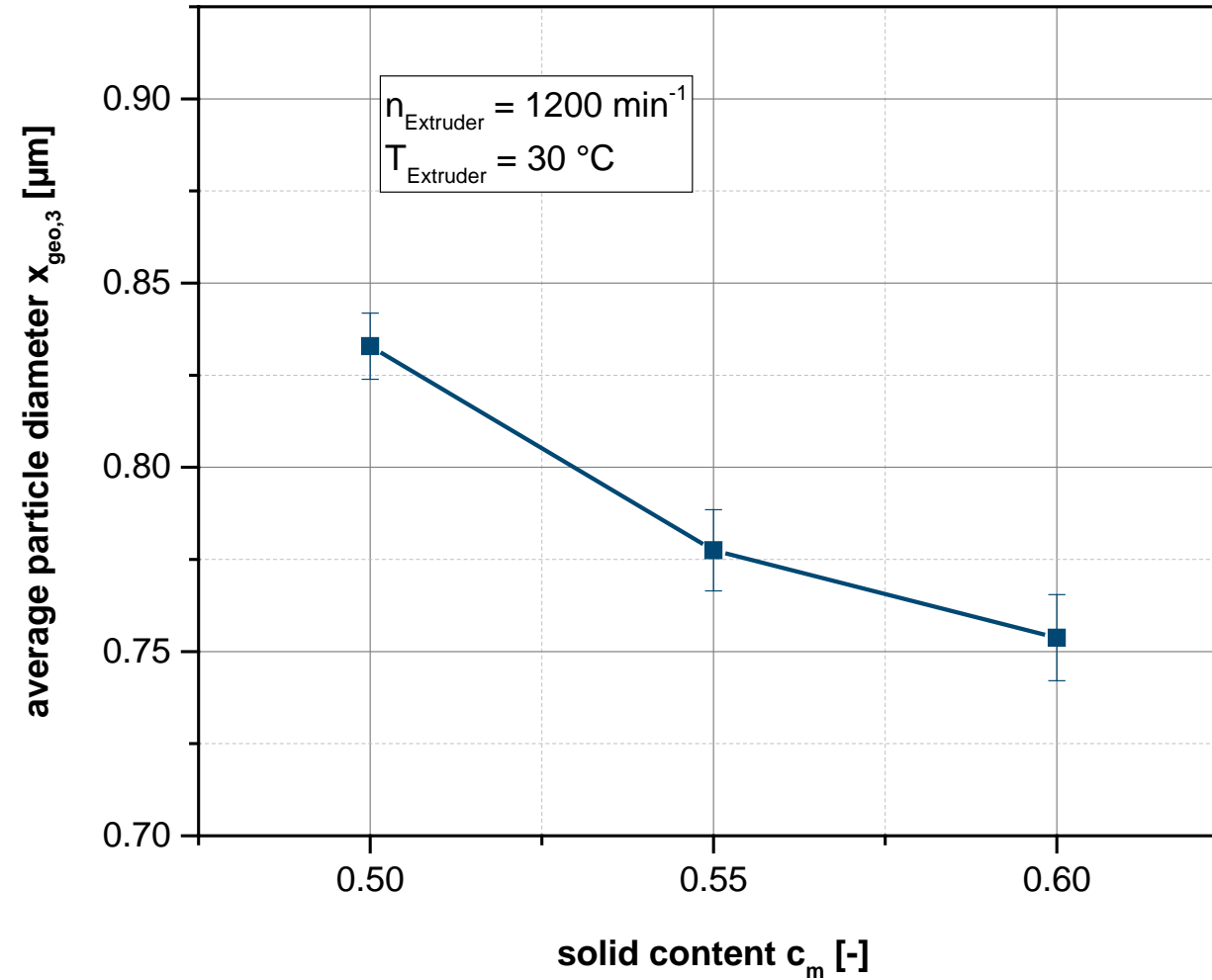
improved adhesive strength

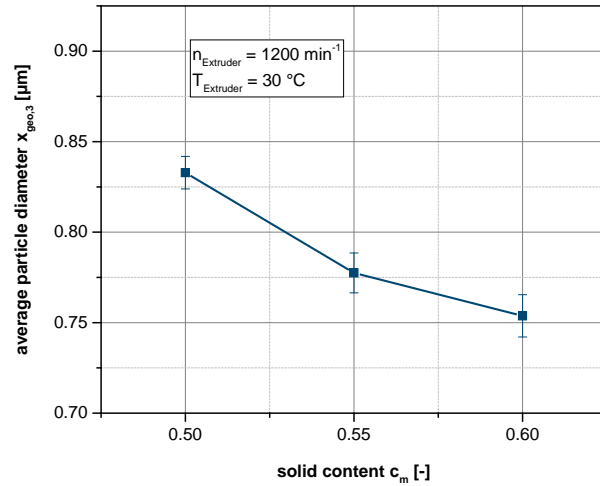
conductivity

- correlation with particle size

- Increasing dispersion → homogenous allocation of carbon black

Influence of Solid Content - Slurry

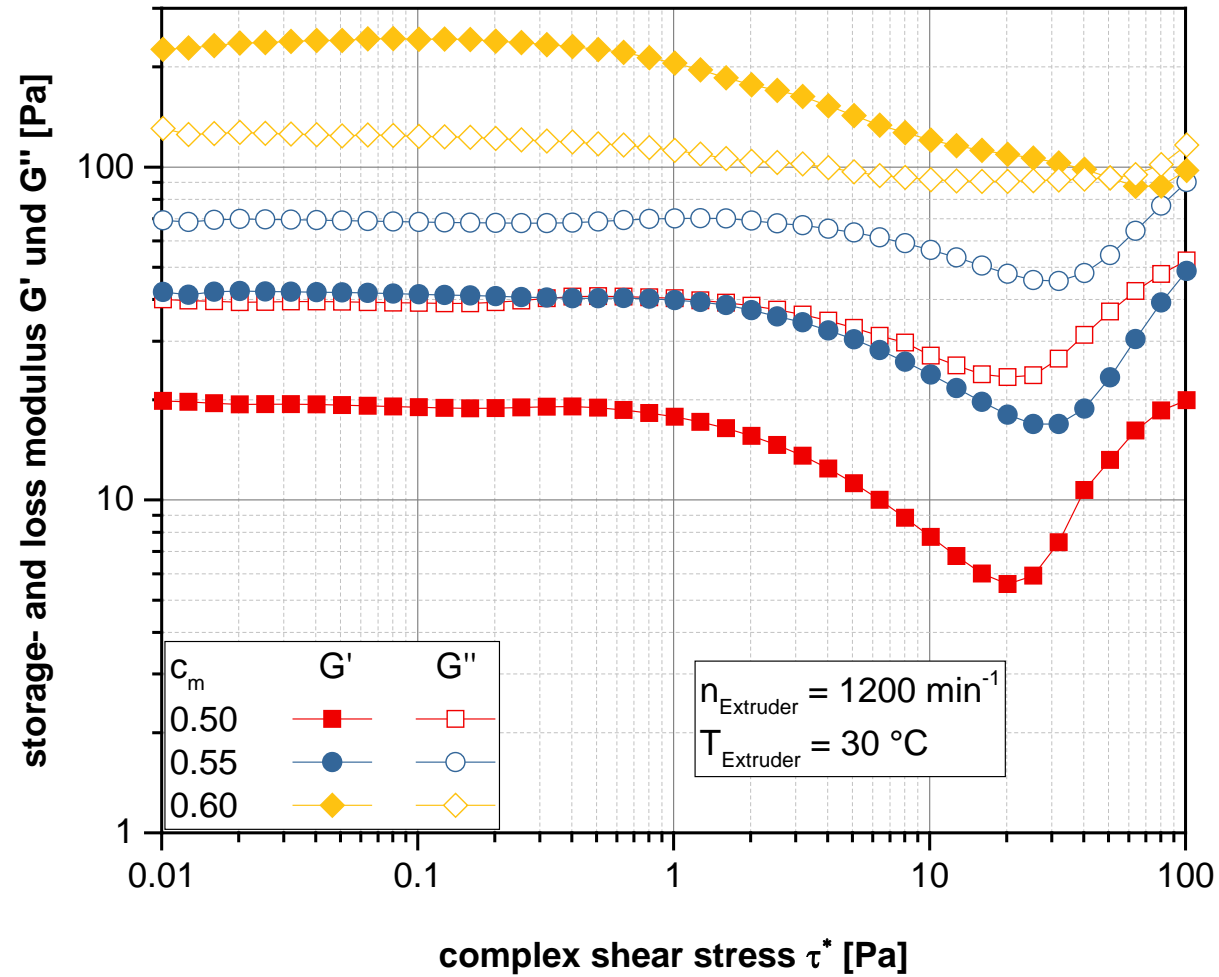


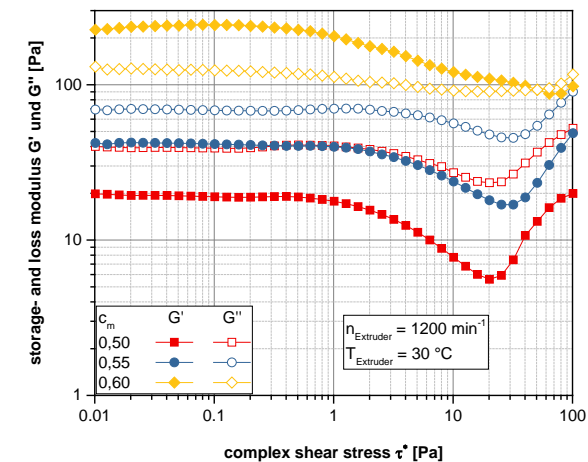
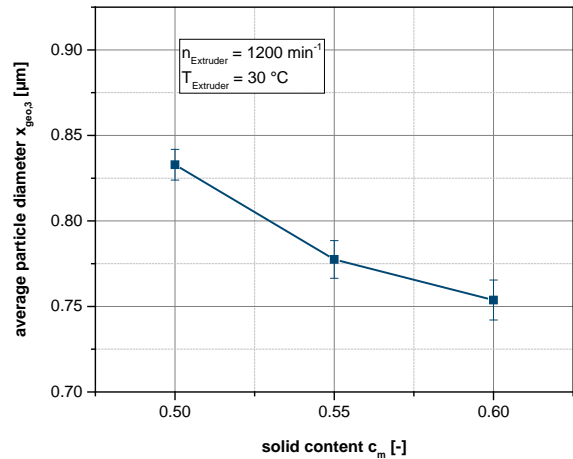


Particle size

- Higher particle concentration \rightarrow stress number and intensity increase
 \rightarrow smaller particles
