Rheology and Microstructure of Battery Electrode Slurries

Jaewook Nam[1,2,†]

[1]Department of Chemical and Biological Engineering, Seoul National University

[2]Institute of Chemical Processes, Seoul National University

[†]email: jaewooknam@snu.ac.kr

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Microfluidics and Coating Process Laboratory

Introduction to coating process

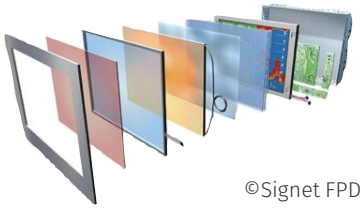
Coating process is the main manufacturing step for many different products.

Conventional products

"High-tech" products

©Watershed

Adhesive tapes



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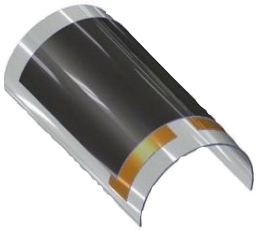
Optical films for LCD



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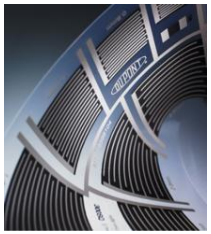
Battery electrodes



©Dupont

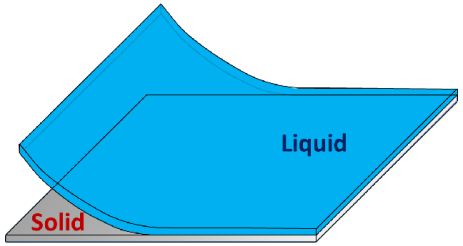
Flexible circuits

©Future Perfect Publishing

e-paper

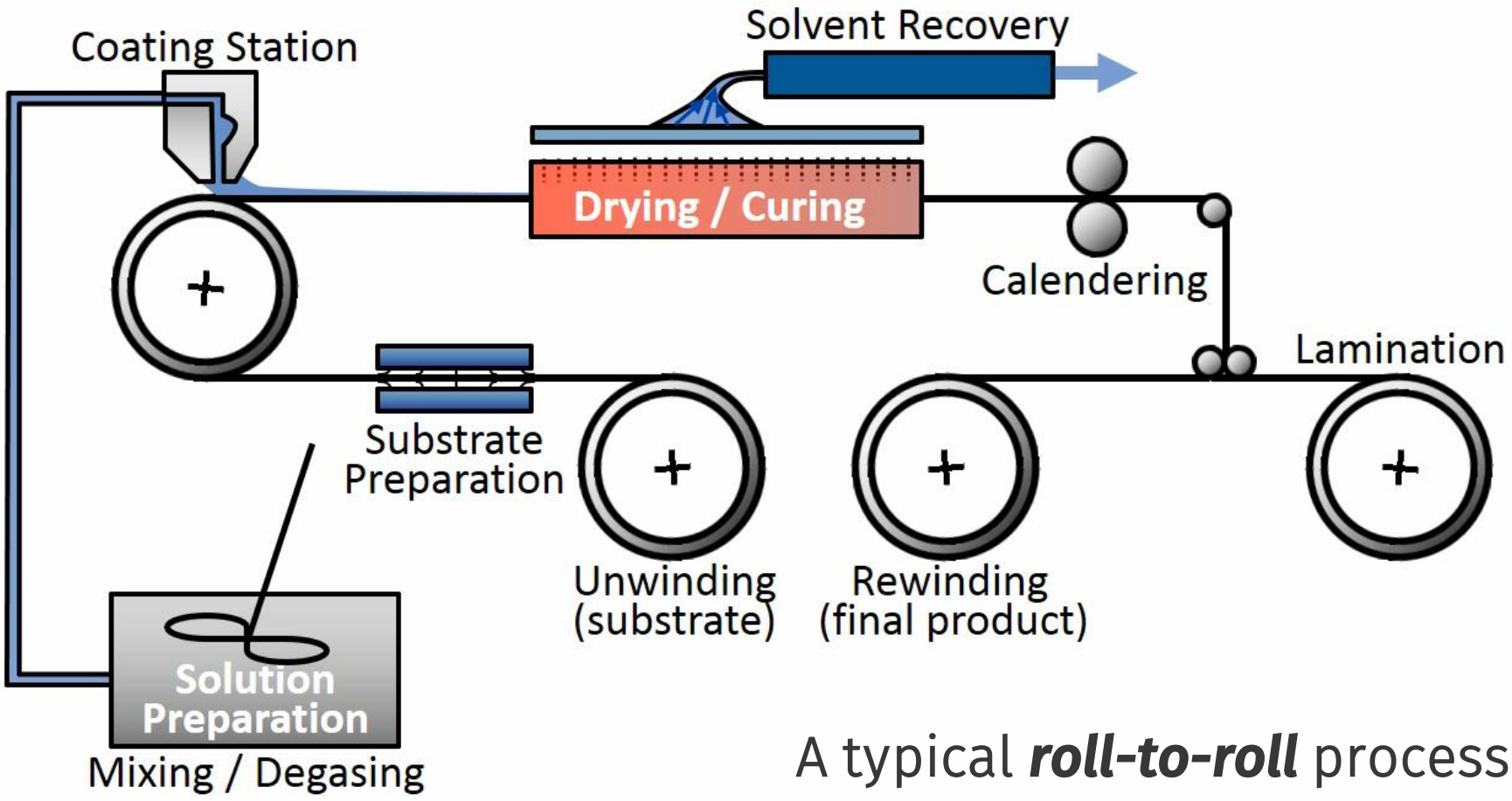
To coat is to place gas at the solid surface
by a layer of liquid.

by L. E. "Skip" Scriven



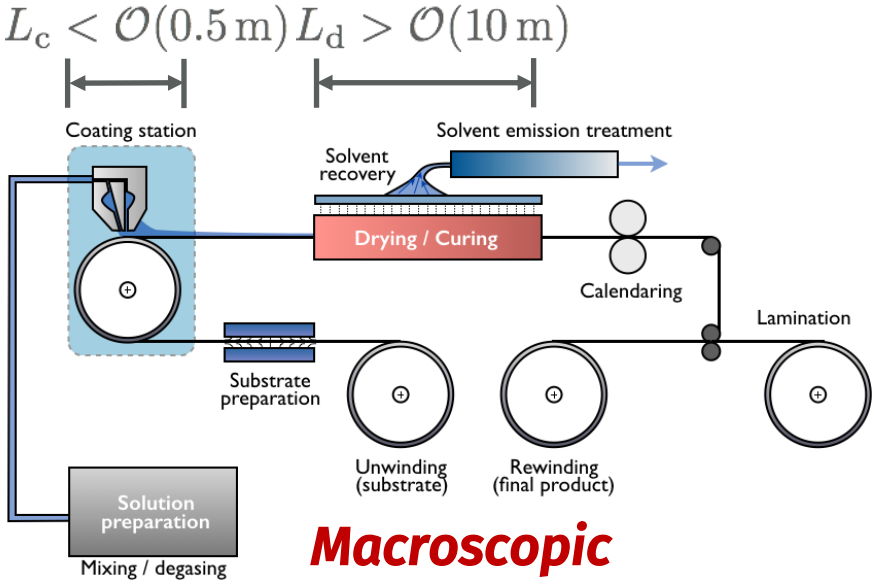
Continuous liquid coating process

Like other chemical process,
coating process consists of numerous unit operations.



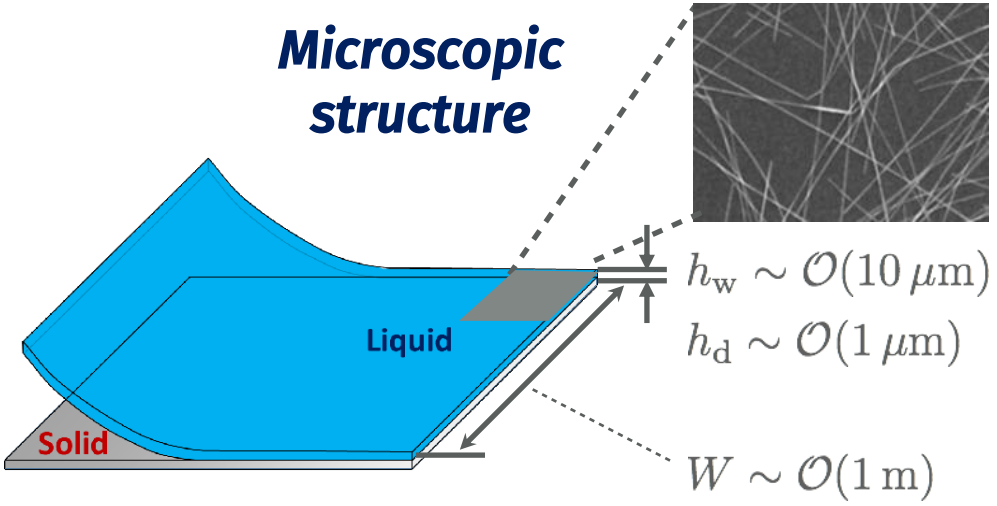
A typical ***roll-to-roll*** process

Key issues in film formation process



Macroscopic process

Microscopic structure



Length of films:

$$L > \mathcal{O}(1\,\mathrm{km})$$

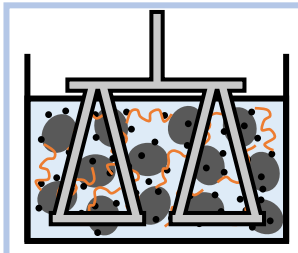
Aspect ratio:

$$\frac{h}{W} \sim 10^5$$

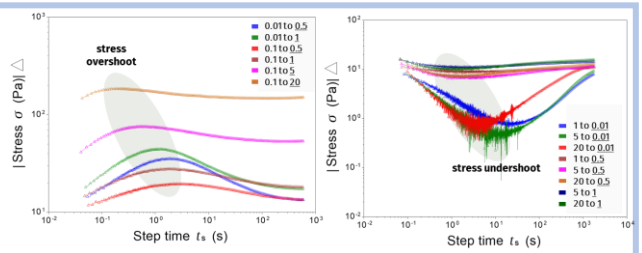
- Maintaining ***uniformity*** and/or creating patterns
  (understanding role of capillarity & wetting @ a given rheological prop.)
- Controlling ***microstructure*** by ***macroscopic*** parameters
  (exploit flow-particle interactions to deposit particles properly)

