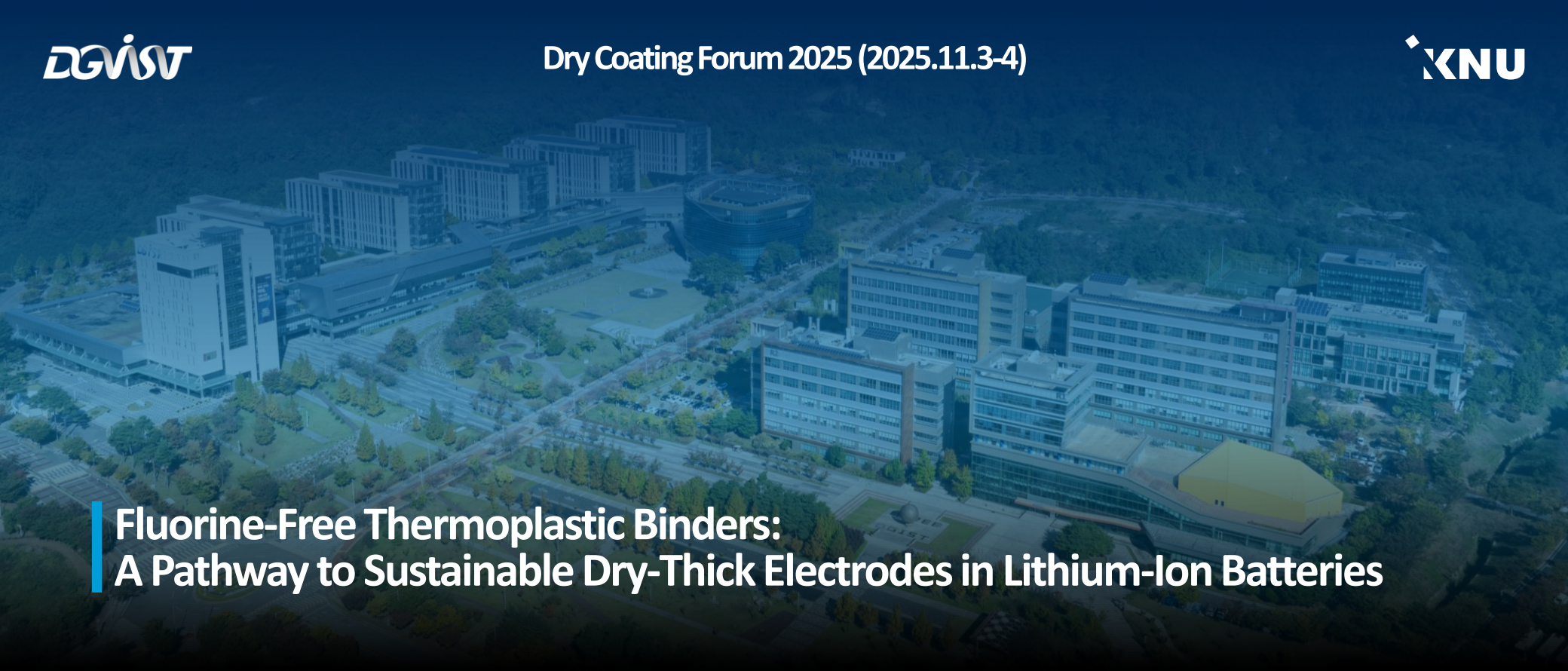




## Fluorine-Free Thermoplastic Binders: A Pathway to Sustainable Dry-Thick Electrodes in Lithium-Ion Batteries

Jinsoo Kim (DGIST, [jinsoo.kim@dgist.ac.kr](mailto:jinsoo.kim@dgist.ac.kr))

Sunghun Choi (Kangwon Nati'l Univ., [s.h.choi@kangwon.ac.kr](mailto:s.h.choi@kangwon.ac.kr))