- Minimal particle size caused by stabilization

Influence of Solid Content - Slurry





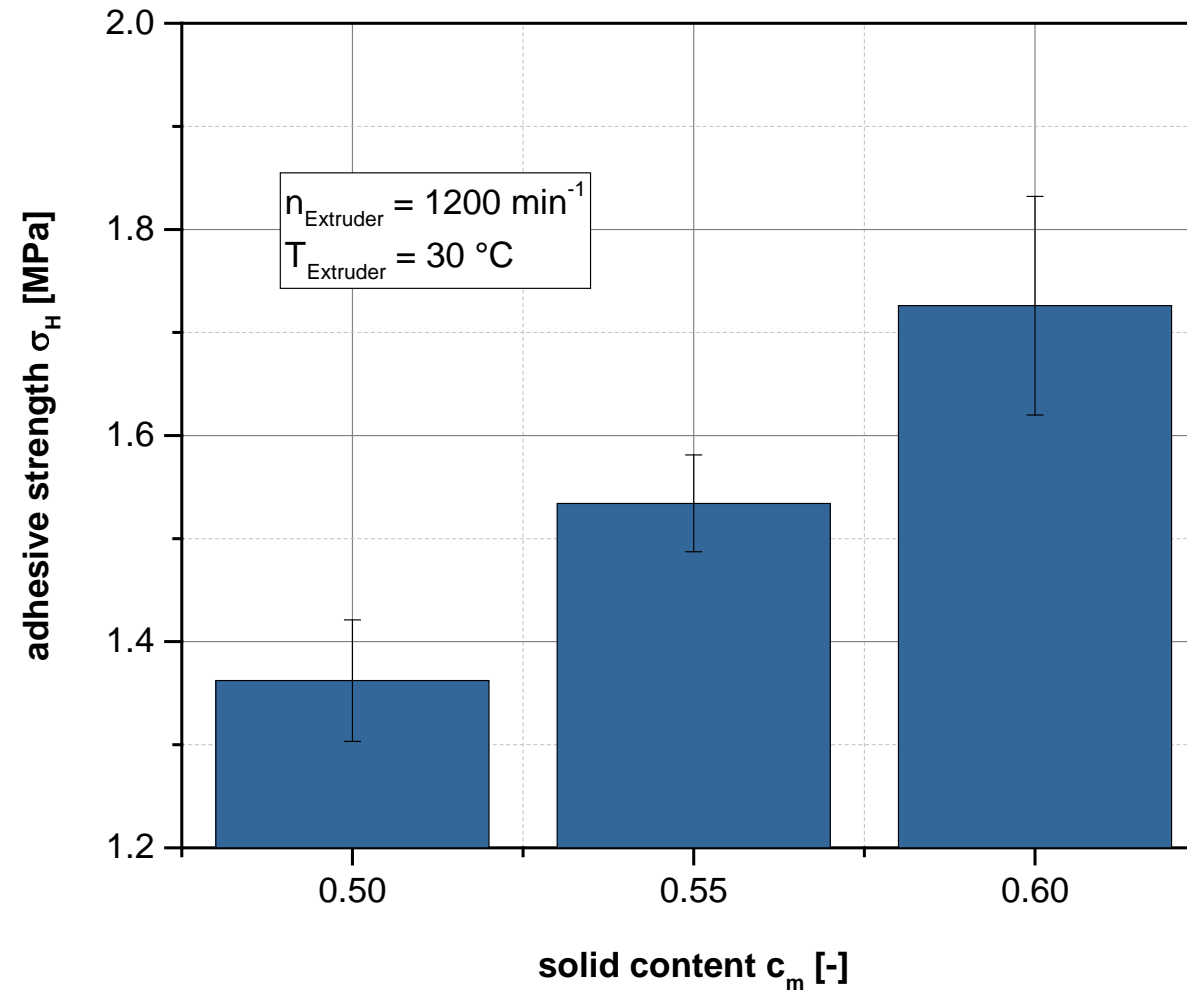
Particle size

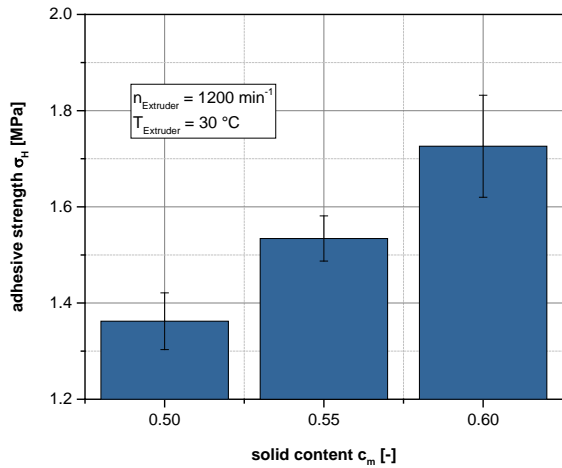
- Higher particle concentration \rightarrow stress number and intensity increase \rightarrow smaller particles
- Minimal particle size caused by stabilization

Rheology

- Viscoelastic solid body for $c_m > 0,60$
- Stability against segregation
- High solid content \rightarrow low mobility, stress number and intensity increase \rightarrow higher viscosity

