Roll-to-Roll Manufacturing of Solid Oxide Fuel Cells

TCF-20-20119

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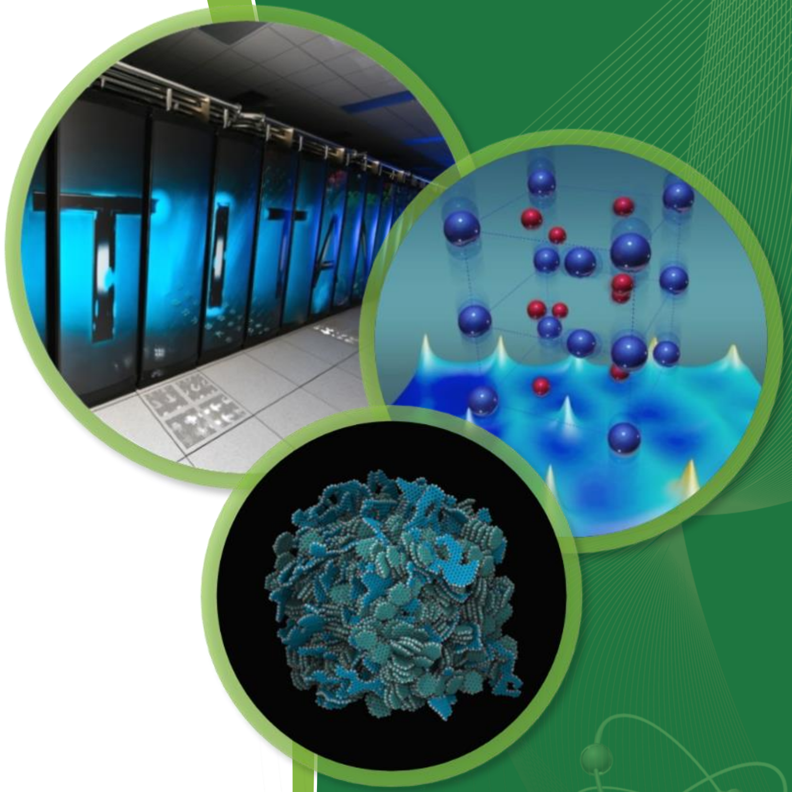

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Project goal and deliverables

Goal: To further develop a high-volume electrode electrolyte assembly (EEA) production capability to significantly increase throughput of SOFC manufacture and reduce the manufacture cost by 30%

Approach:

- Optimize the lamination process using calendering
- Quantity scale-up of the lamination process to demonstrate > 10 ft of EEA
- Further increase EEA throughput via slot-die coating and demonstrate > 5 m/min coating of ASL (10X increase vs tape casting)
- Minimize the anode supported layer (ASL) thickness and reduce material cost by >10%

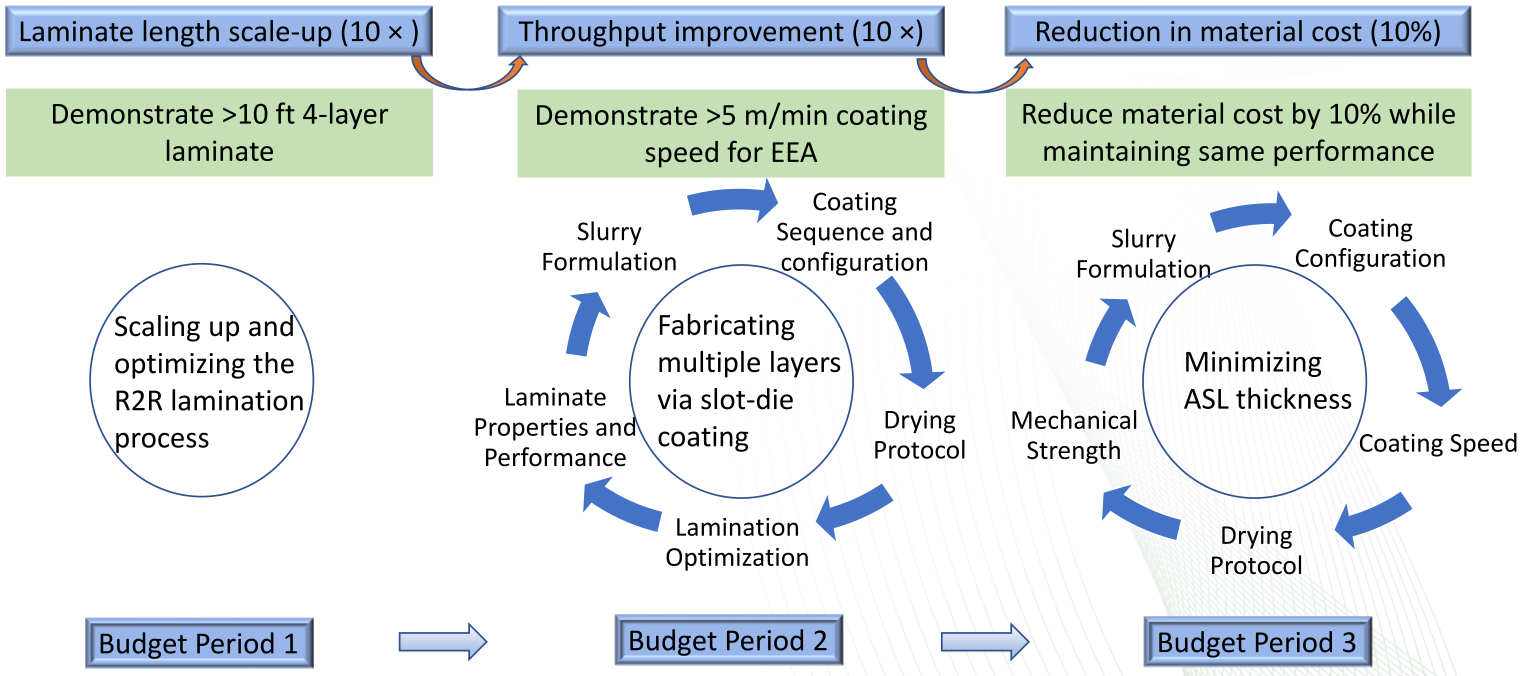
Deliverables:

- **Budget Period 1:** Optimization of the lamination conditions and demonstration of >10 ft 4-layer EEA; sintering the EEA, characterizing the EEA morphology and properties, and testing the cell performance at ORNL and Redox.
- **Budget Period 2:** Fabricating multiple layers via slot-die coating, demonstration of >5 m/min in coating ASL, laminating them into EEA to reduce interfacial resistance, testing the cell performance and characterizing the laminate properties at ORNL & Redox.
- **Budget Period 3:** Further reducing SOFC cost by minimizing ASL thickness and enabling >10% material cost reduction

Project period: 3 years (May, 2022-April 2025)

Project budget: $1.2 M

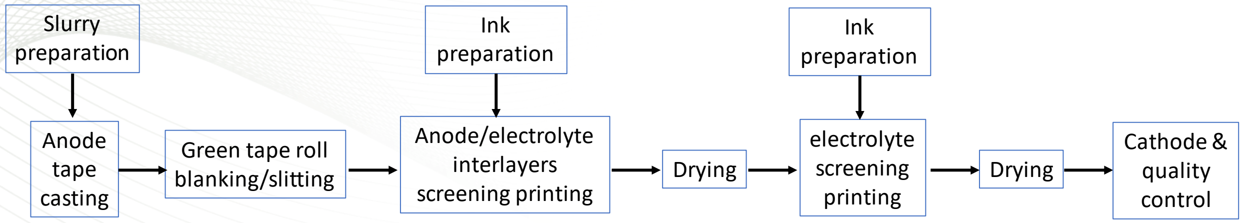
Completion: 25%



Work scope flow chart.