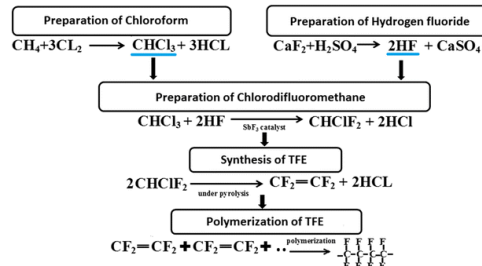


# PTFE Dilutes Environmental Benefits of DBE

## PTFE is magical, but it is not perfect dry electrode binder

rooted from energy intensive and emissive production process

### PTFE: energy intensive & emissive production

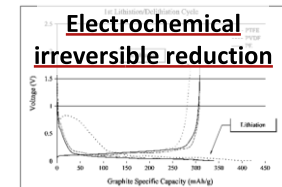


### PFASs restriction in brief

- If releases are not minimised, adverse effects are inevitable
- Broad group restriction proposal
- (Time-limited) derogations for certain uses
  - Industry: Effort needed to switch to alternatives
  - Environment: Emission reduction of 95 %
- If no action is taken societal costs will exceed costs associated with a restriction

➔ Stakeholders invited to provide input during consultation

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- Fluorine-rich chemicals → PFAS restriction (battery binder/electrolyte is still being discussed)
- Non-sticky (used in cooking pans) → adhesive primer coating by wet process (contradictory)
- Hydrophobic → wettability issue to LE (especially to the higher loading, density, large-area)
- Electrochemically reduced at lower potential (vs. Li/Li<sup>+</sup>) → anode might be problematic
- Weak mechanical strength of F/S electrode → Tension problem for R2R manufacturing
- [143.7 kg<sup>CO2</sup> / kg<sup>PTFE</sup>] vs. [8.5 kg<sup>CO2</sup> / kg<sup>PVDF</sup>] & [3.5 kg<sup>CO2</sup> / kg<sup>SBR</sup>]

# Endeavor toward Alternatives to Derisk PFAS in DBE

**Still, there is an unexplored chemical space of DBE binder without fluorine containment**

it is closer than our imagination

1.

*Paraffin & polyethylene*


$$\left( \begin{array}{cc} \text{H} & \text{H} \\ | & | \\ -\text{C} & -\text{C}- \\ | & | \\ \text{H} & \text{H} \end{array} \right)_n$$

2.

*Styrene butadiene rubber (SBR)*


$$\left[ \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right]_n \left[ \text{CH}_2 - \text{HC} \left( \text{C}_6\text{H}_5 \right) \right]_m$$

*and still many more thermoplastics*



- DBE is simple, and simple is best: utilization of universal plastic materials can make bigger impact
- There are tons of fluorine-free thermoplastics that are cheaper and immediately ready-to-use
- Alternative thermoplastics can have different processing concept vs. PTFE-based manufacturing

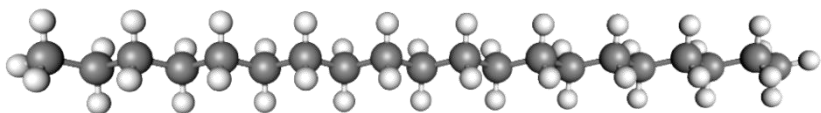
# Fluorine-Free Parafilm<sup>®</sup> M-Based DBE Binder

J. Kim<sup>\*</sup> et al. *Nat. Commun.* accepted (2025), J. Kim et al. PCT/KR patents filed (2024)

# Alternative Dry Electrode Binder and Processing Concept

**Thermoplastic paraffin based dry electrode manufacturing**  
for simpler material and processing concept

## Paraffin



## Source of this research: Parafilm®M



### Parafilm® M All-Purpose Laboratory Film Specs

- Permeability
- Oxygen: (ASTM 1927-98) 150 cc/m<sup>2</sup> d at 23°C and 50% RH
  - Carbon Dioxide: (Modulated IR Method) 1200 cc/m<sup>2</sup> d at 23°C and 0% RH
  - Water Vapor: (ASTM F1249-01)
    - Flat: 1 g/m<sup>2</sup> d at 38°C and 90% RH
    - Creased: 1 g/m<sup>2</sup> d at 38°C and 90% RH