Influence of Solid Content - Electrodes

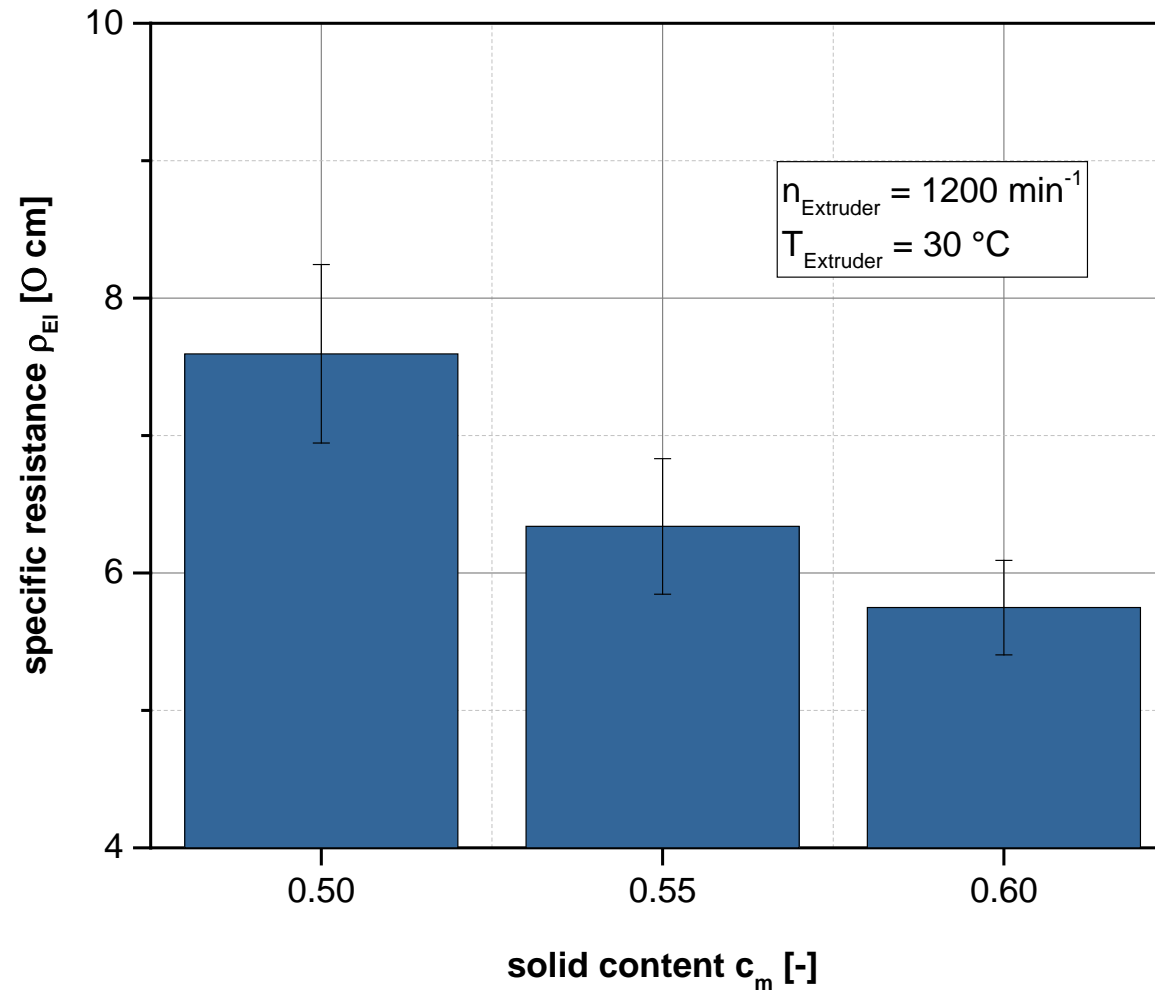


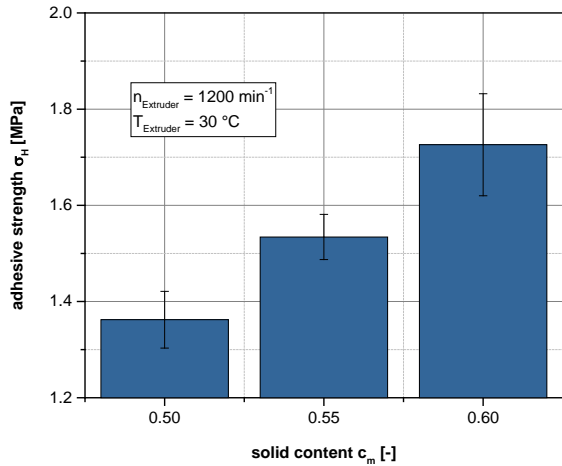


Adhesive strength

- Mainly adhesive caused collapse
- Smaller particles \rightarrow bigger specific surface and more contact points \rightarrow better adhesive strength
- Segregation of inactive material due to the low solid content \rightarrow lower adhesive strength

Influence of Solid Content - Electrodes



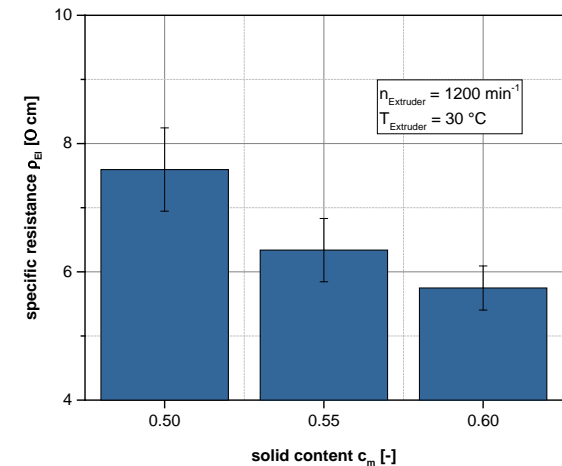


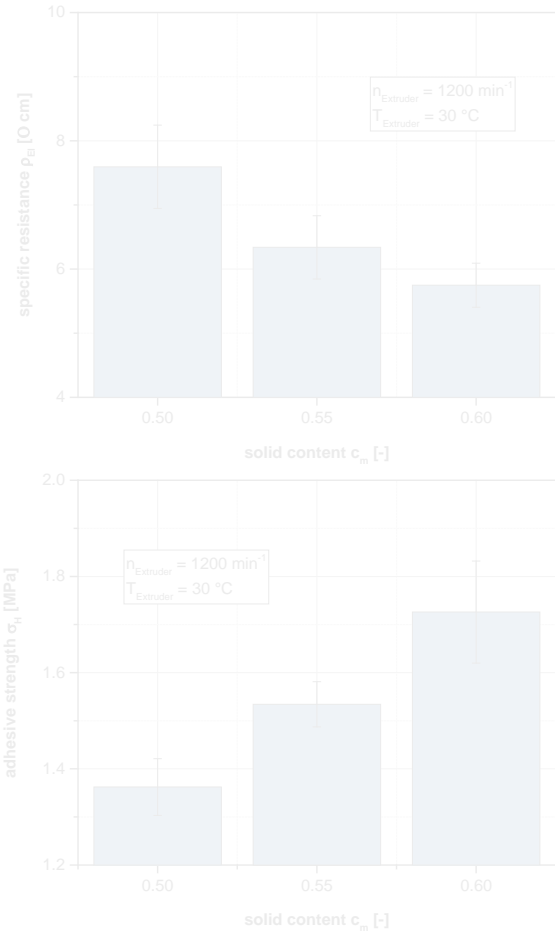
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Electric conductivity

- Correlation with particle size
- Segregation of inactive material due to the low solid content \rightarrow lower adhesive strength





Adhesive strength

- mainly adhesive caused collapse

- smaller particles → bigger specific surface and more contact points → better adhesive strength

Influence of high solid content

+ Reducing drying costs

+ Adhesive strength

+ Conductivity

- Processability

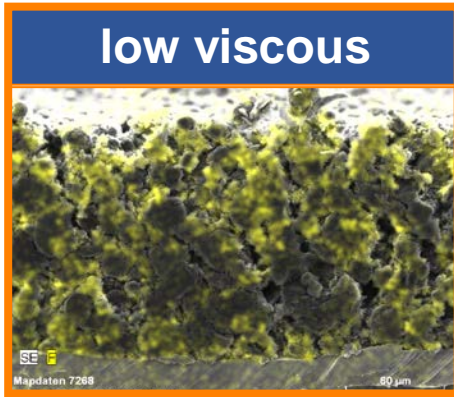
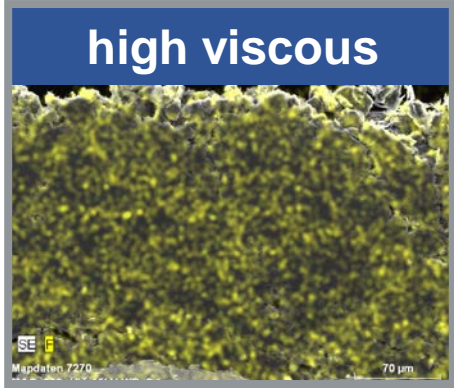
- Segregation of inactive material due to the low solid content → lower adhesive strength

electric conductivity

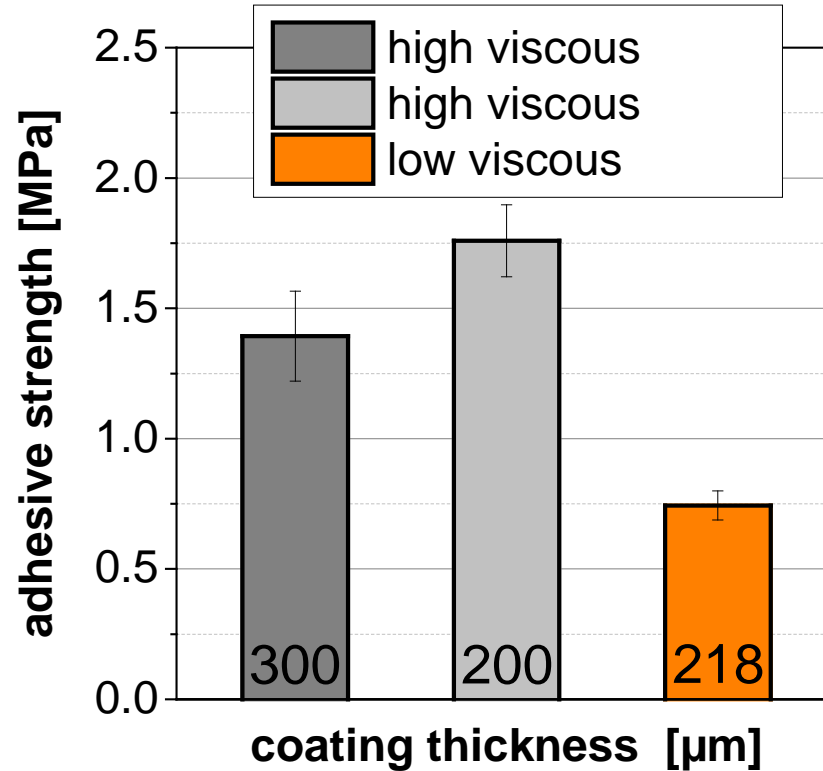
- correlation with particle size

- Segregation of inactive material due to the low solid content → lower adhesive strength