SOFC/SOEC manufacturing involves many steps and the manufacturing cost highly depends on the scale

An example of an EEA manufacturing process

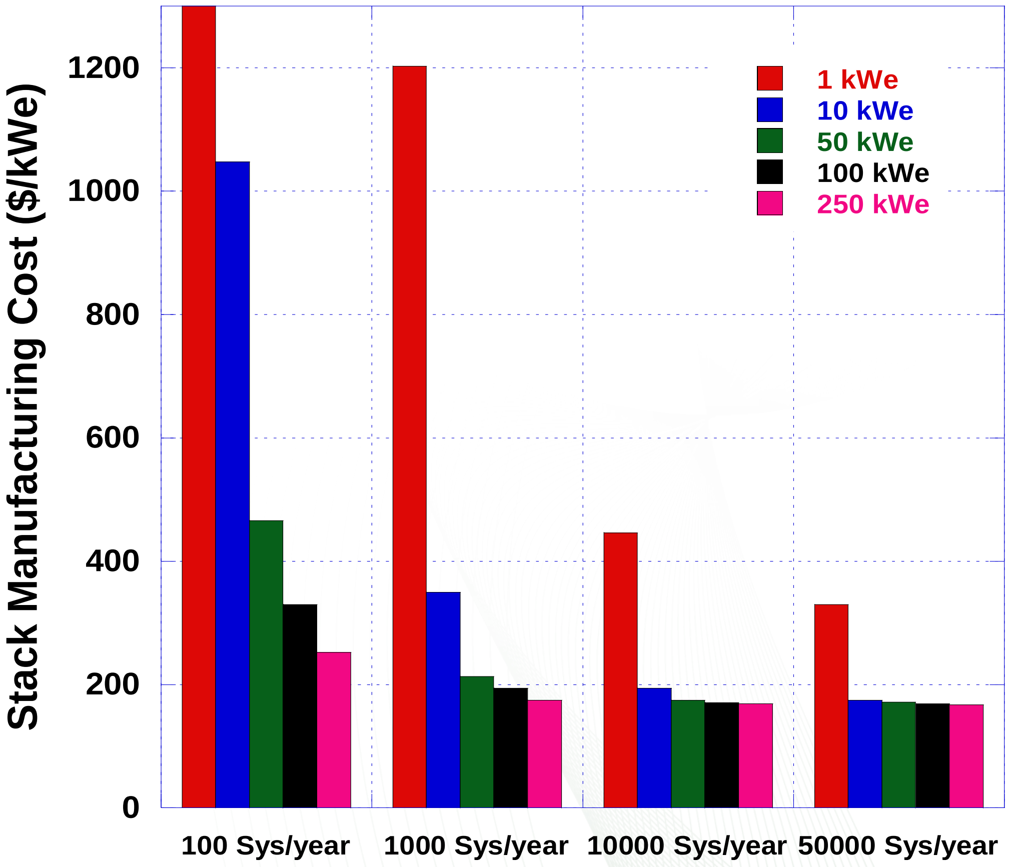


Electrode and electrolyte were coated via tape cast and screening printing in sheet-to-sheet manner

- Low manufacturing volume
- High manufacturing cost
- Conventional method throughput is typically 5-8 min/laminate

Manufacturing cost can be significantly reduced by increasing manufacturing volume and system size

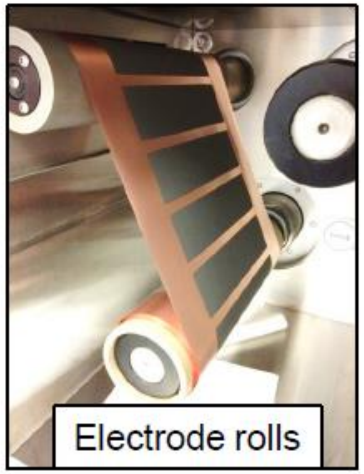
Stack manufacturing cost variation with system size.

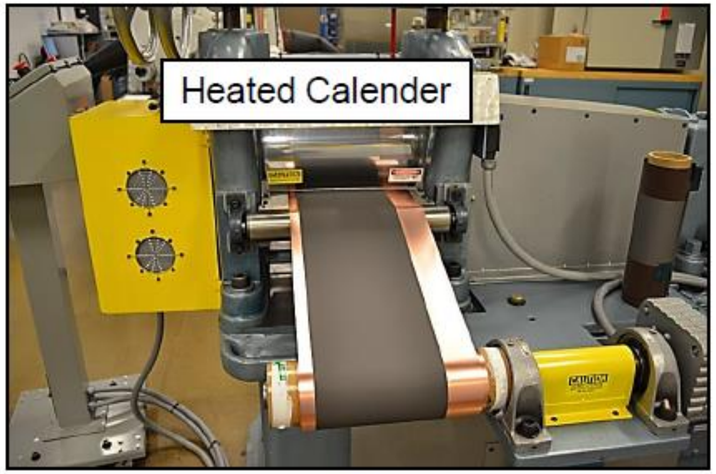


R. Scataglini, et. al., "A total cost of ownership model for solid oxide fuel cells in combined heat and power and power-only applications", Lawrence Berkeley National Laboratory, December 2015

Roll-to-roll manufacturing capabilities at BMF

Battery electrode fabrication





- Planetary mixer
- ½ gallon

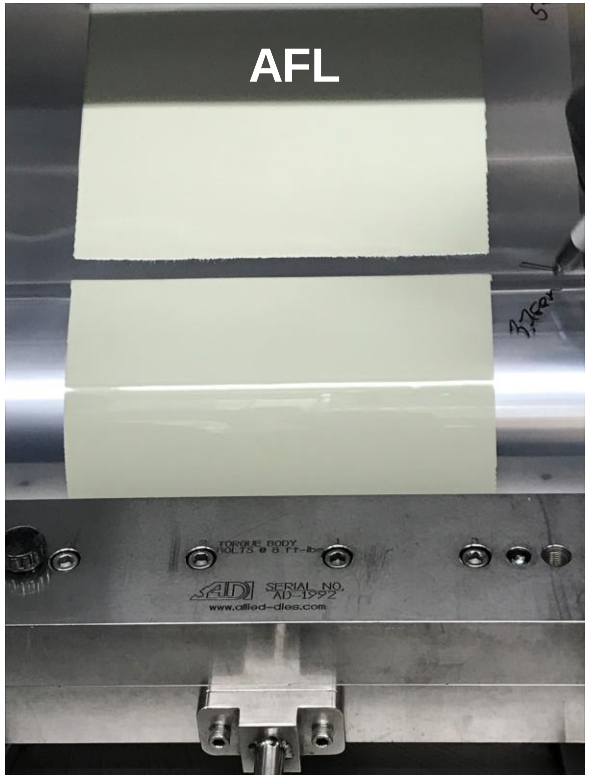
- Single and double sided
- Continuous and intermittent coating
- Capable of simultaneous multi-layer coating
- Up to 15 ft/min

- 9 drying zone including 2 IR zones

- 80,000 lbf
- Temperature up to 250^{o}C
- Up to 15 m/min

Fabricated AFL and GDC via Slot-Die Coating

- Successfully developed slurry formulation for slot-die coating
- Fabricated both defect-free AFL and GDC with a very thin thickness (>5 m/min)
- Fabricated thick ASL via slot-die coating (>5 m/min)



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Rheology experiments for probing fluid behaviors of slurries

A concentric cylinder rheometer (Discovery HR3, TA Instruments) with TRIOS software was calibrated and test cup equilibrated to 25 °C prior to transferring slurries volumetrically into the test cup.