### Effects of Common Reagents

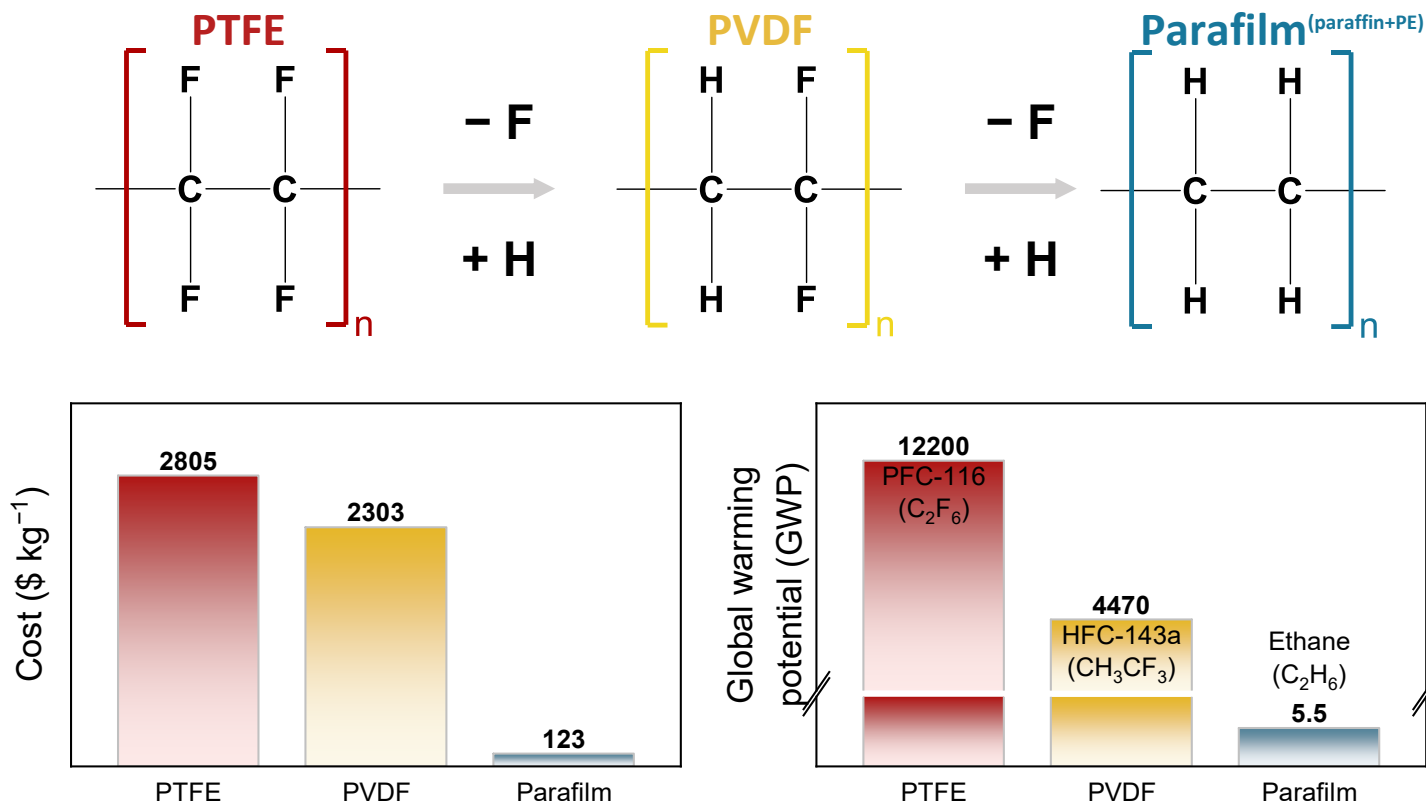
- Potassium Permanganate
  - 5%: No apparent effect except permanent dark brown coloration in 18 hours
  - 0.1%: Same as 5% except slightly less color
- Iodine solution (0.1N)
  - No effect except staining brown in 18 hours
- Ethyl Alcohol (95%)
  - No apparent effect except some face whitening in 24 hours
- No apparent effect in 24 hours:
  - Hydrochloric Acid conc. (12N) dil. (5n)
  - Sulphuric Acid conc. (36n) dil. (5n)
  - Nitric Acid conc. (16n) dil. (5n)
  - Sodium Hydroxide conc. (22%)
  - Ammonium Hydroxide conc. (28% NH<sub>3</sub>)
  - Salt (NaCl) solution (20%)
  - Isopropyl Alcohol (99%)
- Not recommended for use with chlorinated, non-polar aliphatic and aromatic solvents
- Film becomes soft and sticky at about 130°F to 150°F (68°C)