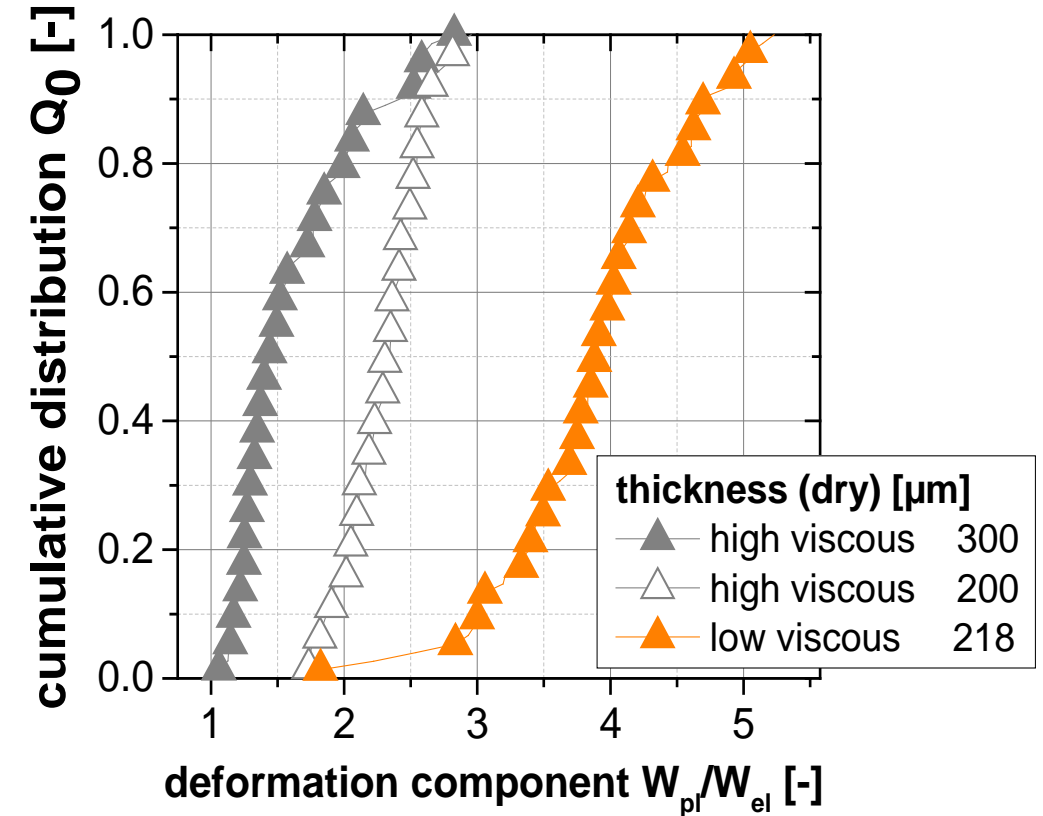
Outlook: High Solid Content $c_m > 60\%$



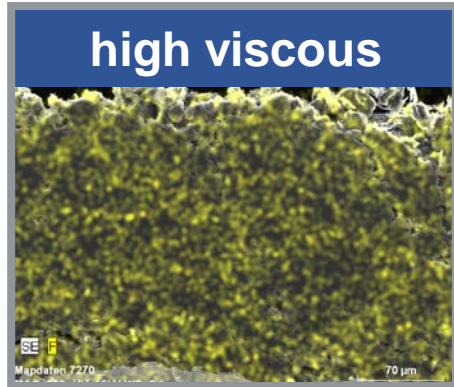
Adhesion



Deformation

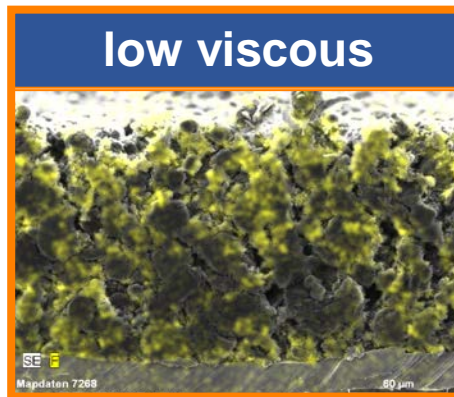


Outlook: High Solid Content $c_m > 60\%$



Benefit:

- No binder segregation
- Improved mechanical properties
- High cycle stability
→ range improvement
- Further reducing drying time/costs



Challenge:

- New coating system required
- Active material can be damaged
→ minimize shear stress