Experimental Procedure:

- Step 1. **Pre-shear** of 5 s^{-1} applied for 60 s.
  - Provides consistent shear history between samples to reduce hysteresis effects.
- Step 2. **Flow Ramp** logarithmic ramp between 5 to 3500 s^{-1} over 5 min
  - Measures stress, providing the samples viscosity as a function of shear rate.
- Step 3. **Oscillation Time Sweep** angular frequency (ω) of 100 rad·s^{-1} and oscillation strain γ of 0.1% for 15 min.
  - Rebuilds the fluid's bridging flocculation network structure which is disrupted at high shear rates.
- Step 4. **Amplitude Sweep** ω = 100 rad·s^{-1}, between γ = 0.01-10%
  - Characterizes strength of network structure by measuring the dependency of G' and G'' on strain.
- Step 5. **Oscillation Time Sweep** angular frequency (ω) of 100 rad·s^{-1} and oscillation strain γ of 0.1% for 5 min.
  - Shorter rebuild time required for amplitude sweep (less destructive than the flow ramp test).
- Step 6. **Frequency Sweep** between ω = 100-0.1 rad·s^{-1} at γ = 0.1%.
  - Frequency sweep within LVR provides insight into the degree of gelling in suspension

Concentric cylinder or "bob and cup" rheology testing GDC slurry. "Skin" formation and solvent evaporation was observed in all GDC slurries.

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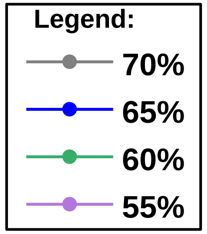
Dynamic viscosity curves demonstrating viscoelastic behavior

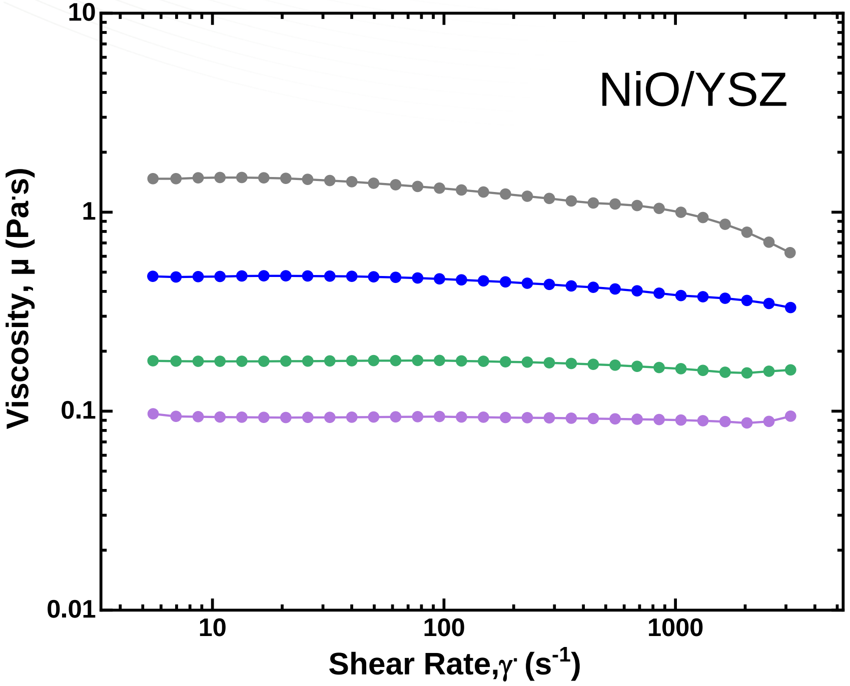
In slot-die coating a slurry with a high LSV (low shear viscosity) and lower HSV (high shear viscosity) is ideal. A high LSV promotes sharper edges while lower HSV values allow higher solids loading and faster coating rates.

$$\text{Viscosity} = \frac{\text{Stress}}{\text{Strain Rate}}$$

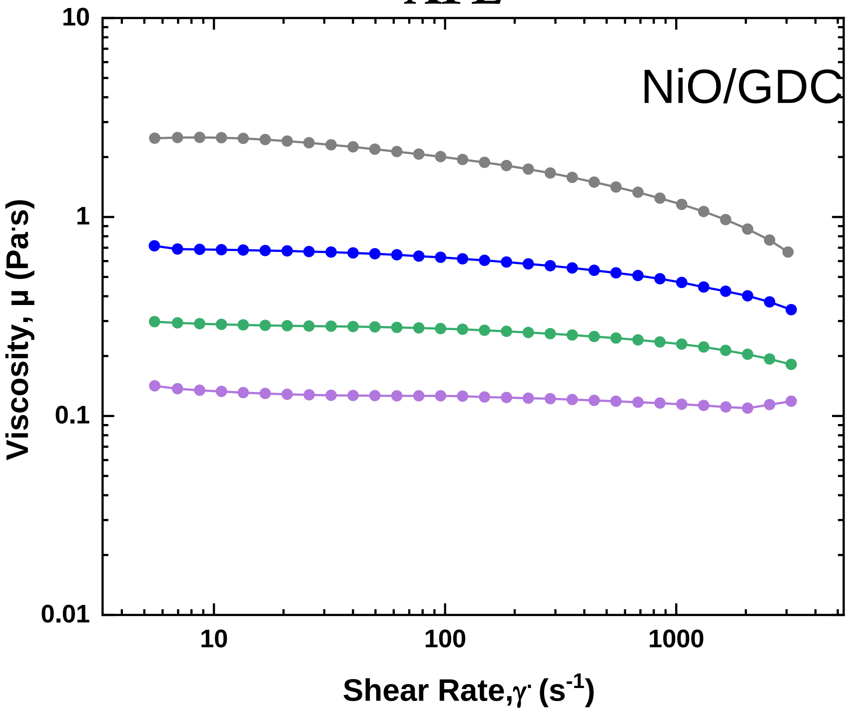
surface area NiO : 2.65 m^2/g
YSZ : 7.0 m^2/g
GDC : 12.5 m^2/g



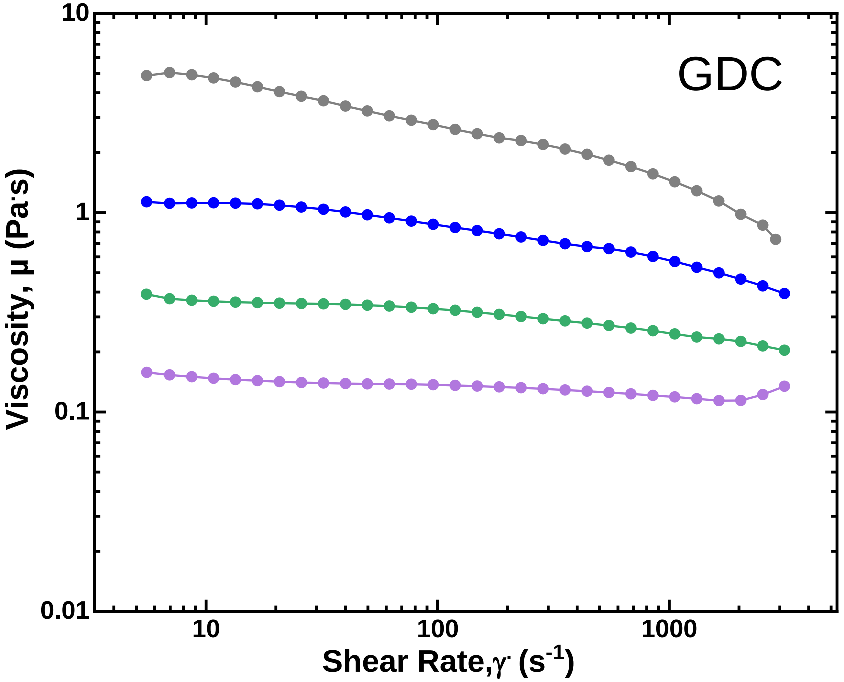
ASL



AFL



GDC



- All slurries show shear thinning behavior
- Shear thinning behavior is more pronounced with higher solid contents
- Viscosity trend follows: GDC>AFL>ASL in agreement with the surface area