- Fluorine-free chemicals → sustainable and low cost (~1/30 vs. PTFE)
- Sticky without adhesive primer coating on current collectors
- Electrochemically stable at low & high potential (vs. Li/Li<sup>+</sup>) → cathode/anode compatible
- Chemically stable (saturated hydrocarbon) → no side reactions
- Direct powder calendering → no tension issue for R2R

# Representative Wet & Dry Electrode Binder Chemistries

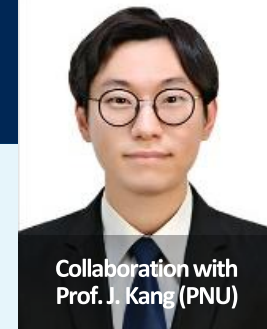
## Structurally identical but differentiated impact

linear carbon chain of polymer terminated fluorine or proton



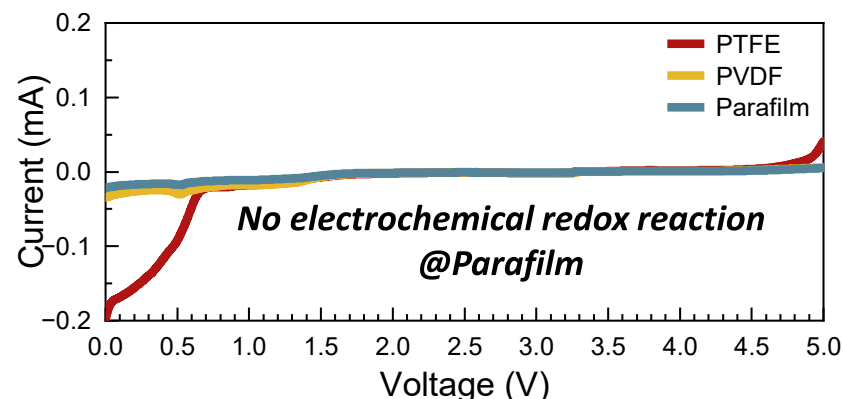
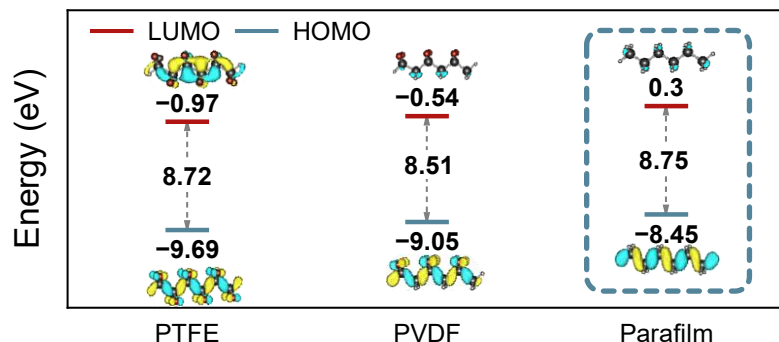
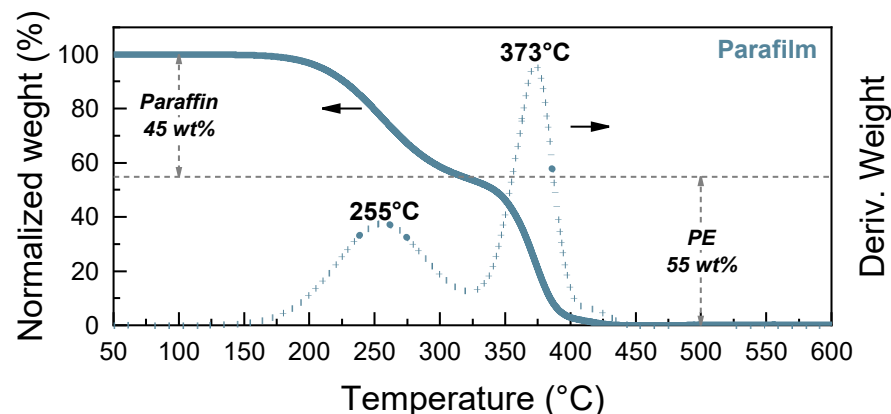
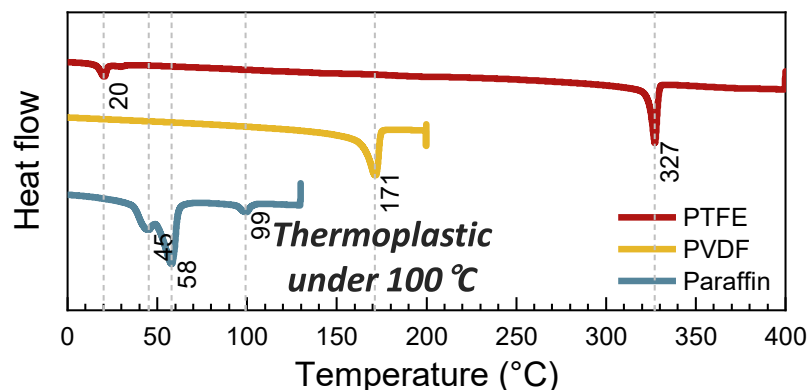
- Parafilm has low cost & global warming potential (relative to PTFE) → zero risk of PFAS