Outline – Slurry rheology and transportation

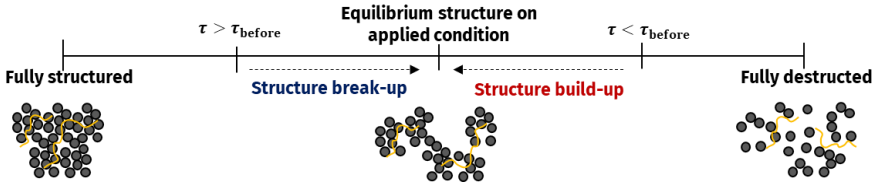
Slurry mixing & Rheology | Transportation | **Coating** | Drying Calendaring ... | Final Product



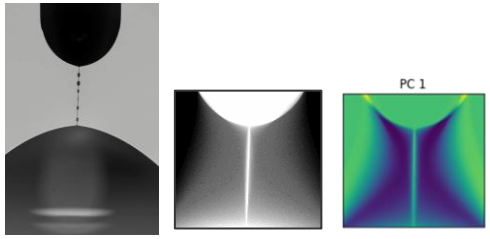
Mixing effect



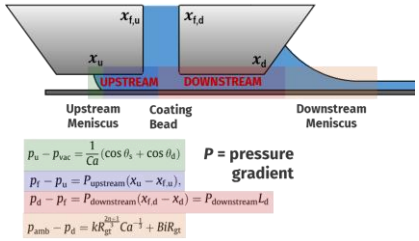
Time-dependent behaviors



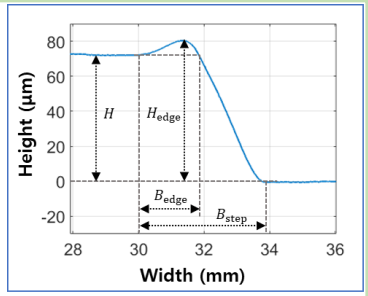
Constitutive equation



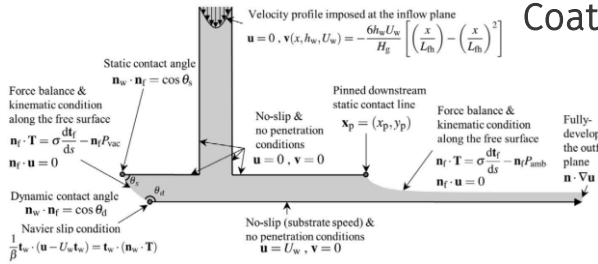
Extensional rheology



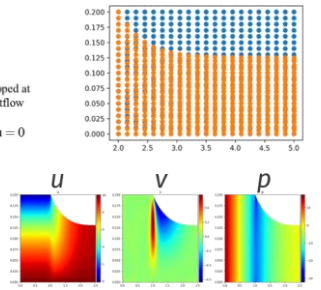
Simple model analysis



Coating edge analysis

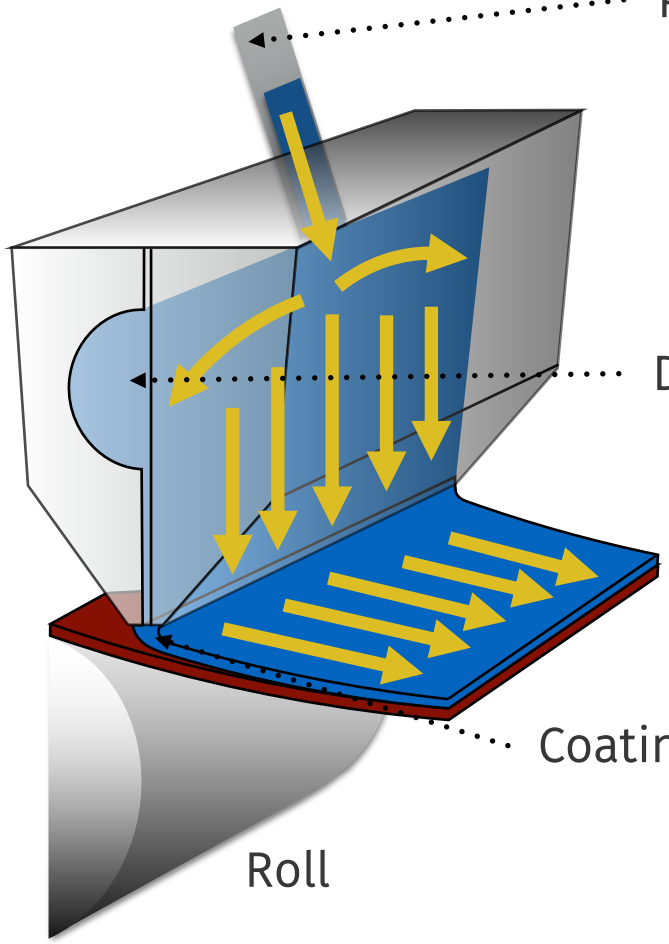


FEM computation



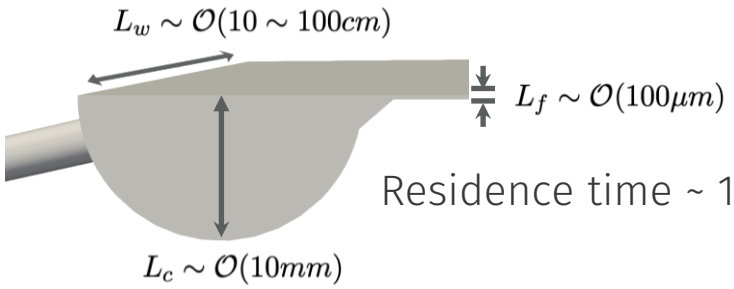
FEM computation

Overview of the slot coating process

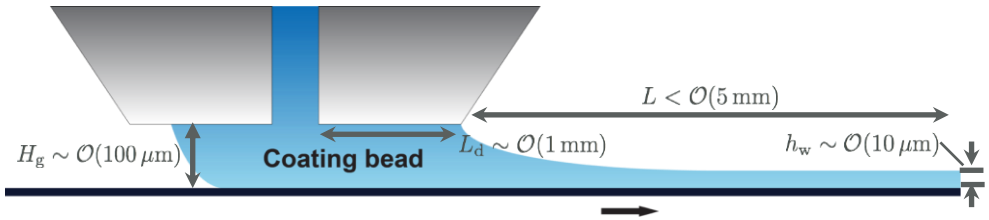


Pipe diameter ~ $\mathcal{O}(1\ \mathrm{cm})$

Maximum shear rate ~ $\mathcal{O}(10\ \mathrm{s}^{-1})$



Residence time ~ 10s



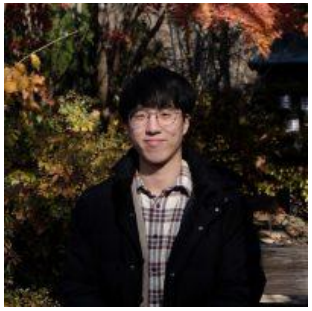
Residence time ~ 0.01s

The slot coating process involves

wide range of time and length scales.

Rheological properties of battery slurry

Nayeon Park



Hyunjoon Jung

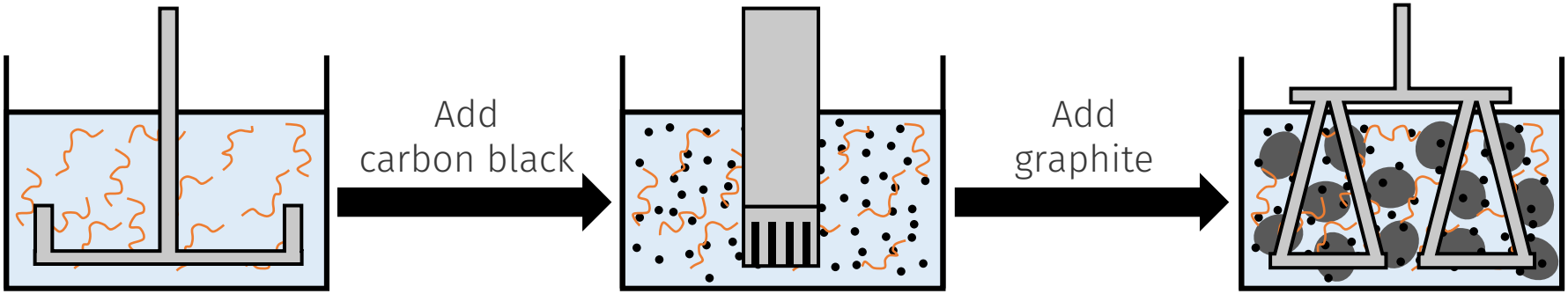
Cheolheon Hyun

Park, N., Lee, M., Jung, H., & Nam, J. Complex rheological response of Li-ion battery anode slurries. ***Journal of Power Sources***. (2024).

Jung, H., Hyun, C., & Nam, J. Shear-driven viscosity enhancement in battery slurry. ***Journal of Rheology***. (2025).