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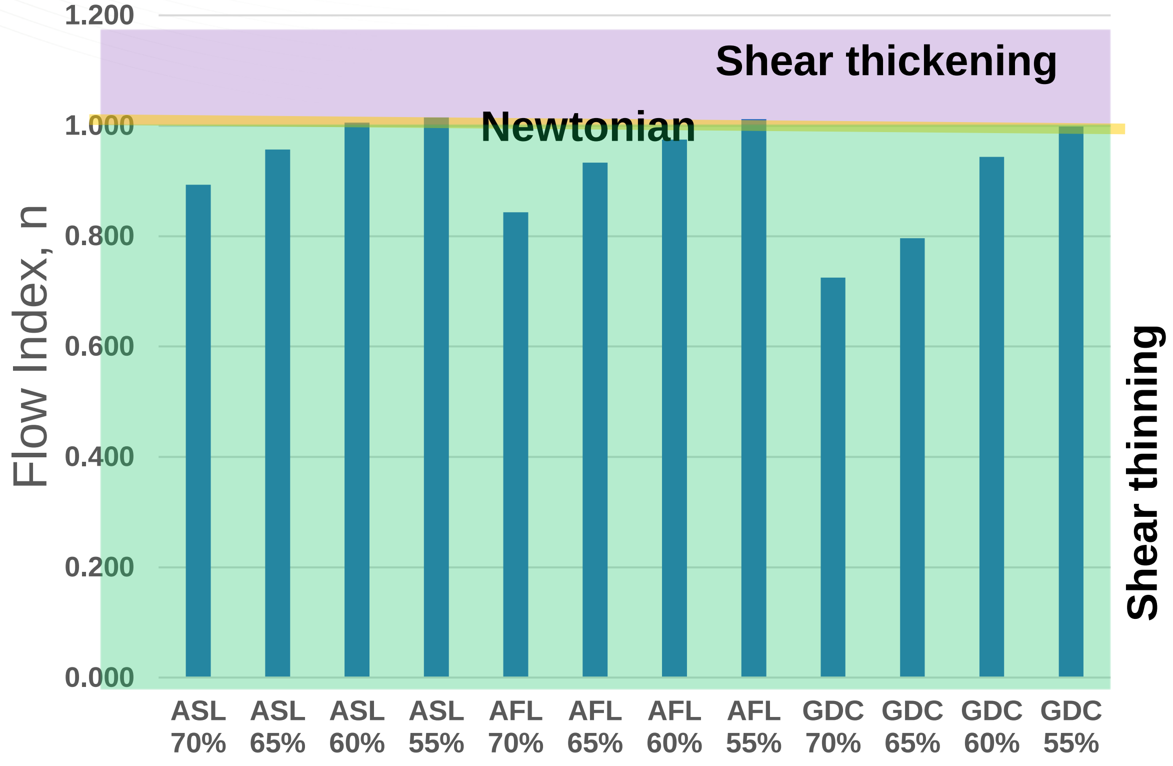
Evaluating shear behavior using Hershel-Bulkley modeling

Hershel-Bulkley modeling is useful for comparing the shearing behavior in similar viscosity slurries.

The **flow index (n)** is indicative of the shear behavior of a fluid.

$$y = y_0 + Kx^n$$

n = 1 Newtonian fluid behavior
n < 1 indicates the degree of <u>shear thinning</u>
n > 1 indicates the degree of <u>shear thickening</u>



All fittings have an $R^2 > 0.999$

- The surface area of oxides influences their intermolecular forces within a fluid.
- The ASL has the lowest surface area, while GDC has the highest surface area.
- GDC has a higher degree of shear thinning than the ASL and AFL at same solid loading.

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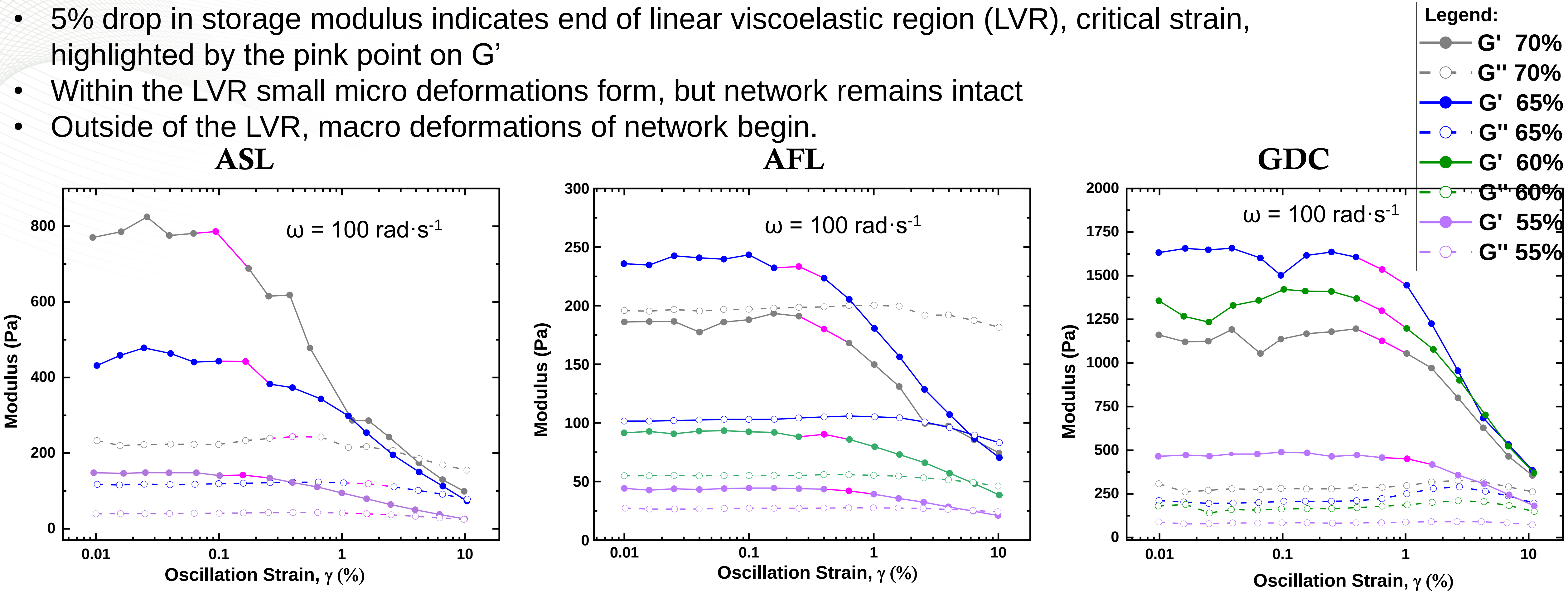
Most slurries show higher storage modulus than loss modulus

- 5% drop in storage modulus indicates end of linear viscoelastic region (LVR), critical strain, highlighted by the pink point on G’
- Within the LVR small micro deformations form, but network remains intact
- Outside of the LVR, macro deformations of network begin.