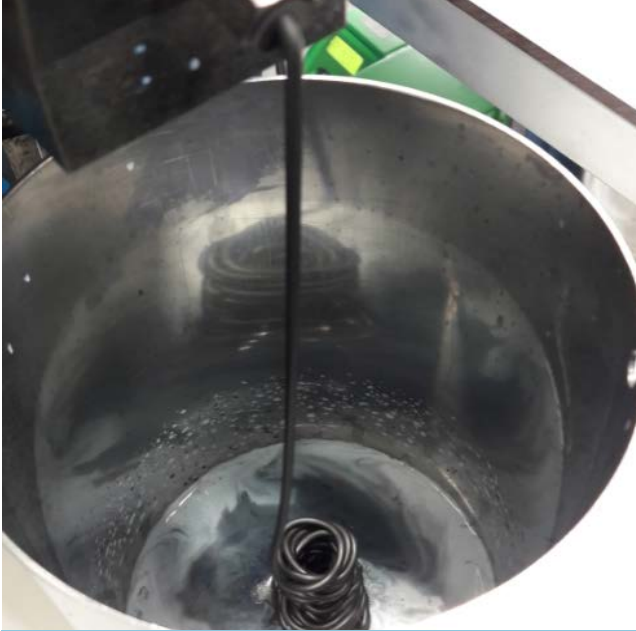
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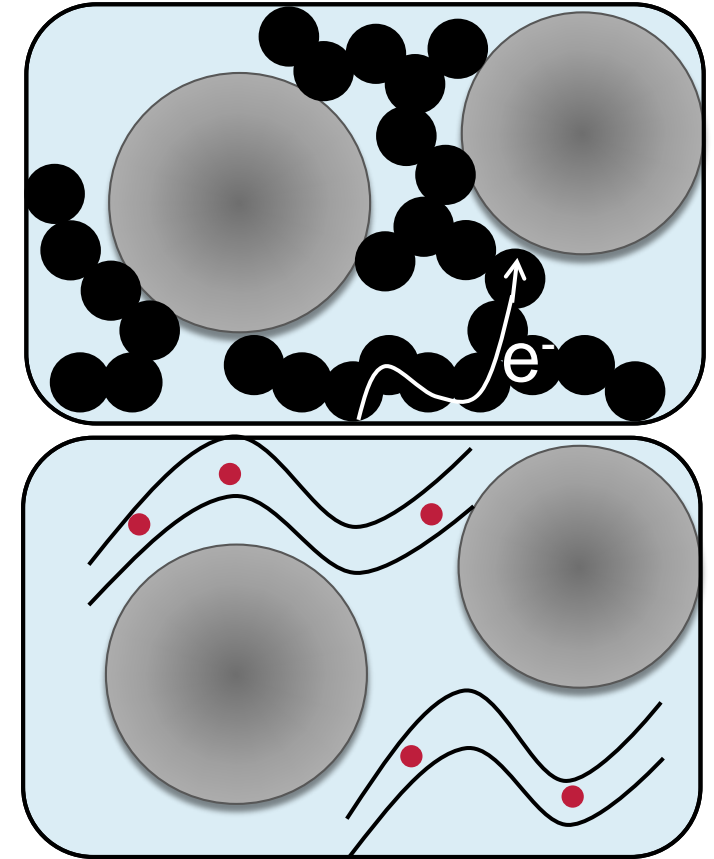
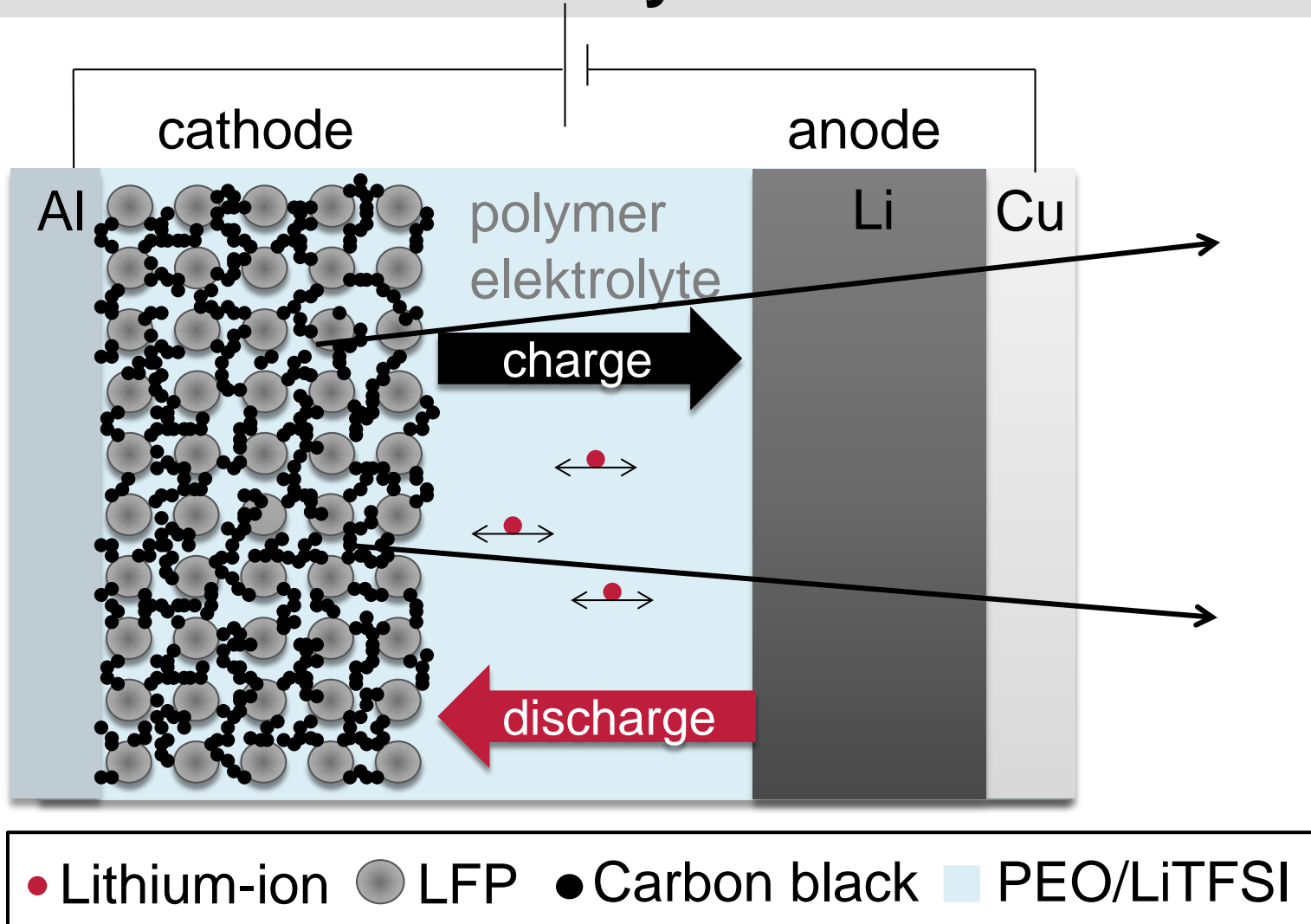
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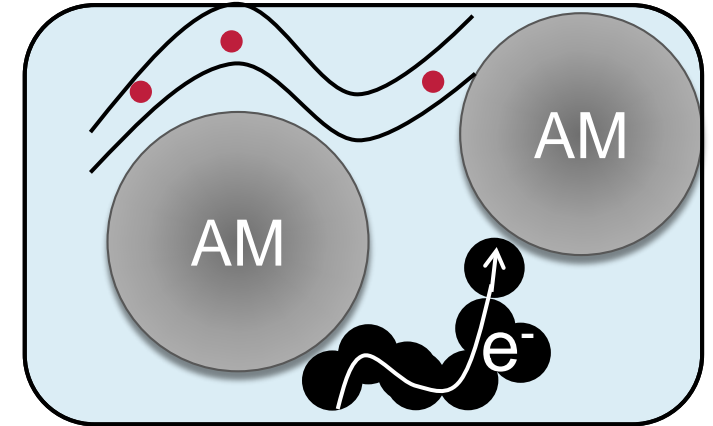
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All-solid-state battery



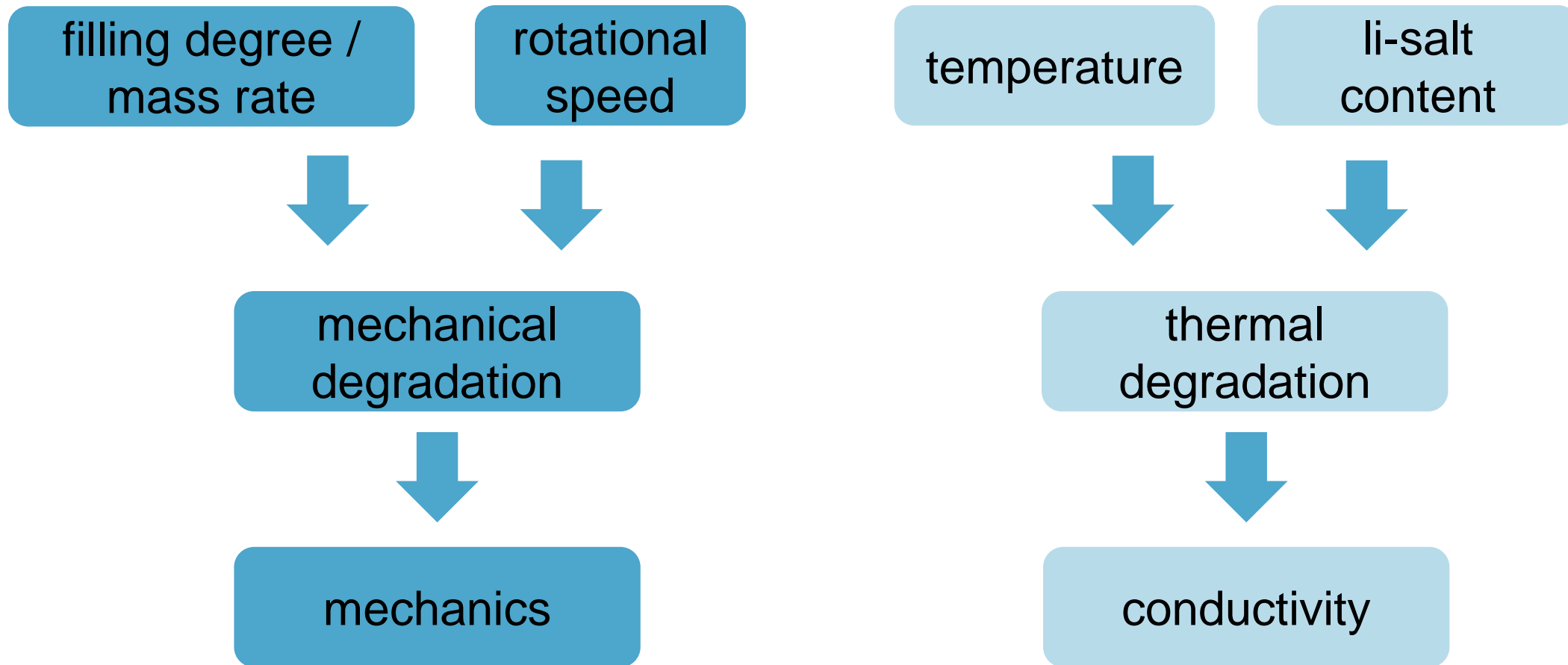
Requirements for All-Solid-State Processing

- Liquid electrolyte is replaced by a solid polymer-salt mixture
- No desired porosity like in classic Li-Ion batteries, goal is zero porosity
- Li-ion transport is dependent on polymer chain movement
- High homogenization degree is needed for high ionic conductivity
- Shear stress has to be minimized as it causes chain-degradation
- Solvent free process chain is used



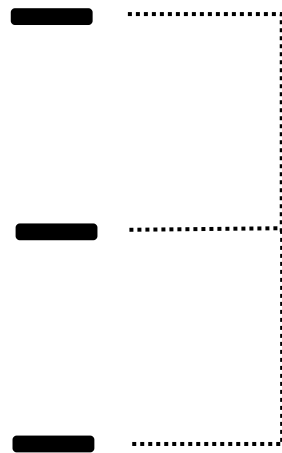
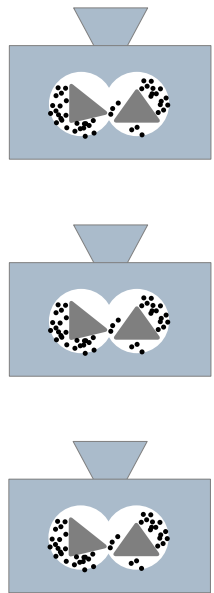
- Lithium-ion
- Carbon black
- LFP
- PEO/Li-salt