Anode slurry preparation

	Material	Size	Concentration
Solvent	Water		
Active materials	Graphite / Silicone	~ 10 μm / ~ 100 nm	35 ~ 50 wt% 20 ~ 30 vol%
Conductive additives	Carbon black	10 ~ 100 nm	~ 1 wt% ~ 2 vol%
Polymer binder	Carboxymethyl cellulose / Styrene-butadiene rubber	100 ~ 1000 kg/mol / ~ 100 nm	~ 1 wt%



CMC solution
Overhead stirrer
100 rpm 12 hours

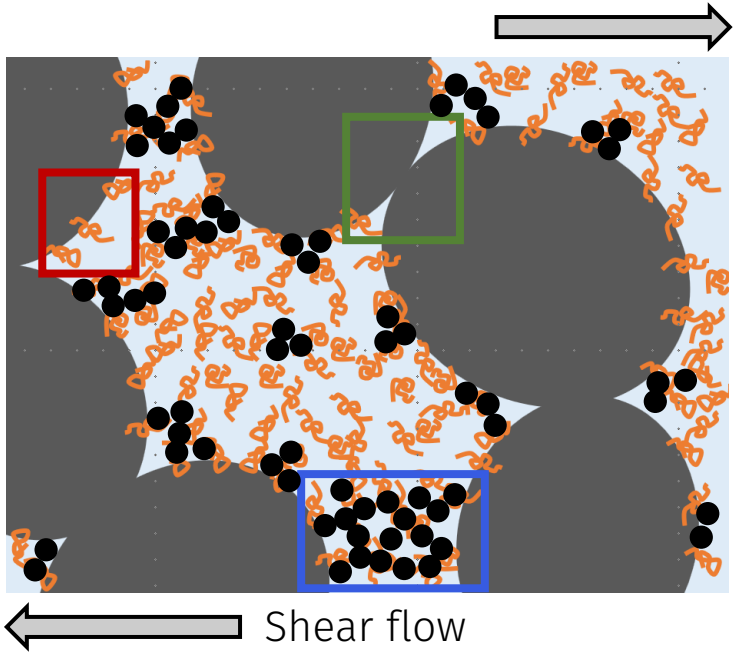
CB suspension
Homogenizer
8000 rpm 10 min

Anode slurry
Planetary mixer
300 rpm 60 min

Battery electrode:

complex, multiscale, dense particle-fluid system.

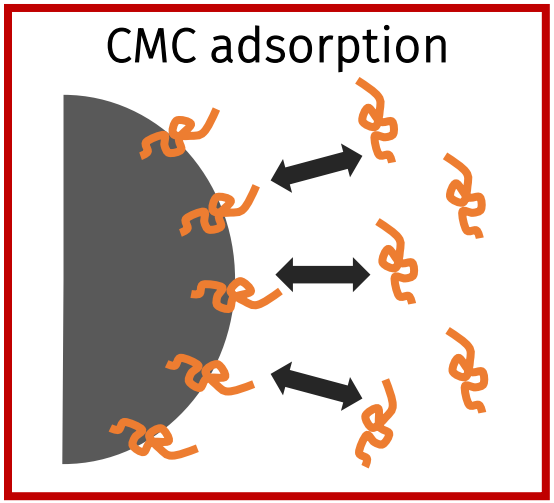
Microstructure of anode slurry

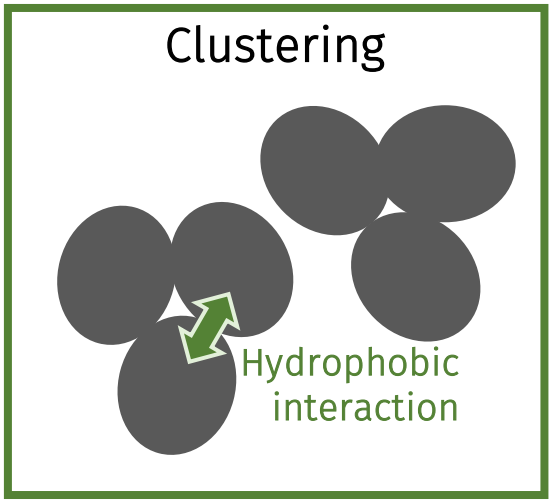


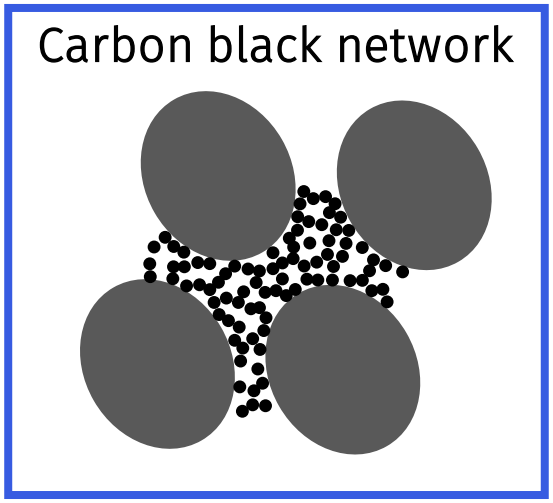
Graphite
~ 10 μm, ~ 30 vol%

Carbon black
~ 10 nm, ~ 2 vol%

Carboxymethyl cellulose (CMC)
~ 10 nm , ~ 1 vol%



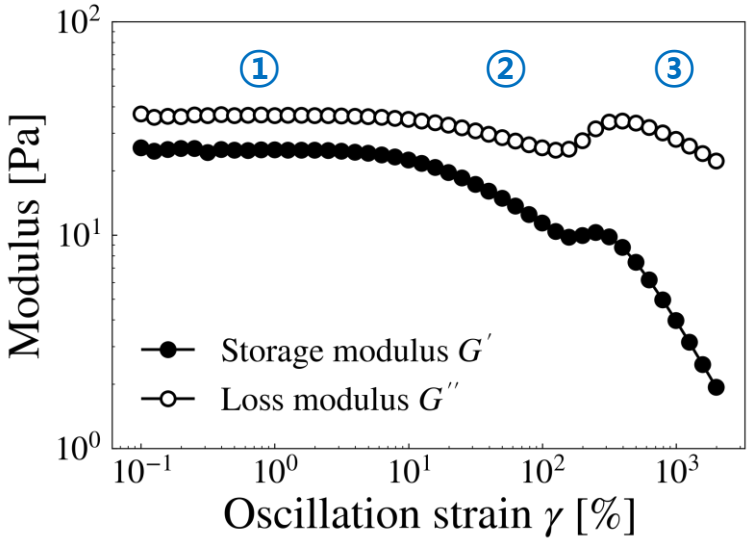


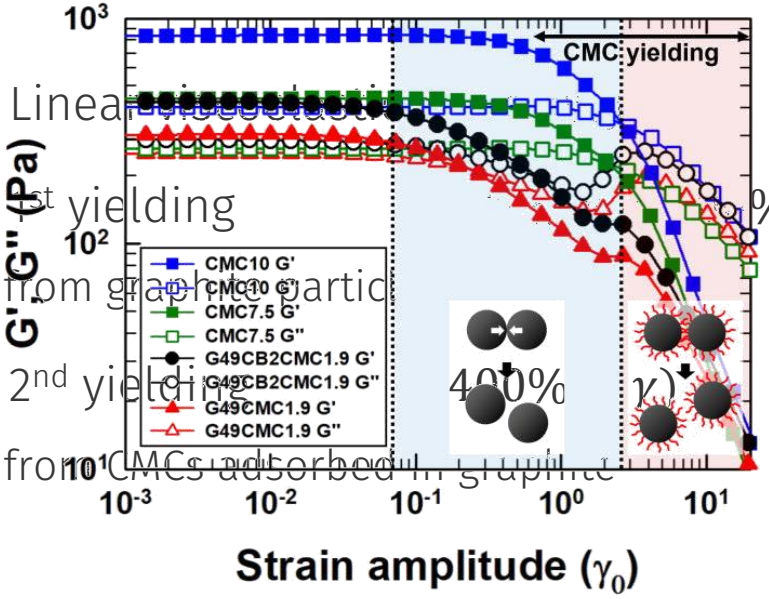


Battery slurry has very complex hierarchical microstructures . . .

Strain amplitude & shear rate sweep

Strain amplitude sweep





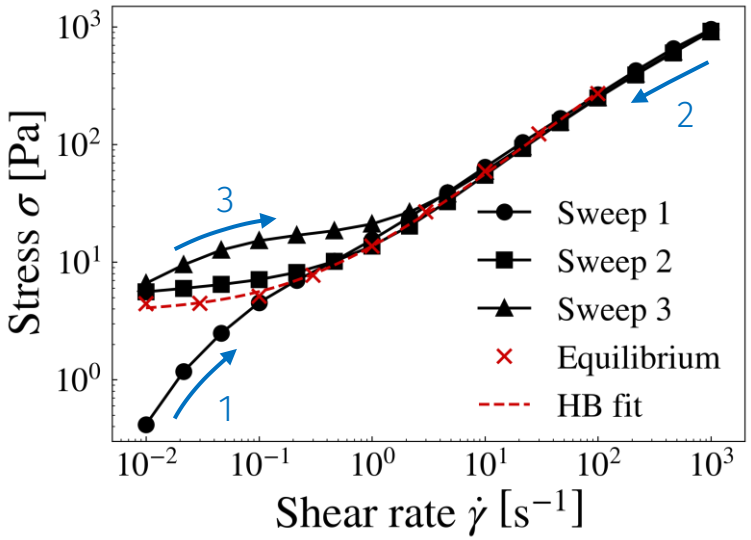
① Linear viscoelastic

② 1st yielding (~40%)
from graphite particle

③ 2nd yielding (~400%, γ_0)
from CMCs adsorbed in graphite

Kim et al., ***Phys. Fluids*** (2022)