- Moduli increases with increasing solid content in general except for the 70wt% in AFL and GDC
- Higher moduli indicate better capability in store energy→solid like material
- LVR ends at smaller oscillation strain with higher solid content

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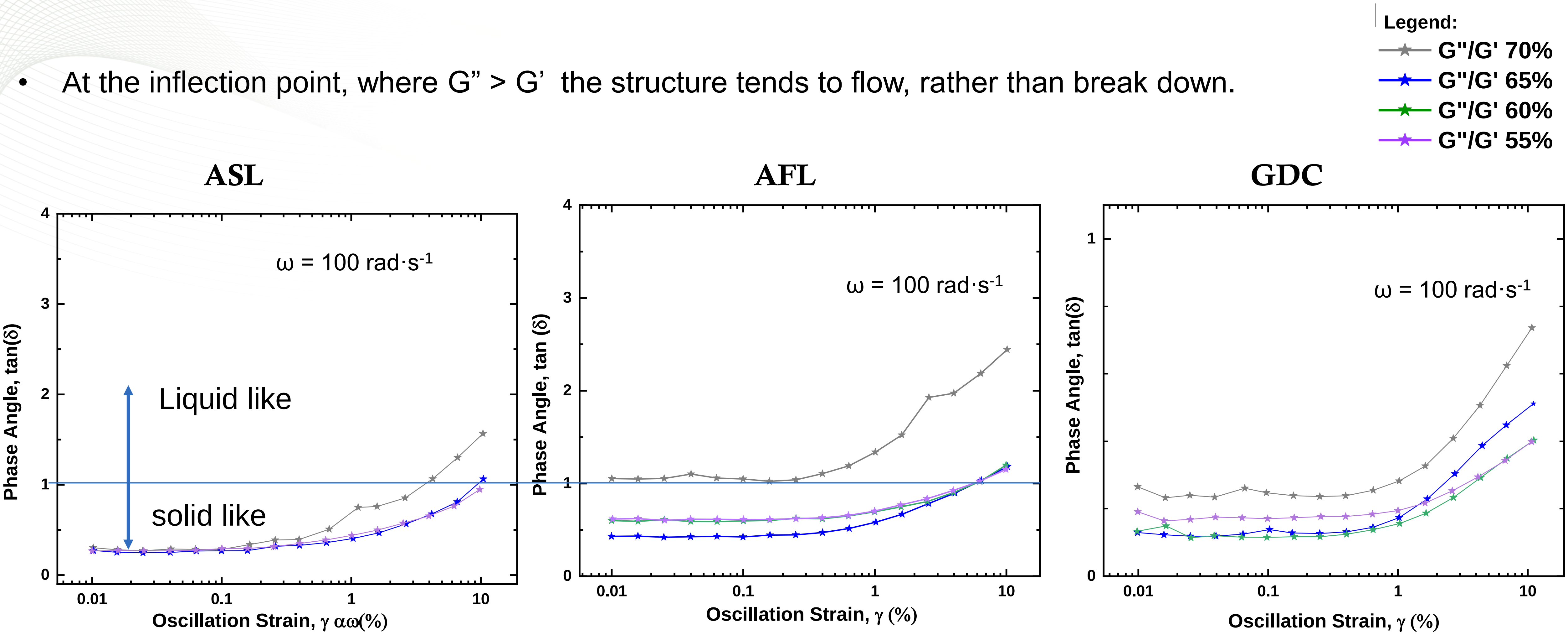
Tangent > 1 indicates fluid behavior

- At the inflection point, where G" > G' the structure tends to flow, rather than break down.



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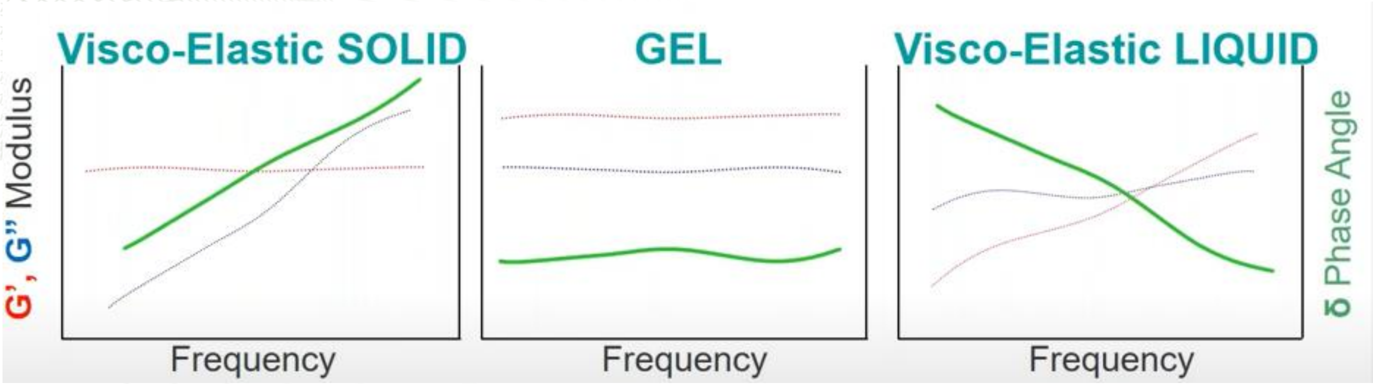
Frequency sweep indicates gel structure for all slurries

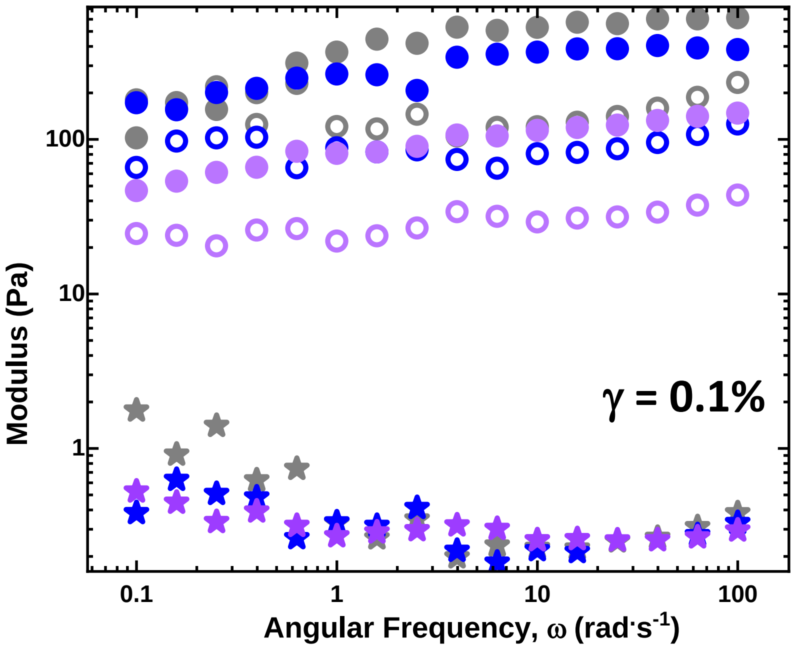


There is no inflection point of storage and elastic moduli, indicating gel behavior throughout entire test region.