Process Parameter Effects on Polymer Properties

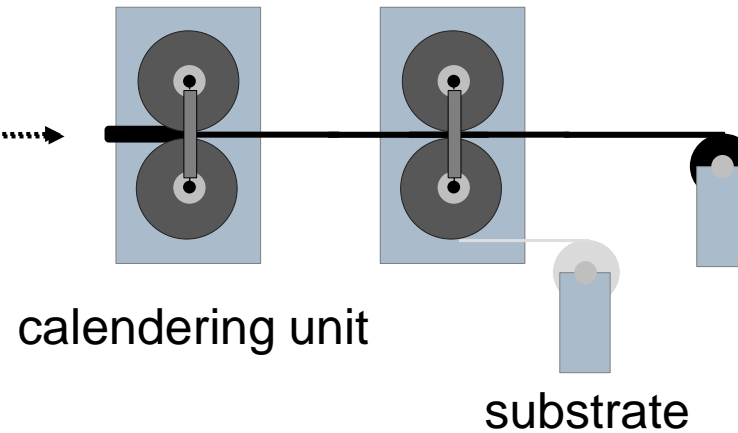


Batch Process for ASSB Production

kneading unit

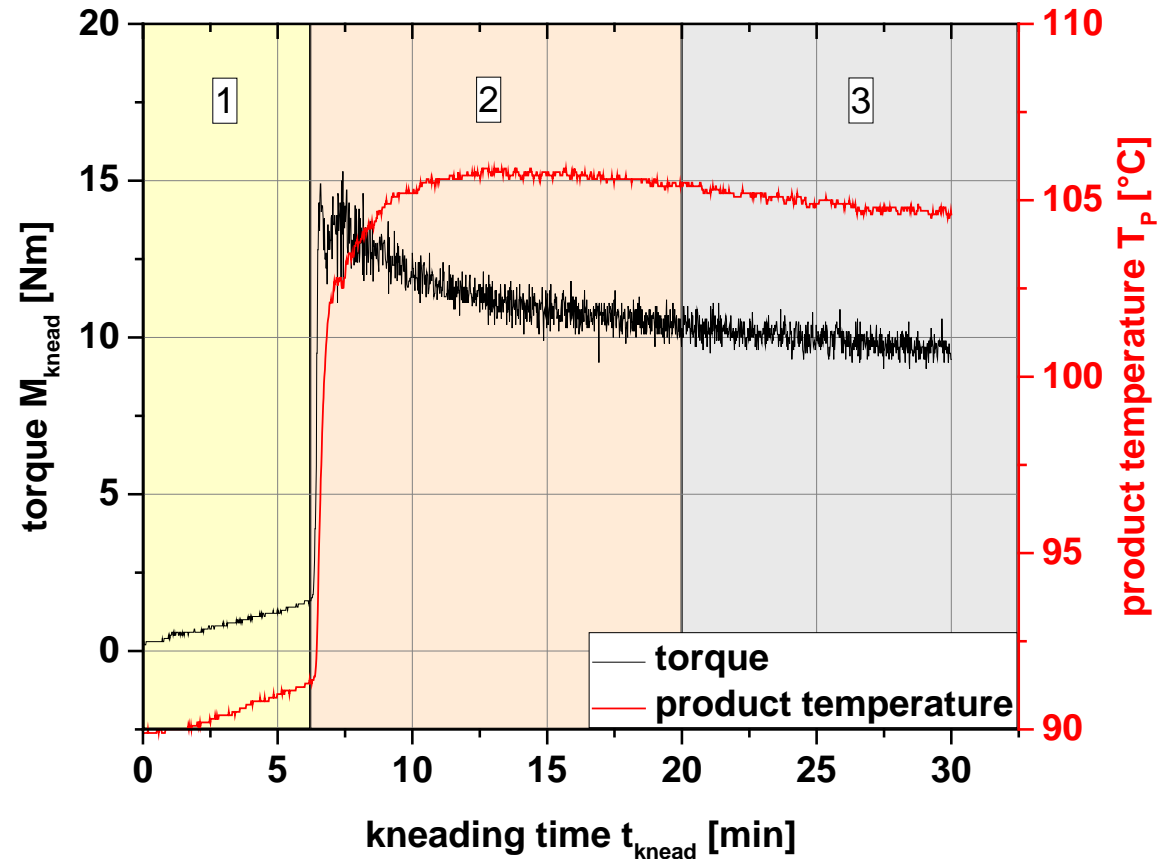


lamination unit



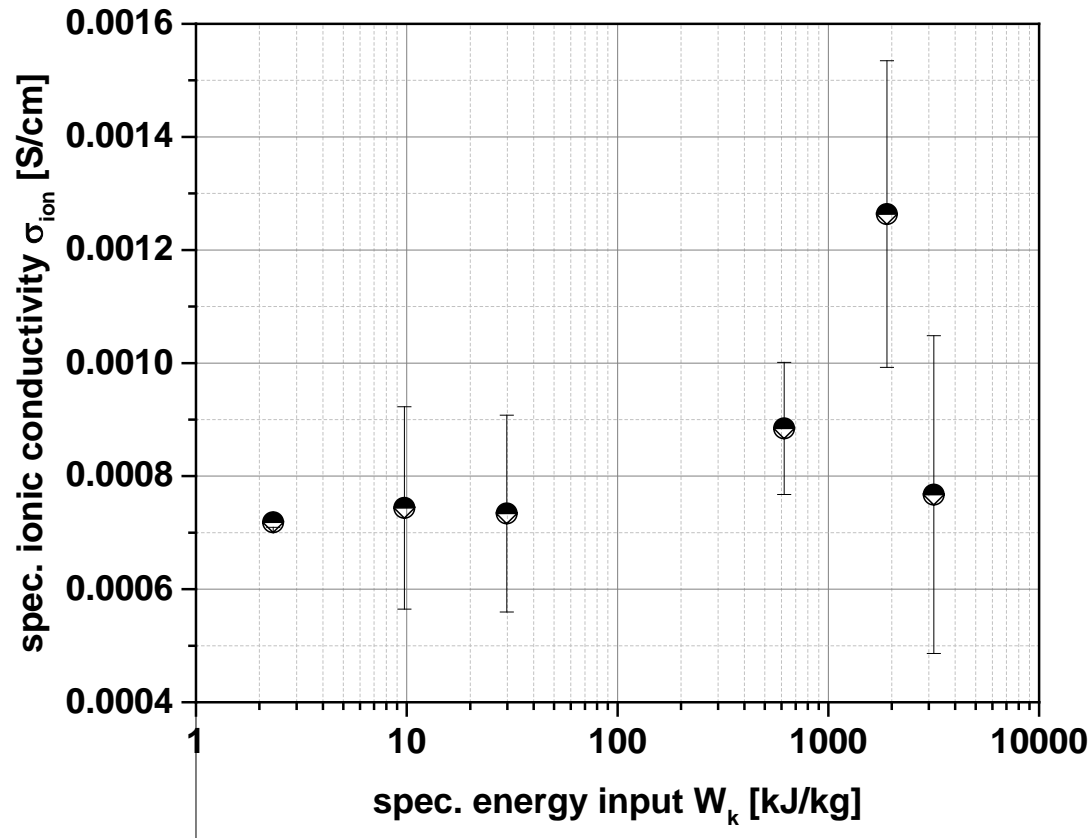
- Time and cleaning intensive
- Low level of automation
- Higher personnel and energetic costs