Shear rate sweep

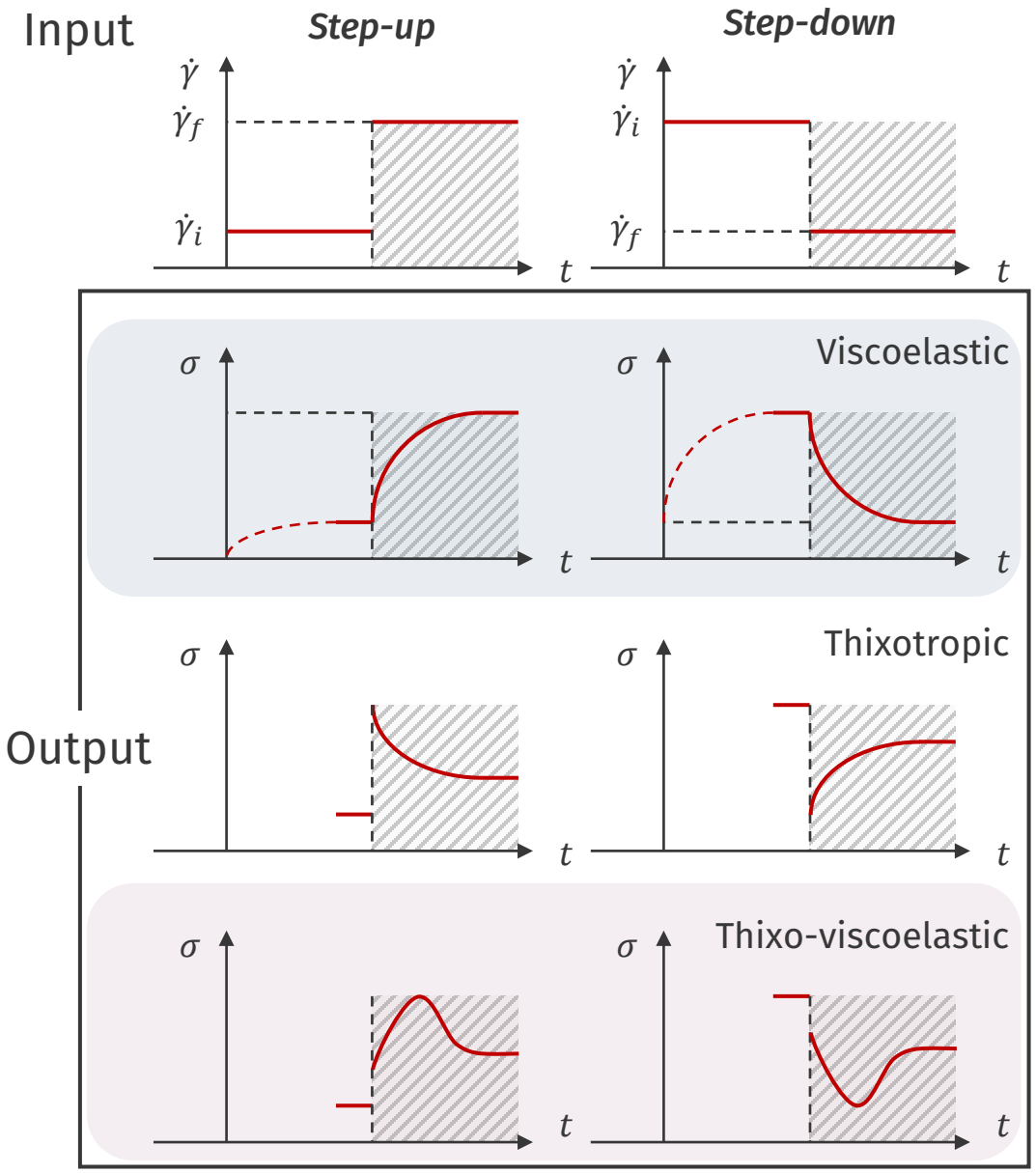


- Hysteresis loop implies thixotropy.
- Equilibrium curve can be fitted to the Herschel-Bulkley (HB) model:

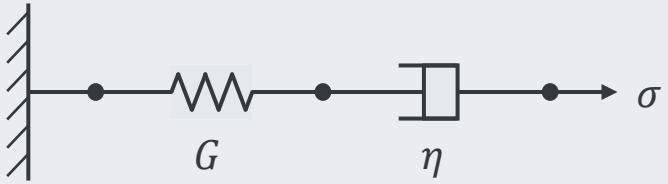
$$\sigma = \sigma_y + K|\dot{\gamma}|^n$$

- Measurement results depend heavily on protocols.

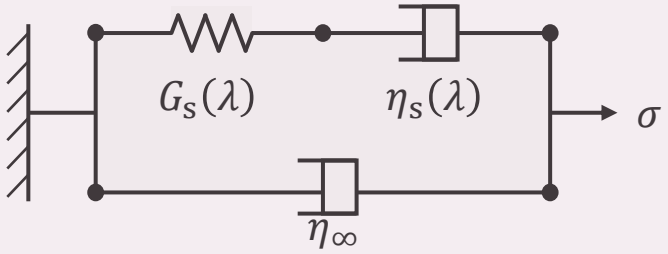
Step shear rate test: Constitutive models