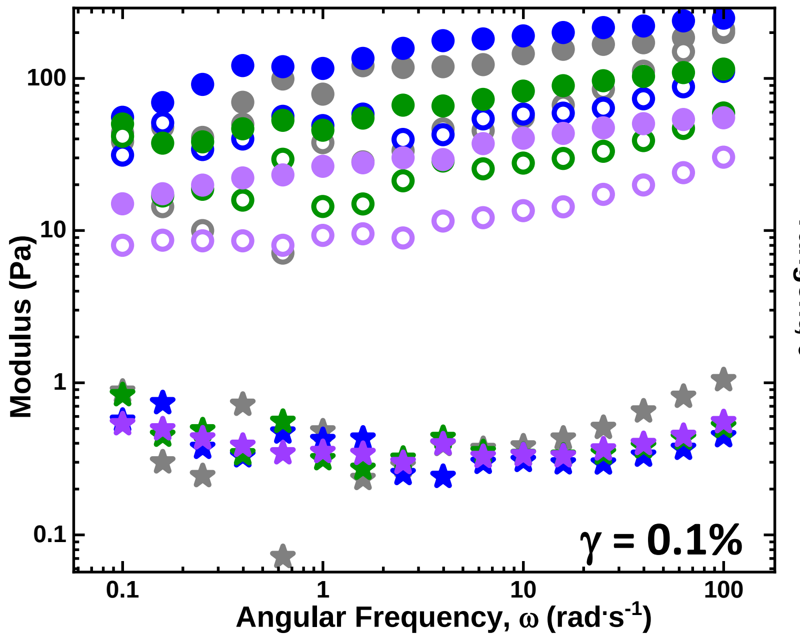
The GDC slurry is on average an order of magnitude higher for both moduli.

Legend:
- G' 70%
- G" 70%
- G' 65%
- G" 65%
- G' 60%
- G" 60%
- G' 55%
- G" 55%
- G"/G' 70%
- G"/G' 65%
- G"/G' 60%
- G"/G' 55%

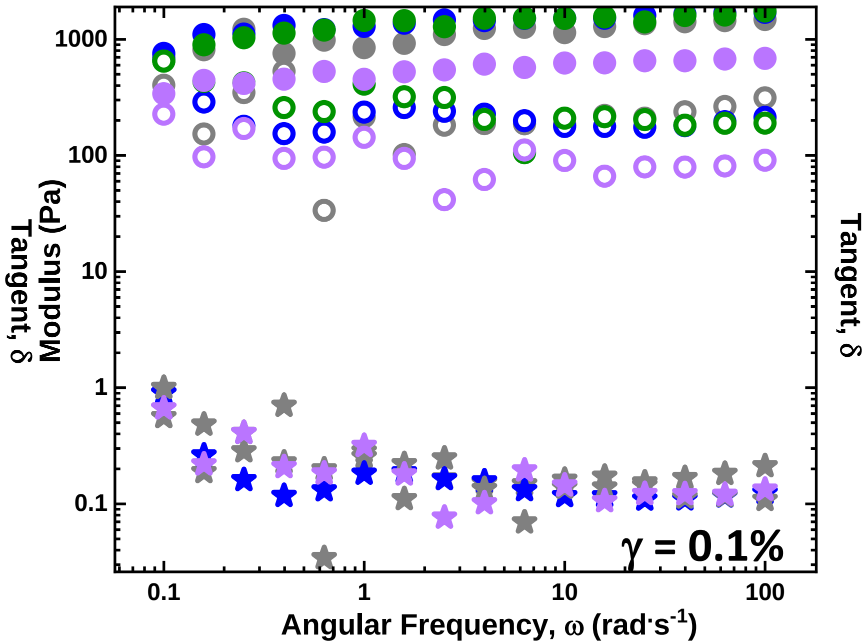
ASL



AFL



GDC



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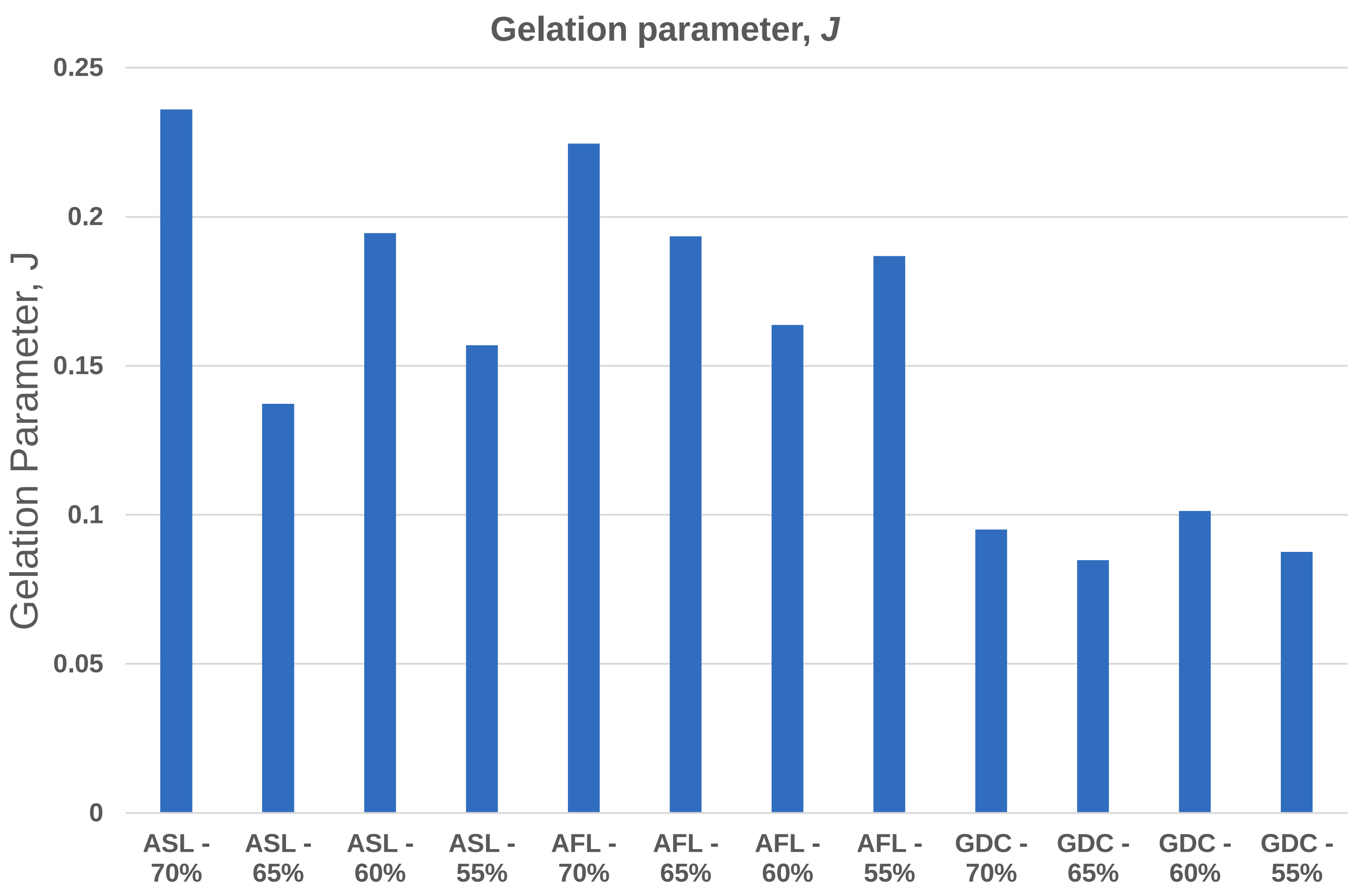
Deriving gelation value from power law of frequency sweep data

A gelation value (J) close to zero, indicates a more solid-like network for the liquid structure.