# Thermal and Electrochemical Characteristics



## Thermoplastic for low temperature & pressure processing

beneficial to sustainable electrode manufacturing

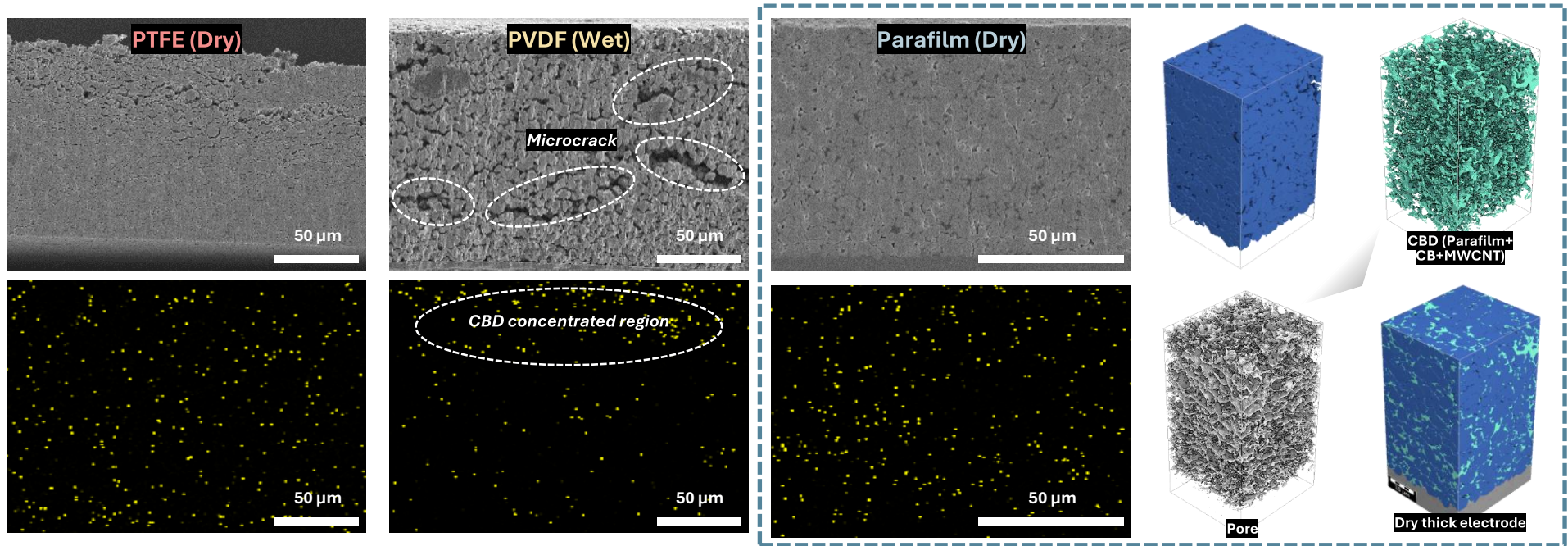


- Low  $T_g \rightarrow$  Feasible phase transition of Parafilm  $\rightarrow$  Potentially low  $E$  processing
- Parafilm has widest electrochemical window (high LUMO – low HOMO,  $e^-$  delocalization)