Short-term: Maxwell model



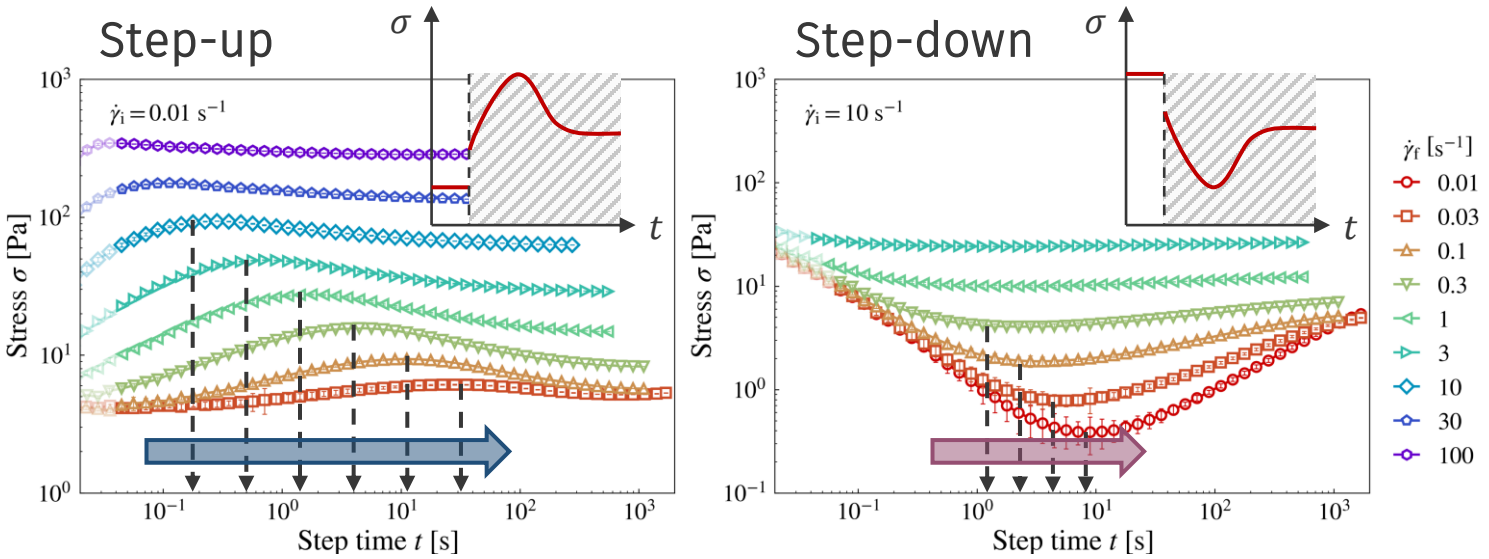
Long-term: TEVP model



Long-term response: Thixo-viscoelasticity

Same $\dot{\gamma}_i$

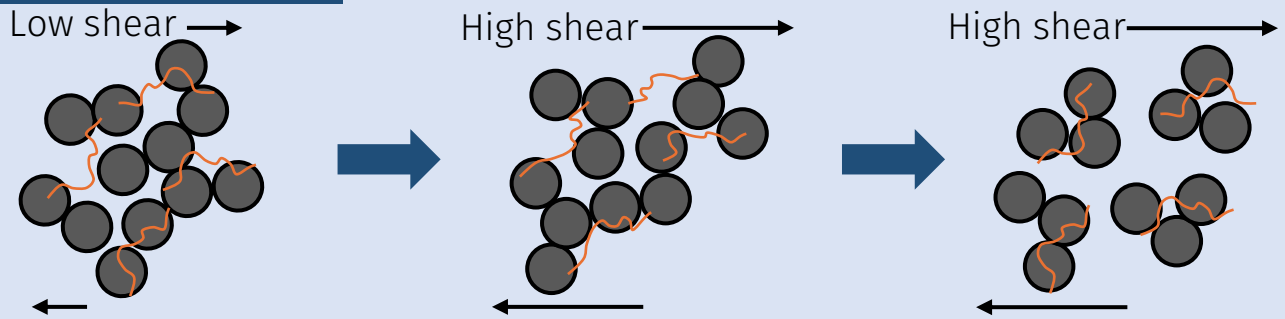
→ Varying $\dot{\gamma}_f$



$\dot{\gamma}_f$ ↓ ⇒ Delay of max. stress peak

$\dot{\gamma}_f$ ↓ ⇒ Delay of min. stress peak

Microstructure evolution during step-up test

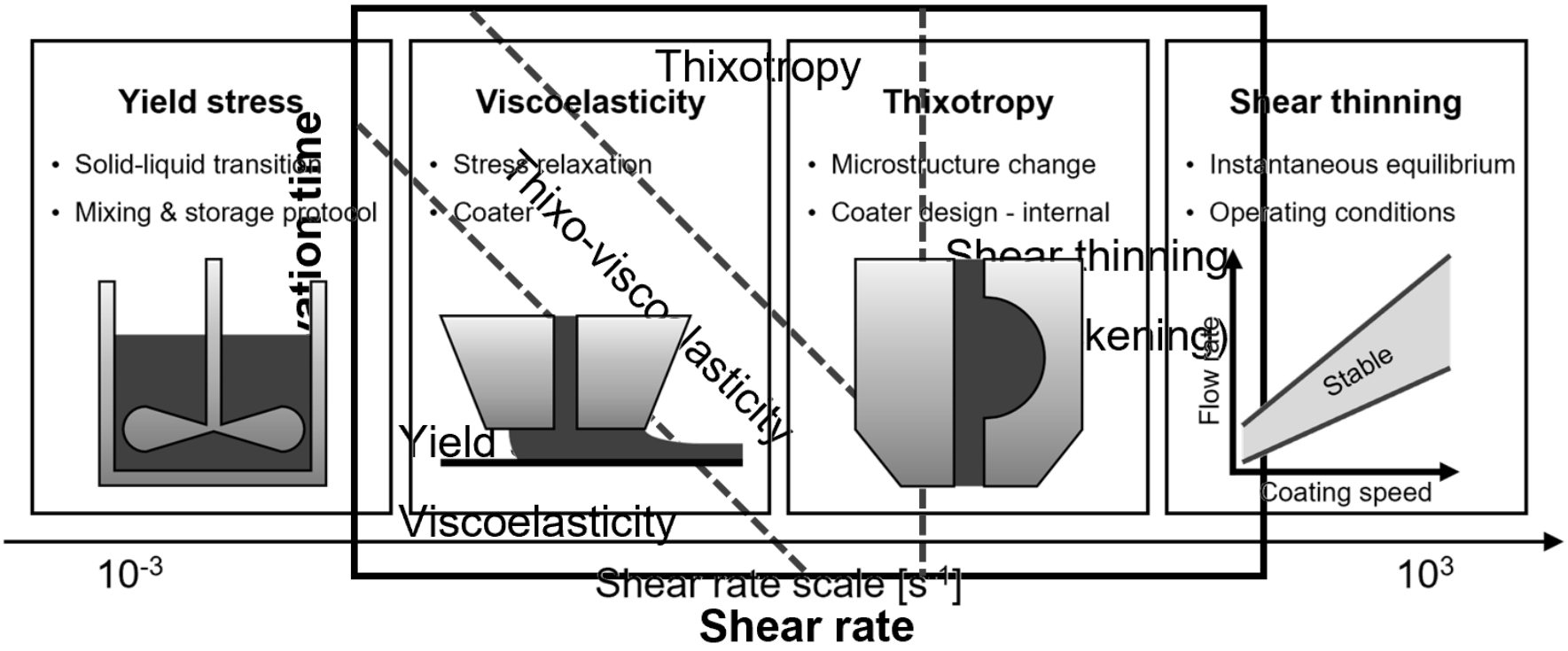


Step shear rate tests reveal

the combined effects of viscoelasticity and thixotropy!

Park, N., Lee, M., Jung, H., & Nam, J. Complex rheological response of Li-ion battery anode slurries. ***Journal of Power Sources***. (2024).

Rheological insights for coating process



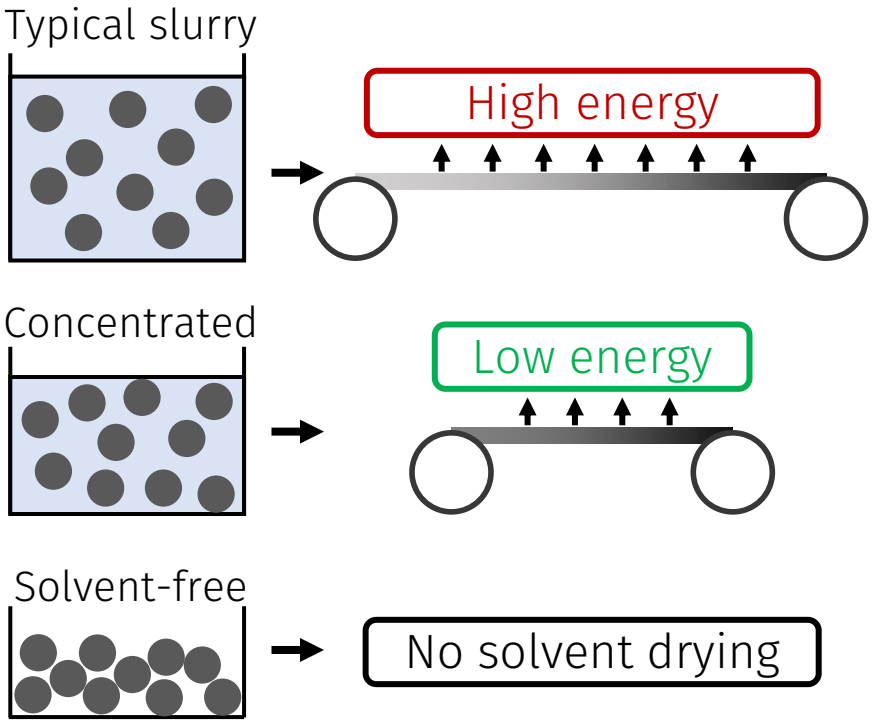
For effective LIB electrode manufacturing analysis,
focus on the shear rate range and
its prevailing rheological characteristics!

Park, N., Lee, M., Jung, H., & Nam, J. Complex rheological response of Li-ion battery anode slurries. ***Journal of Power Sources***. (2024).

Concentrated slurry

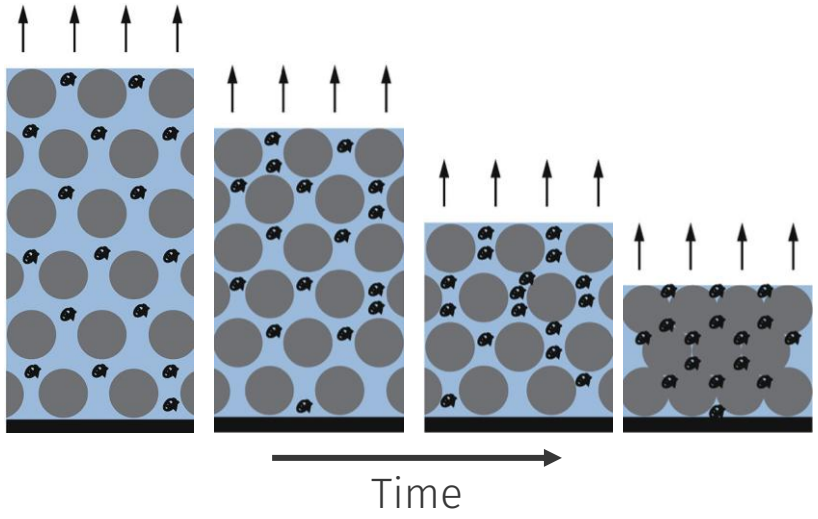
Industrial demand for higher slurry concentrations

Energy consumption



- Drying requires **high energy** and raises solvent **environmental concerns**.

Binder migration

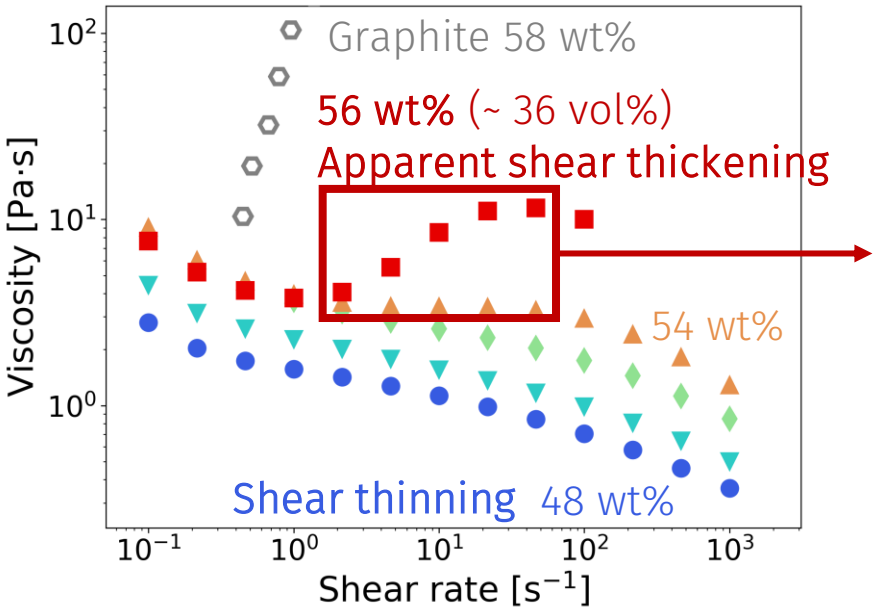


Font et al., ***J. Power Sources*** (2018)

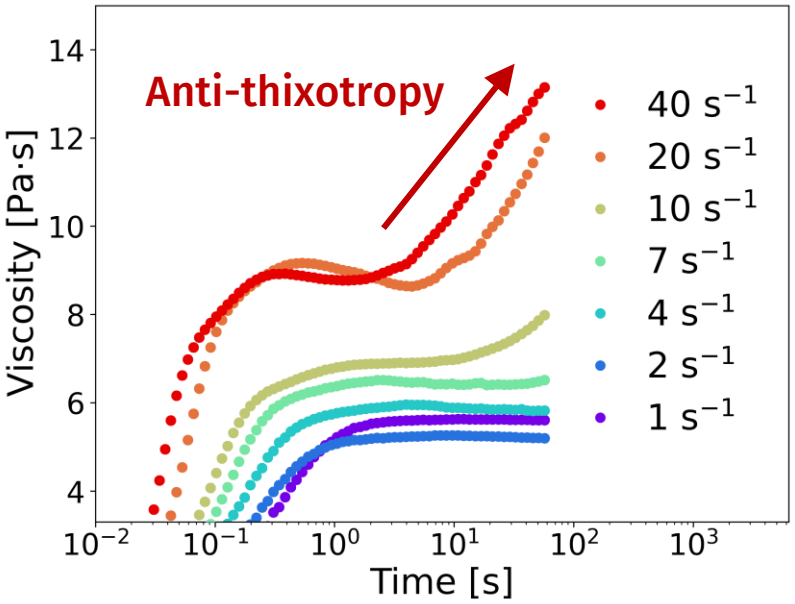
- **Thick films** are required to increase energy storage density.
- Binder/small particle **migration** intensifies in thick films.

Viscosity enhancement

- Flow curves



- Transient viscosity



Apparent shear thickening is observed at high graphite concentration.

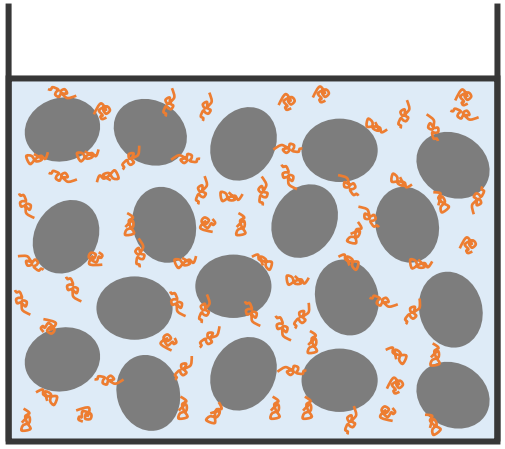
The viscosity increases over time when subjected to strong shear.