$$G' = \alpha\omega^{J}$$

In general, degree of gelation is higher with lower solid content



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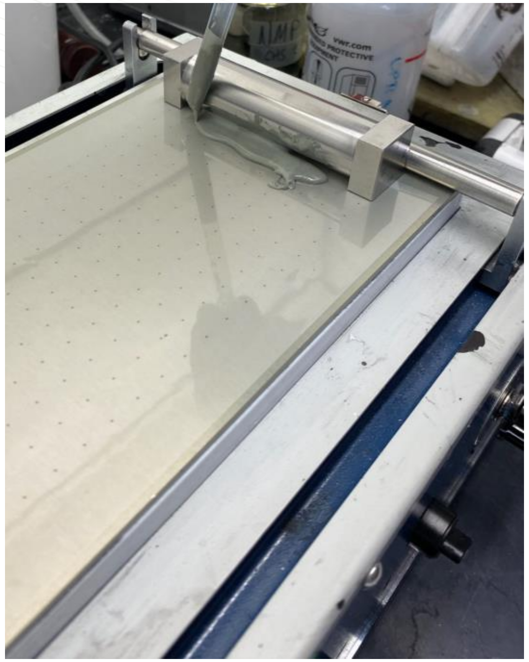
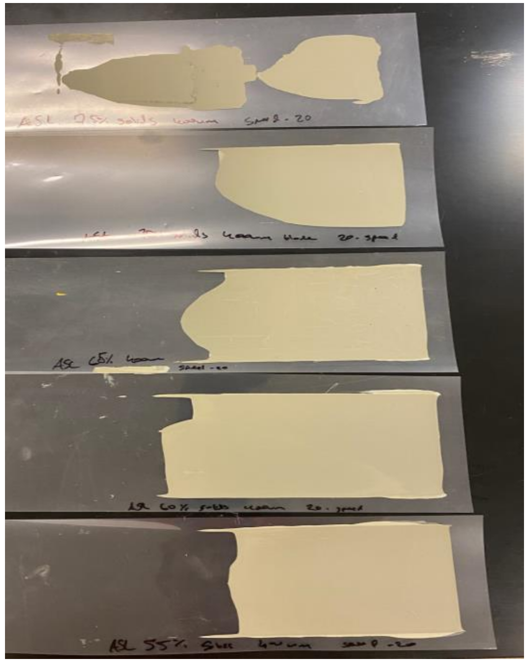
Surface evaluation of doctor's blade cast slurries

Initial coating quality evaluation:

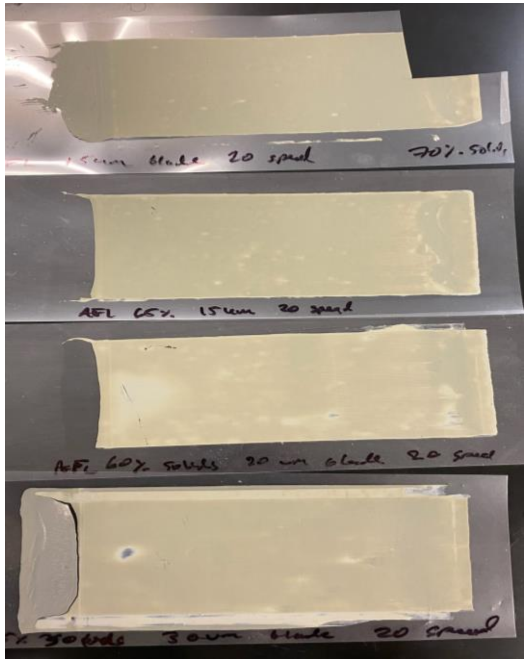
- controlled with similar dry thickness
- Surface morphology characterized by optical microscope