Batch Kneading Process for ASSB



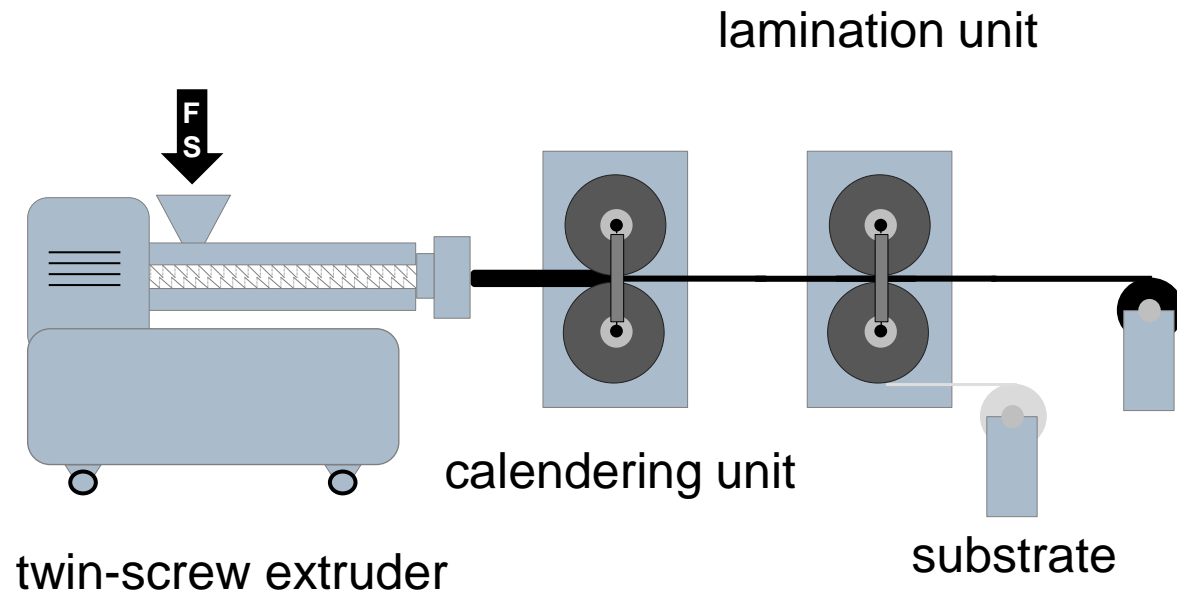
1. Homogenization of PEO particles
2. Plasticizing PEO melts and flow resistance decreases
3. Mechanical degradation of PEO

Batch Kneading Process for ASSB



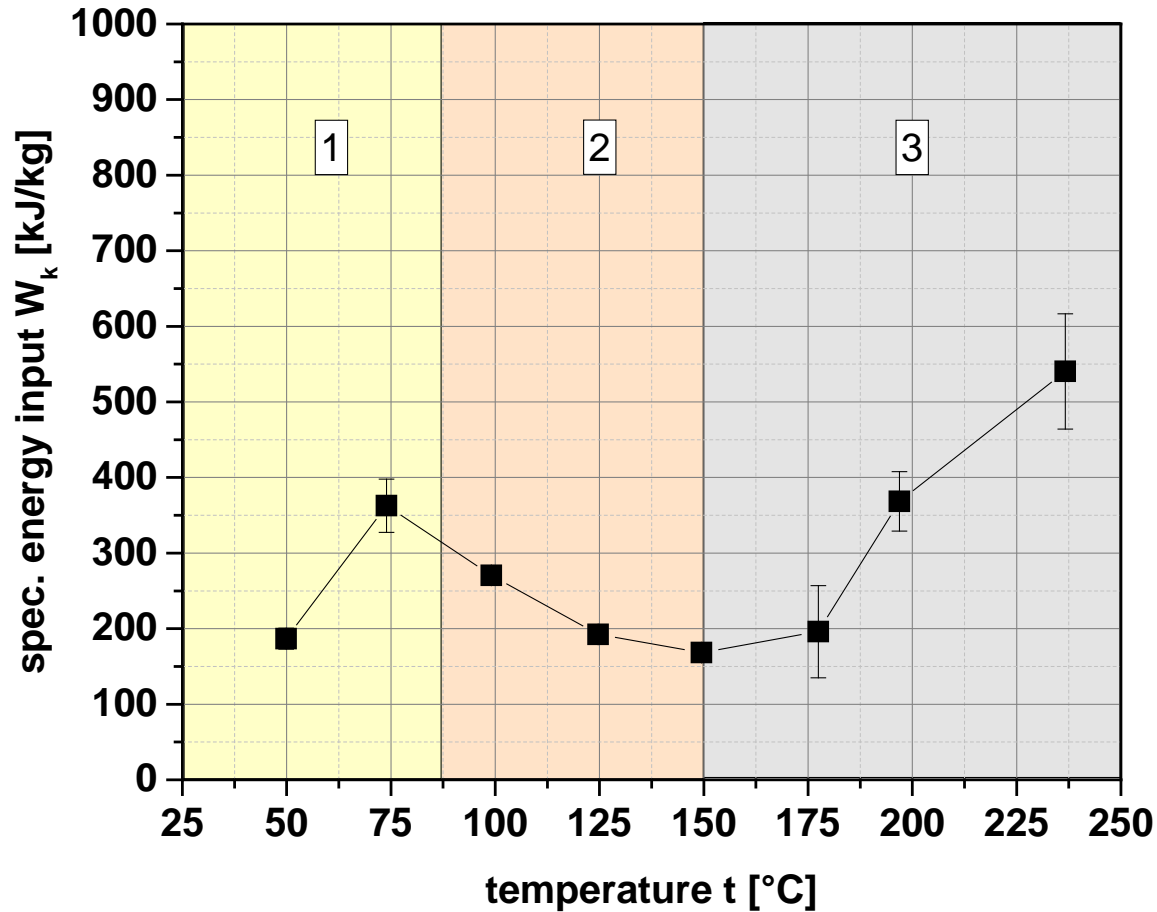
- Specific ionic conductivity increases with rising energy input through homogenization and chain-degradation
- For $W_k > 2000$ kJ/kg degraded polymer chains probably cross-link and the reduced chain mobility cause a decreased ionic conductivity

Continuous Process Chain for ASSB Production



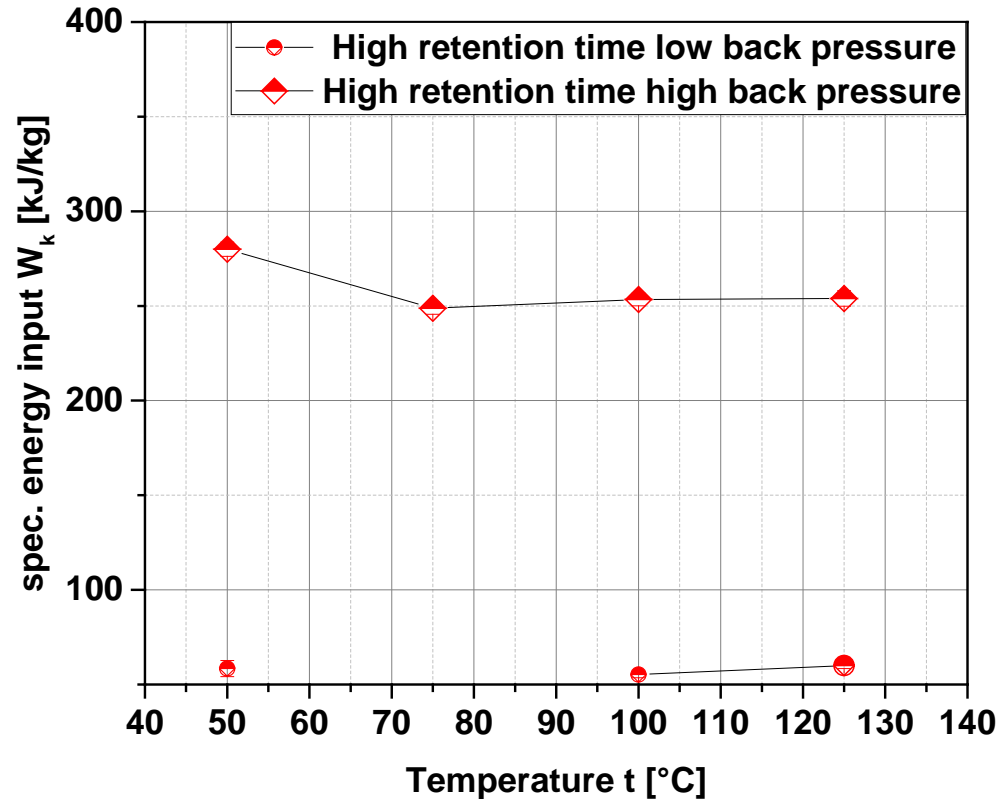
- Through solvent free process drying unit is saved
- For direct calendaring thin and broad extrudates are desired
- Utilization of same process route for cathodes and separator

Influence of Temperature on Specific Energy Input



1. Homogenization of solid PEO particles
2. Plasticizing of molten PEO causes decrease in flow resistance
3. Thermal degradation and solidification of PEO