Concentrated slurries exhibit distinctive rheological behaviors, particularly apparent shear thickening and anti-thixotropy.

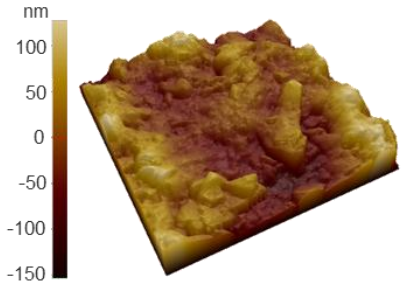
Jung, H., Hyun, C., & Nam, J. Shear-driven viscosity enhancement in battery slurry. ***Journal of Rheology***. (2025).

Friction contact between graphite particles

We studied **graphite/CMC aqueous slurry** for simplicity.

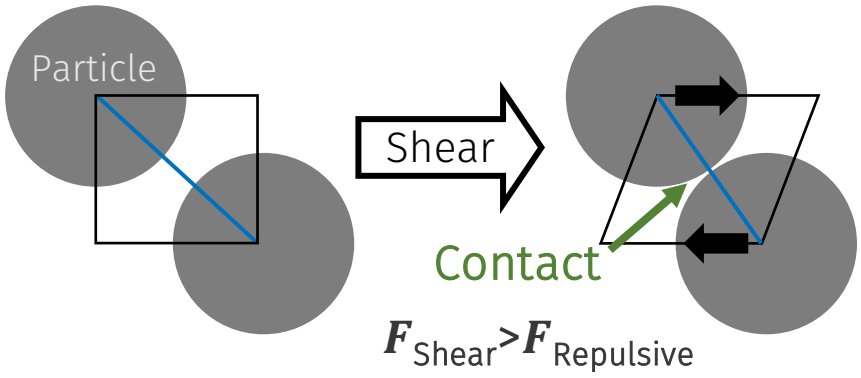


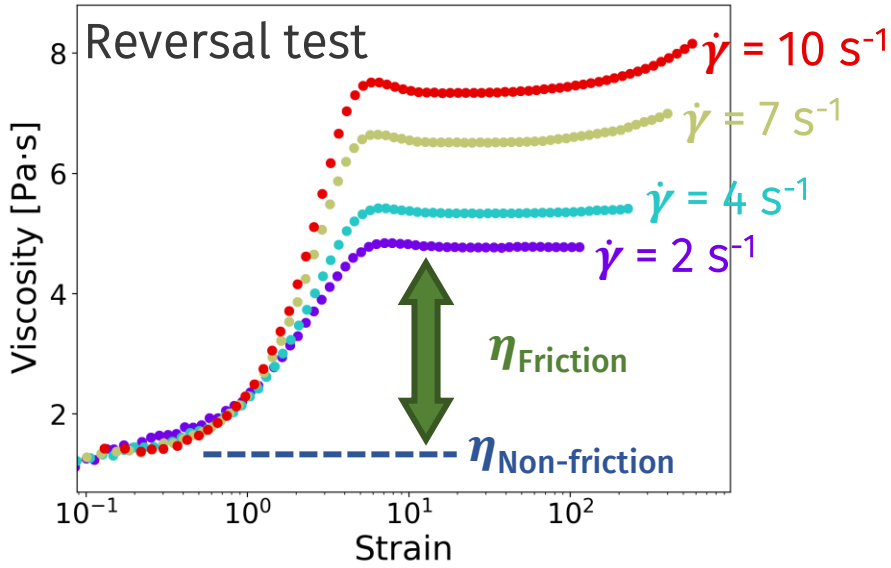
- Graphite surface profile (AFM image)



Roughness ~ 56 ± 13 nm

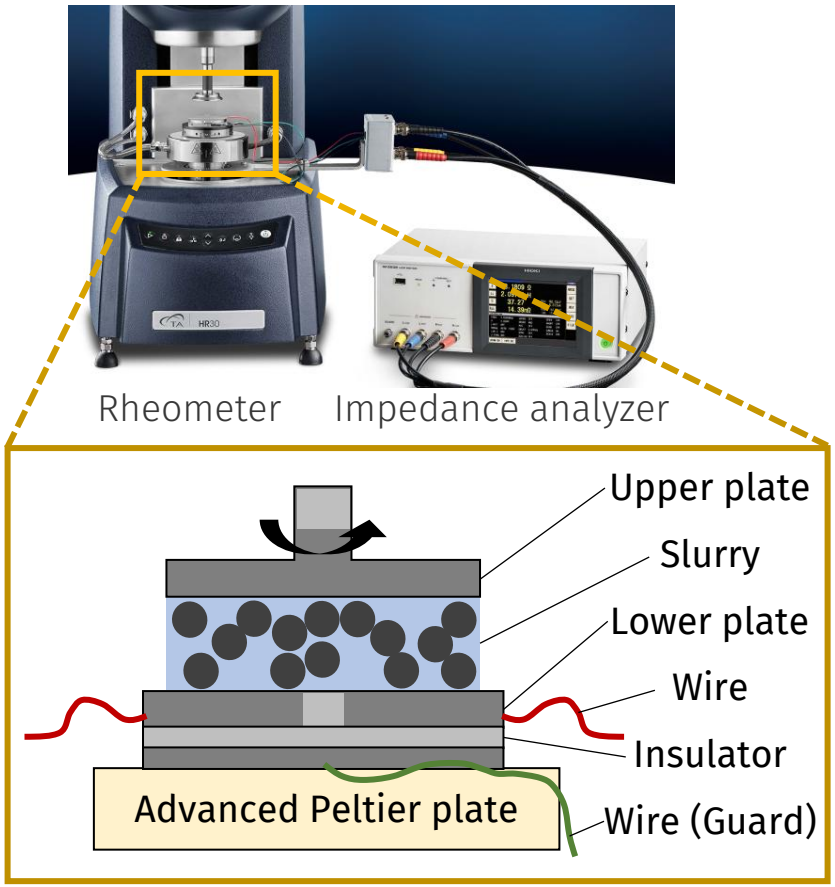
Friction contact mechanism

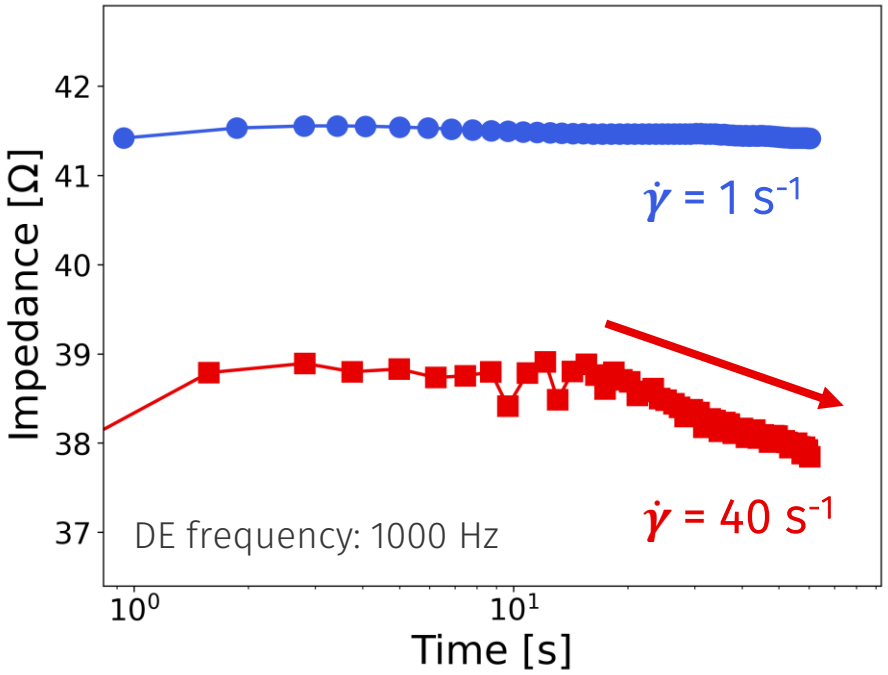




Graphite surface is sufficiently rough to generate shear-induced friction contact.

Rheo-impedance



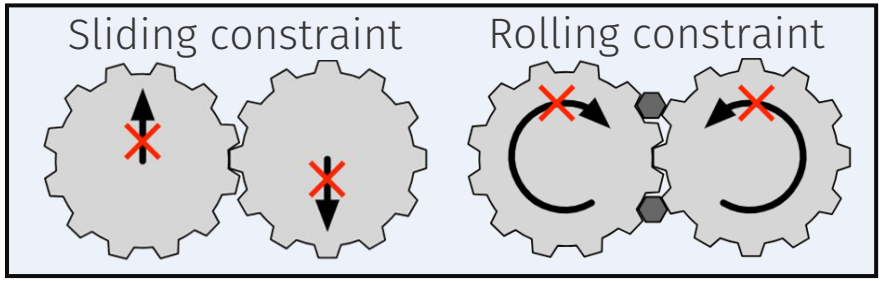


Higher shear rates and longer shearing times lead to a denser particle network.

The rheo-impednace meausrements provide information about microstructure under shear flow.