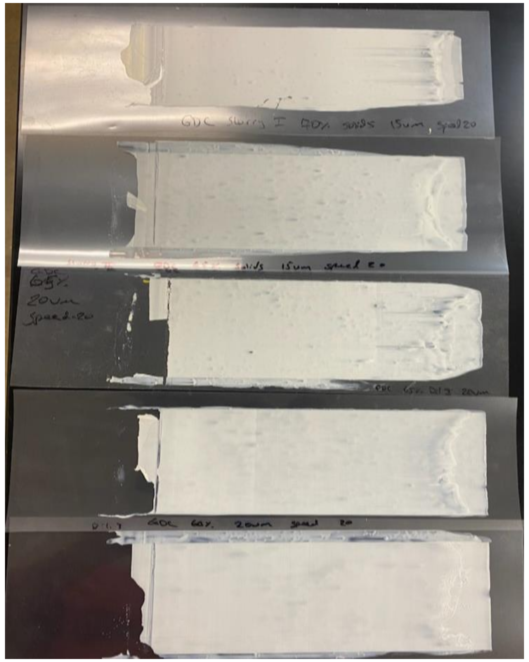
Doctor's blade casting of AFL slurry



ASL:
75% - 400 μm
70% - 400 μm
65% - 400 μm
60% - 400 μm
55% - 400 μm

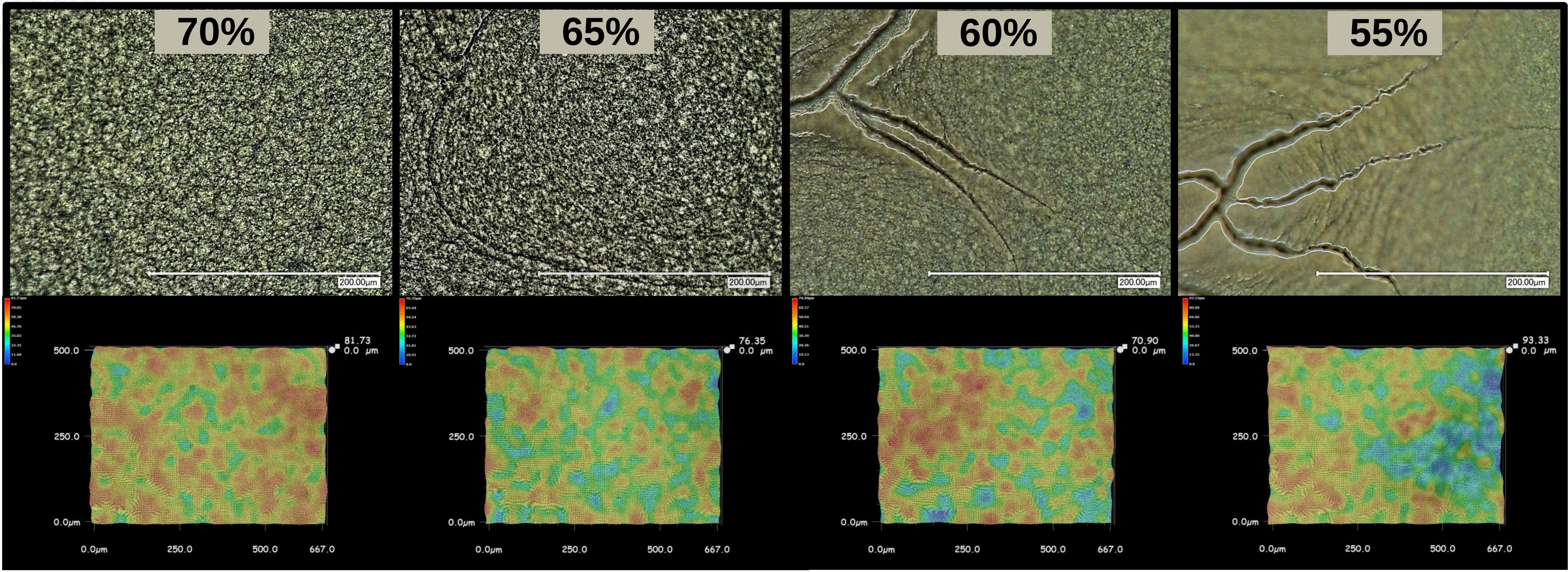


AFL:
70% - 15 μm
65% - 15 μm
60% - 20 μm
55% - 30 μm



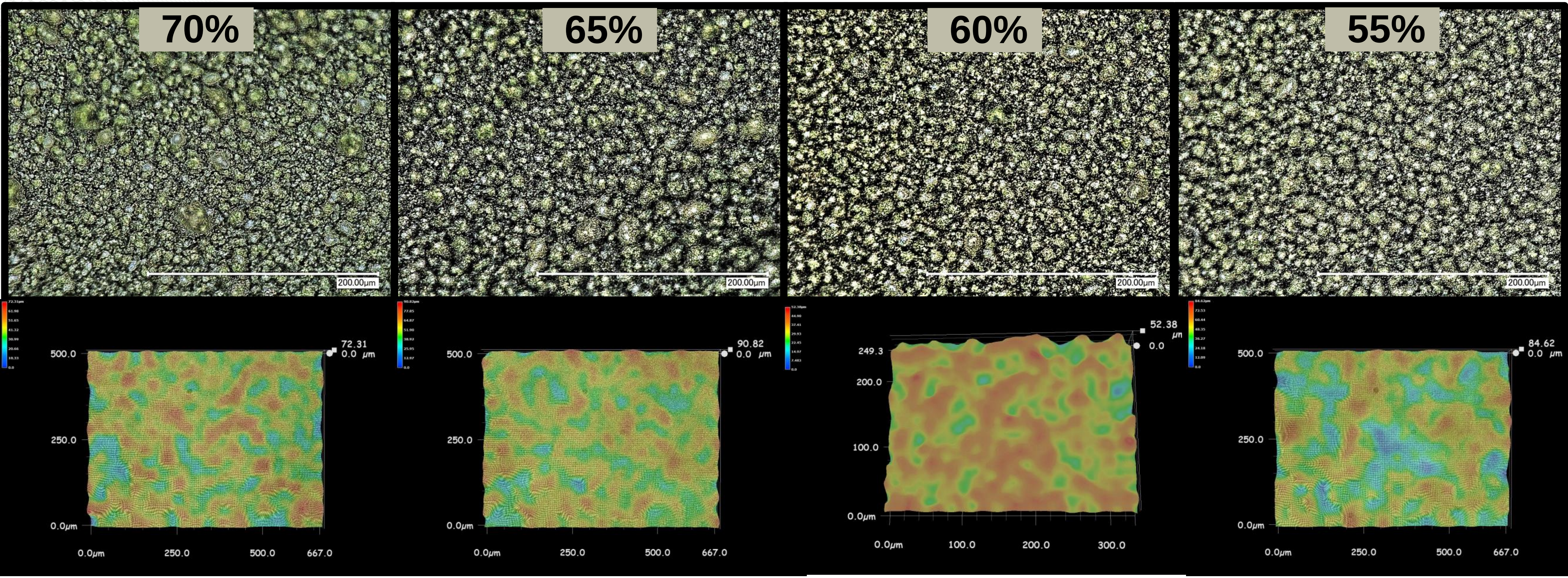
GDC:
70% - 15 μm
65% - 15 μm
65% - 20 μm
60% - 20 μm
55% - 30 μm

ASL Microscopy – Cracks form in dilutions below 70% solids



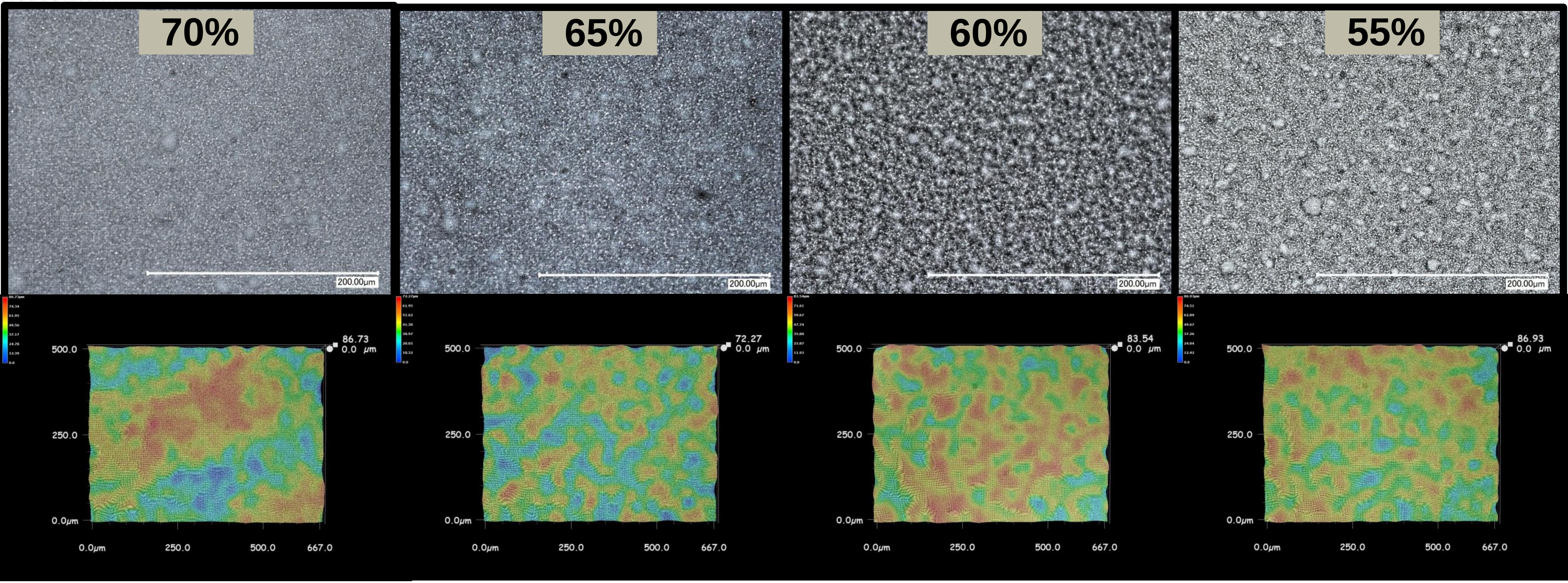
(Top row) the 70% sample lacks surface defects, with all 3 further diluted samples exhibiting surface crack formation. (Bottom row) 3D surface profile shows large continuous cavities indicative of surface cracks. These defects are likely due to the high solvent fraction evaporating and causing the coating to contract.

AFL Microscopy – agglomerate size more homogenous upon dilution



(Top row) Large and small agglomerates form the grain structure for each level of dilution and this distribution tends to become more homogenous upon dilution. (Bottom row) 3D profile of surface roughness, the 60% sample has the most uniform surface structure with a majority of the surface being at the peak heigh level of 52.36 *um*, and containing the fewest surface cavities as well as the smallest delta between the highest and lowest surface points..

GDC Microscopy – Air entrainment defect increases with dilution



The GDC is a very thin layer (on the order of 10’s of um) (Top row) Clear air entrainment is a present defect which significantly worsens upon dilution. The 60% solids sample is the worst as seen by extent of surface roughness from air entrainment. (Bottom row) Significant surface roughness is seen in the 3D analysis and air entrainment is visible in each sample. Degassing will be more critical for dilute slurry..

Summary

- Fabricated ASL, AFL and GDC via roll-to-roll slot-die coating at > 5 m/min.
- Evaluated theological properties of ASL, AFL and GDC slurries with various solid contents

Future Plan

- Predict coating window of various slurries
- Coat ASL, AFL and GDC via slot-die in roll-to-roll operation
- Laminate the slot-die coated single or muti-layers
- Sinter the multilayer and compare the properties with those from traditional batch process
- Assemble SOFC cells and evaluate electrochemical performance

Acknowledgements

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- ORNL Team
- Redox Power Systems Team

Thank You

Any Questions?