Influence of Temperature on Specific Energy Input

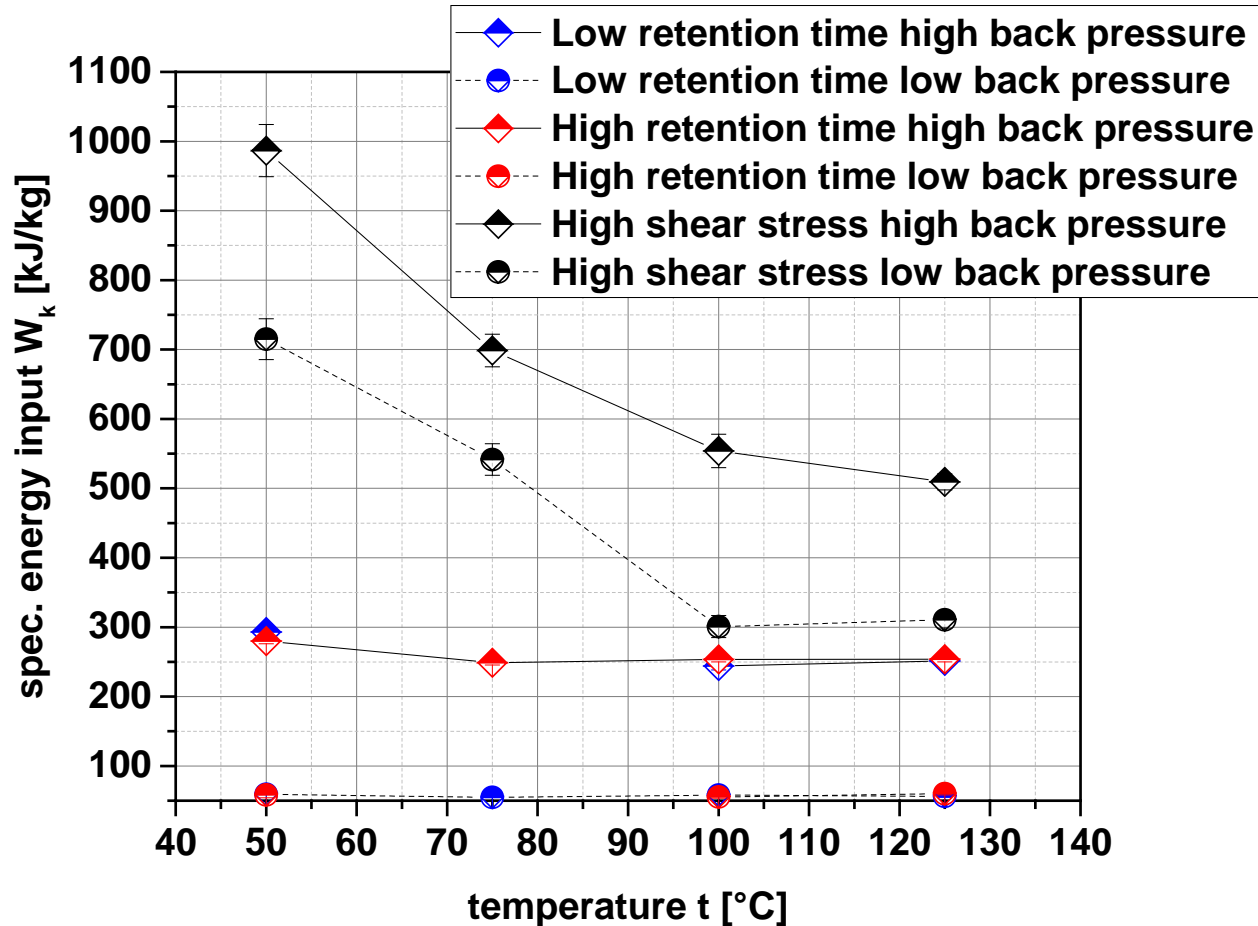


- Lithium salt works plastifiing
- For the high retention screw configuration the temperature impact on the specific energy input is neglectalbe
- High back pressure leads to increased specific energy input

Influence of Operating Temperature



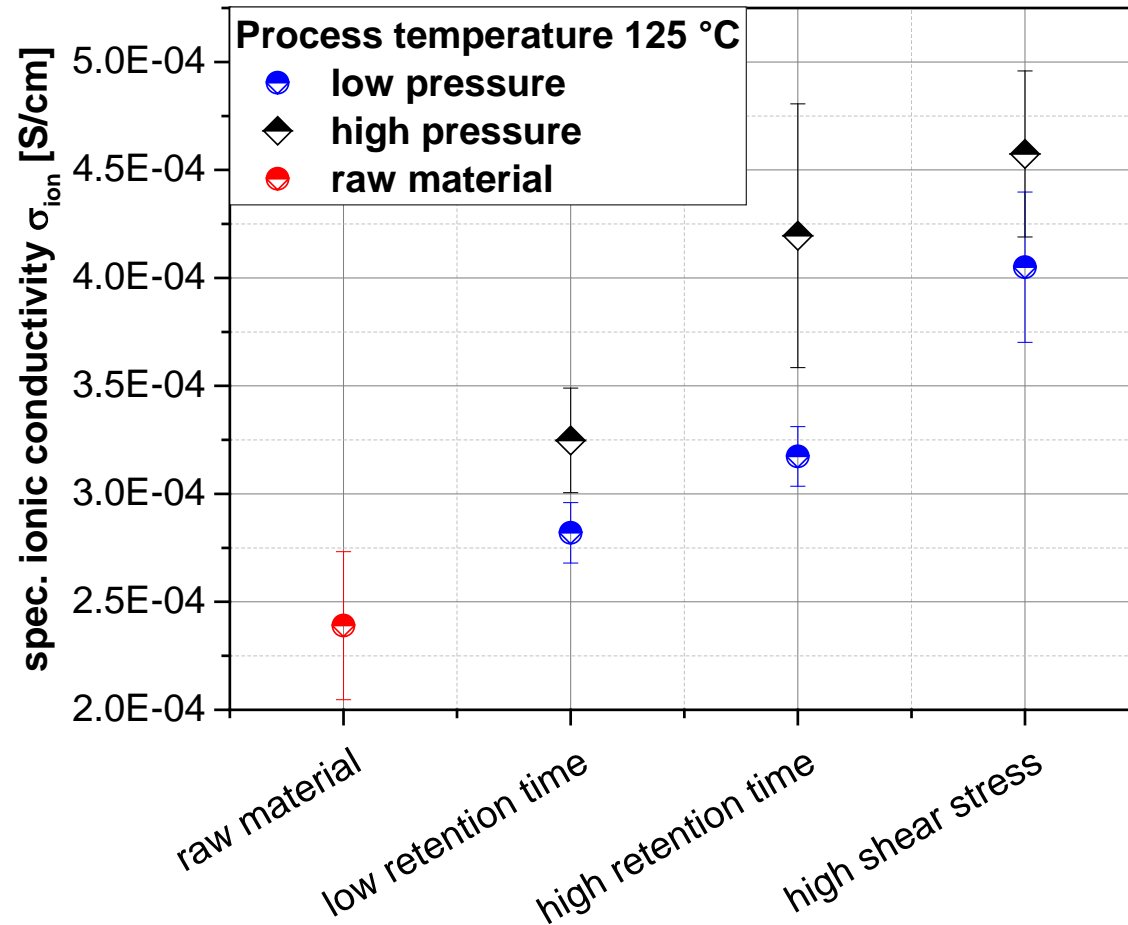
Influence of Screw Config. on Specific Energy Input



- Use of kneading elements leads to temperature dependency
- High shear stress causes thermal degradation for a temperature > 100 °C

Influence of Screw Config. on Specific Energy Input





- Higher retention time and higher shear stress lead to increased homogenization
- High shear stress and high retention time cause thermal degradation for 125 °C

Conclusions

- For kneading and extrusion process the polymer passes three phases depending on the specific energy input
- Batch kneading: higher energy input increases ionic conductivity
- Thermal degradation for $W > 2000$ kJ/kg
- Extrusion process: low retention time leads to low homogenization
- High retention time and high shear stress cause degradation

Conclusions

- Process window limited through thermal and mechanical degradation
- Continuous extrusion process: specific energy input controllable through screw configurations causing a specific retention time
- Solvent free processing of separator in the extruder is possible
- Reached ionic conductivities are slightly lower

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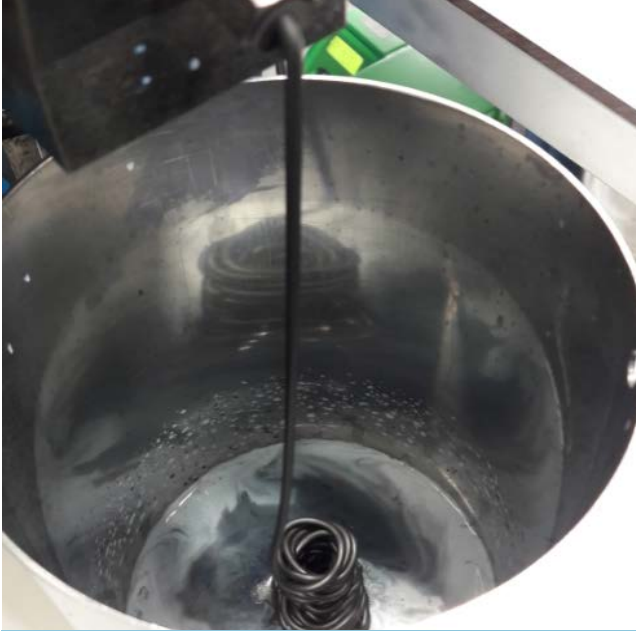
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