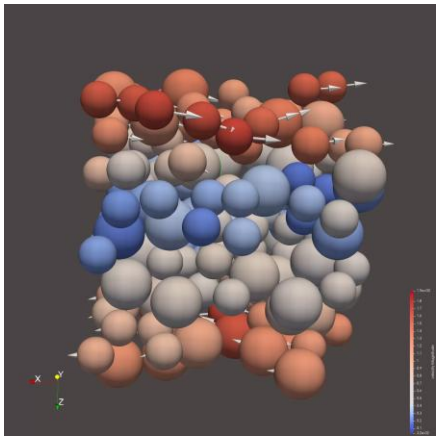
Future works

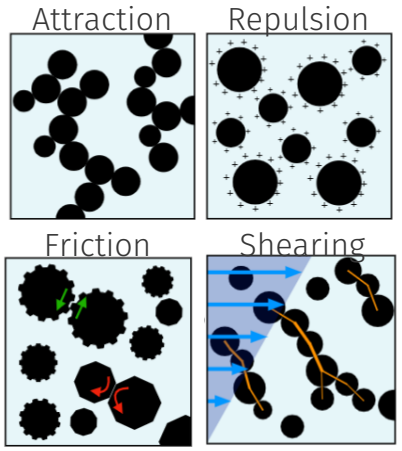
Frictional contact contribution



Singh et al. ***Phys. Rev. Lett.*** (2020)

DEM simulation

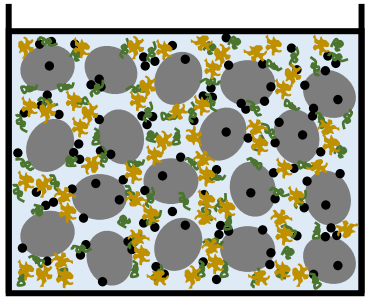




Ness et al. ***ARCMP.*** (2022)

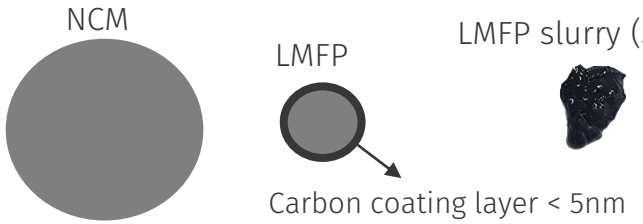
Other battery slurry systems

- All-solid-state battery slurry



Understanding particle interactions becomes more complex with solid electrolyte addition.

- Olivine structure cathode slurry



✓ Surface carbon coating
✓ High BET

} Particle agglomeration

New binders and **CA** are required for olivine-type materials.

Understanding particle-level interactions across diverse battery slurry system.

Edge Profile Control in Battery Electrode Slot-Coating

Jihwan Yoon

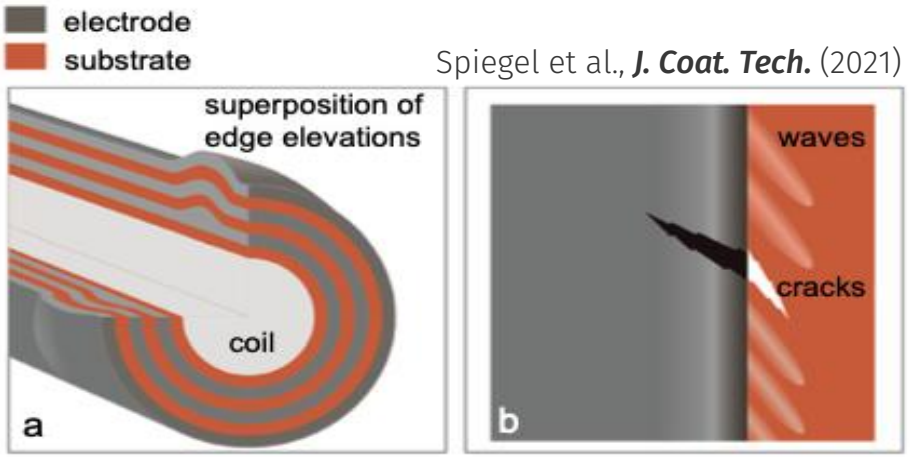
Kyengmin Min

Jisoo Song

Yoon, J., Min, K., Song, J., & Nam, J. Controlling Slot-Coating Edge Profiles of Battery Electrodes. ***ACS Applied Materials & Interfaces***. (2025).

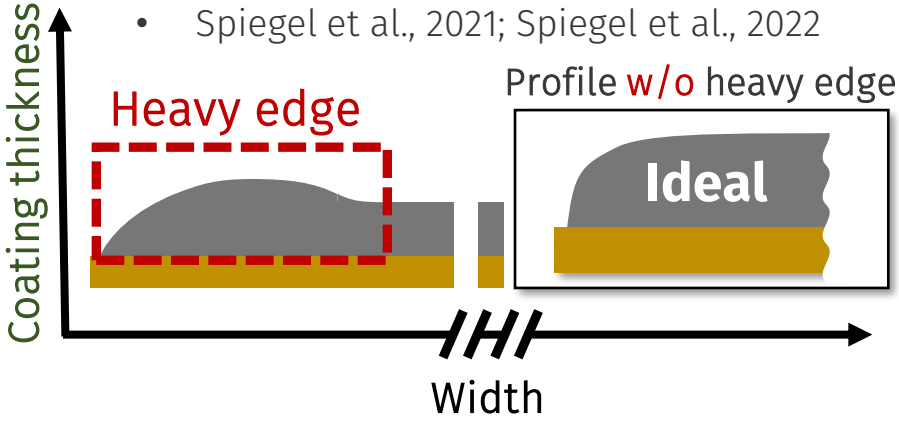
Issue: edge profile & quality window

- Edge elevation (heavy edge)

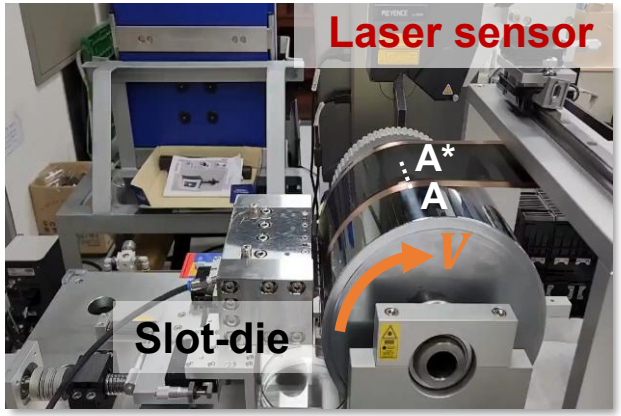


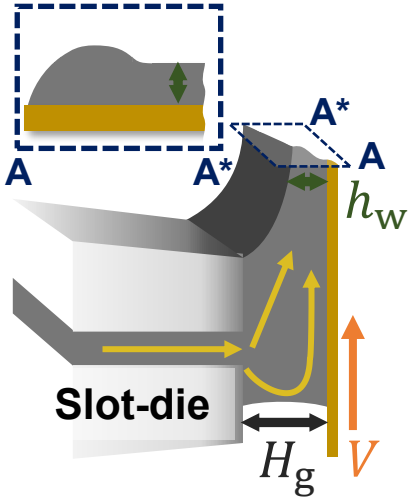
Spiegel et al., ***J. Coat. Tech.*** (2021)

- Edge (profile) quality control
  - Bitsch et al., 2014
  - Spiegel et al., 2021; Spiegel et al., 2022

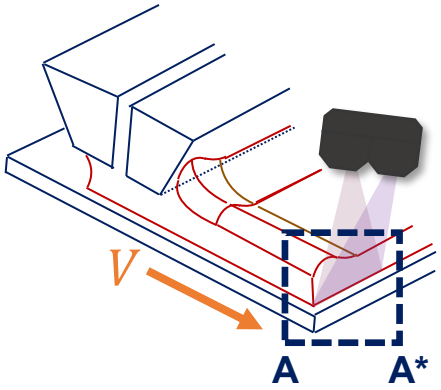


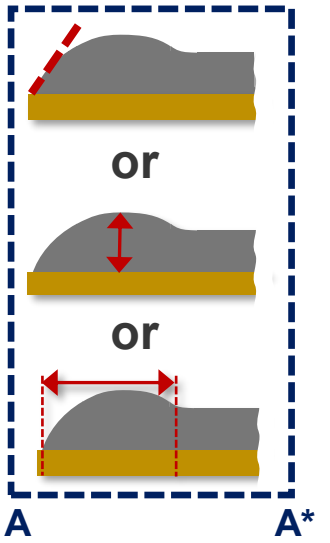
- Edge profile detection system





- Automated system



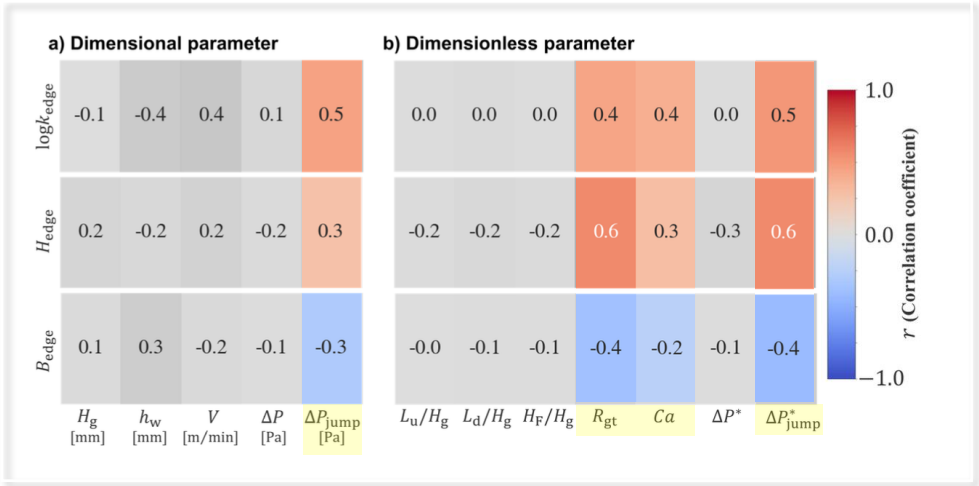


We investigated quality window for edge quality control in thick-film coating.

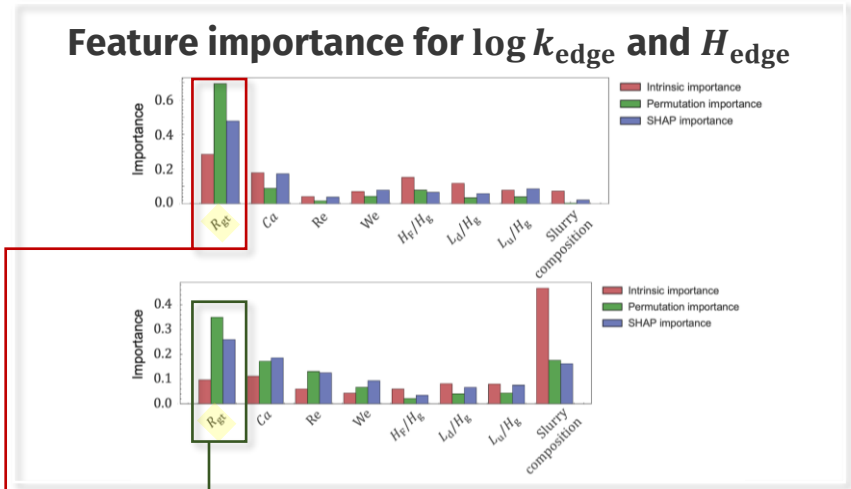
Result: Edge profile data analysis

- Identified the most influential variables using both statistical and machine learning methods.

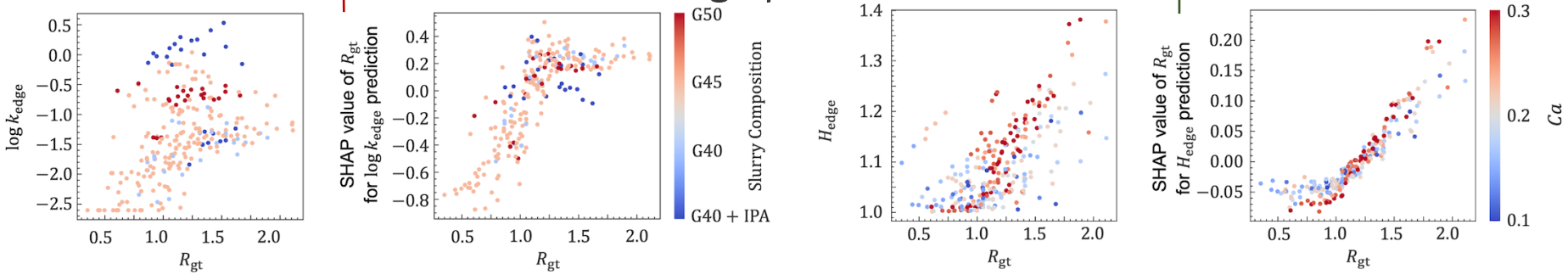
Statistical method (Spearman correlation matrix)



Machine learning (XGBoost model)



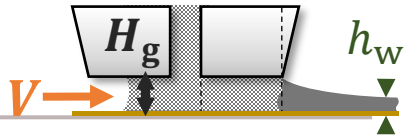
- Subsequently, SHAP analysis was performed on the key variables to evaluate their influence on the edge parameters.



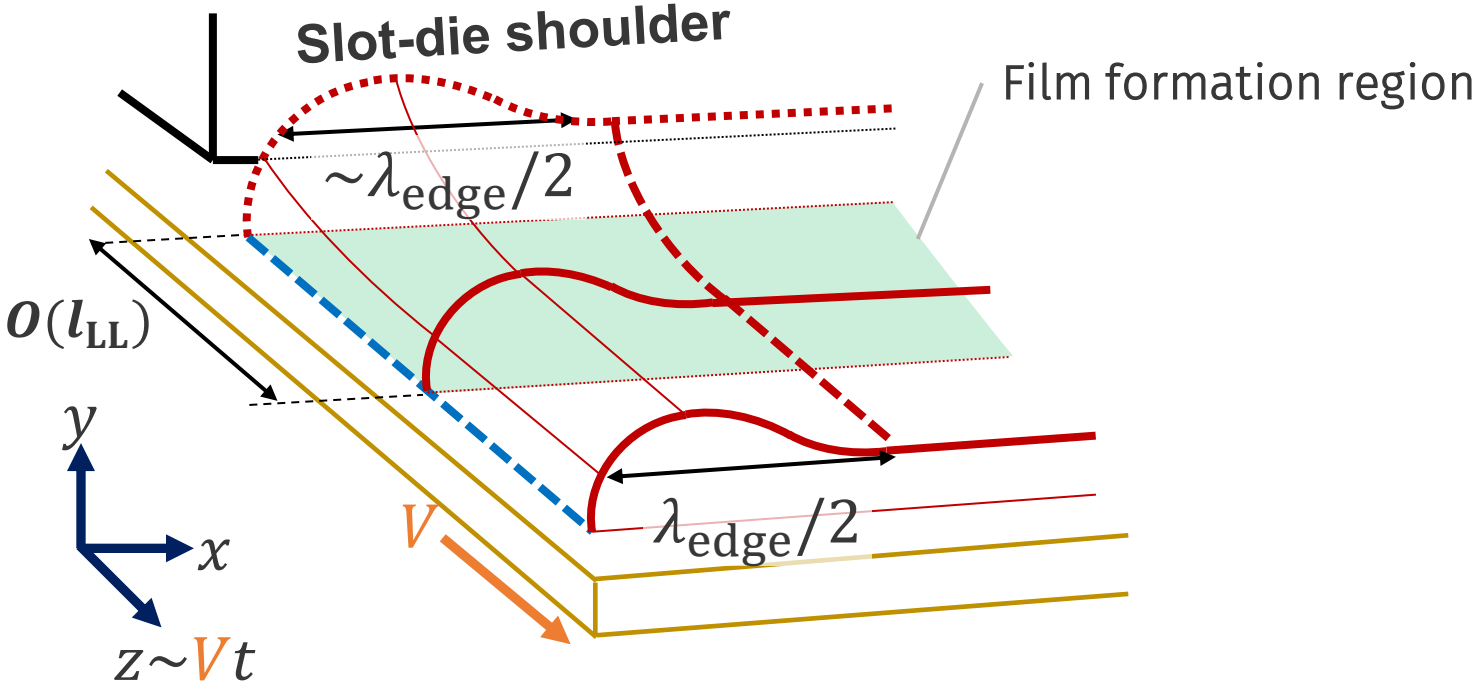
We established quantitative relationships between process parameters and edge profiles.

Edge formation modeling

❖ $R_{gt} = \frac{H_g}{h_w}; Ca = \frac{\mu V}{\sigma}$



- Leveling effect ~ τ_{level} (time constant for leveling flow).
- Available time for leveling (τ_{pass}).

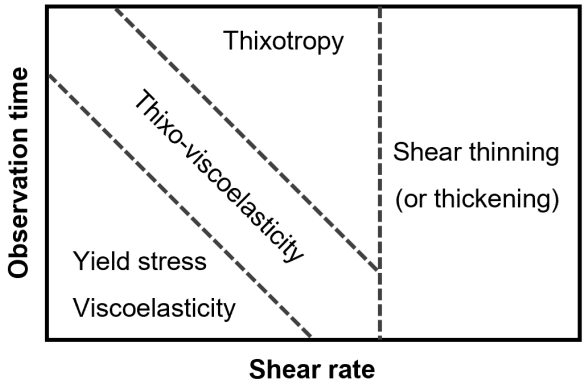


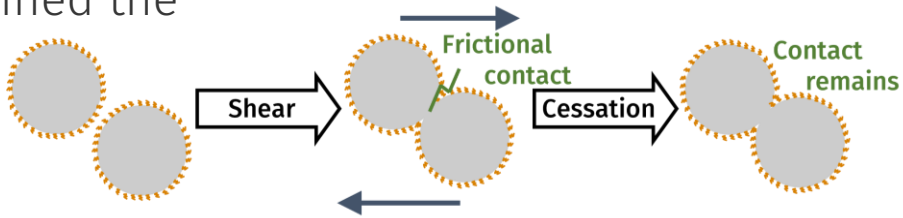
$\tau_{level} \sim \frac{\eta \lambda_{edge}^4}{\sigma h_w^3} \sim O(10^{-3} - 10^3)$ s V.S. $\tau_{pass} \sim \frac{l_{LL}}{V} \sim \frac{H_g}{V}(3Ca)^{-1/3} R_{gt}^{-1} \sim O(10^{-1} - 10^0)$ s

λ_{edge}^4 & τ_{pass} ($\sim R_{gt}^{-1}$) are crucial for edge quality control.

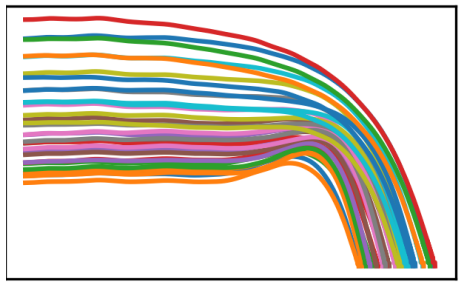
Final Remarks

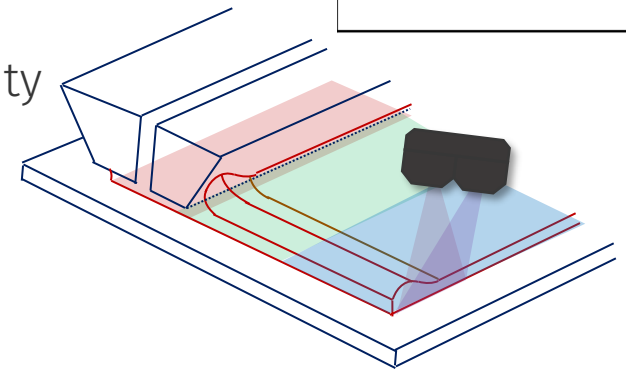
- Battery slurry rheology
  - ✓ Characterized rheological responses of Li-ion battery anode slurries across various **time** and **shear rate scales**.
  - ✓ Investigated **shear-induced viscosity enhancement** in concentrated anode slurries and clarified the underlying mechanisms.





- Edge profile in slot coating
  - ✓ Comprehensive analysis of 500+ experimental data identifying key factors in edge profile formation.
  - ✓ Successfully explained **edge formation mechanisms** and developed practical quality management **guidelines.**





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