# Microstructure of Wet and Dry Thick Electrodes

## Uniform distribution of CBD through the DBE thickness

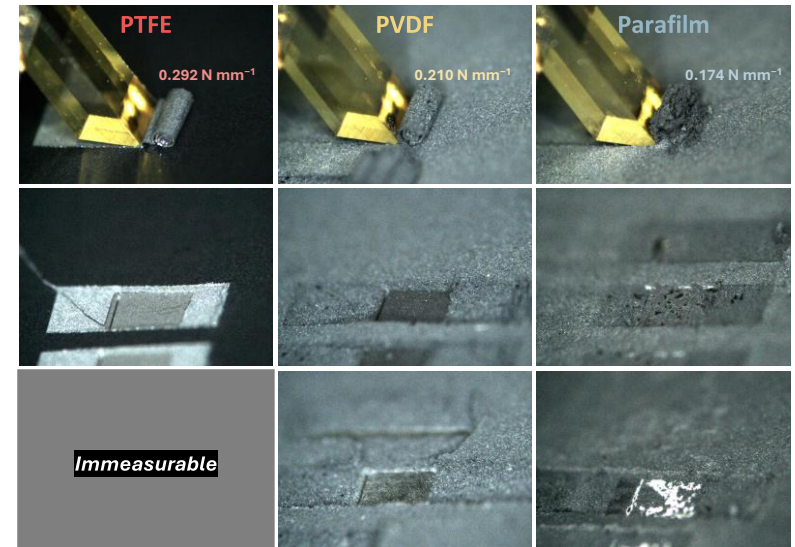
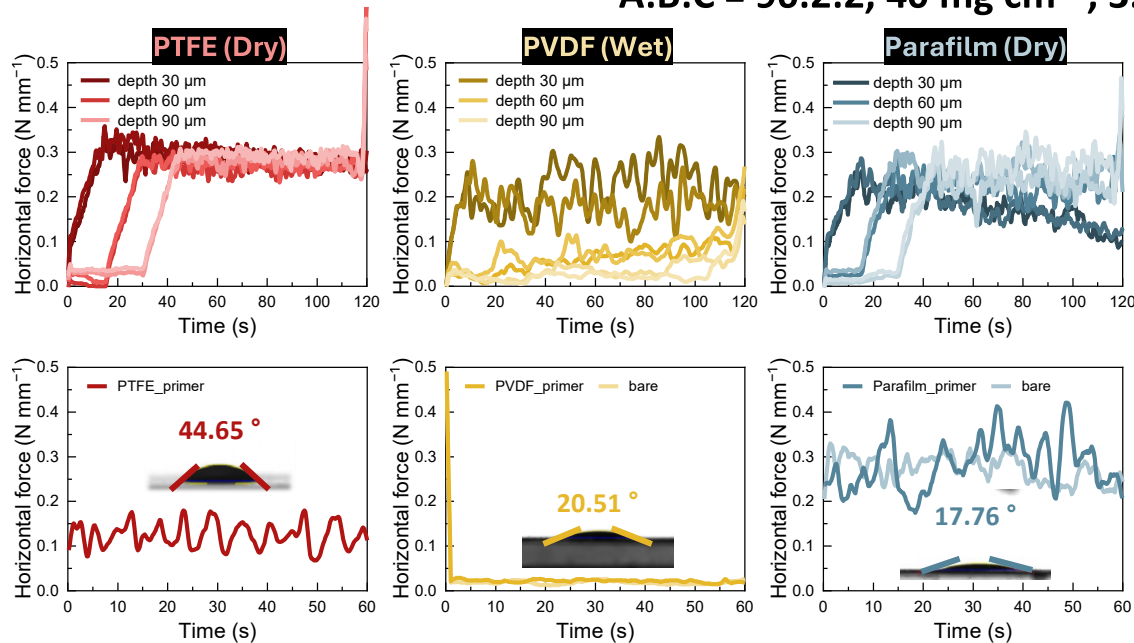
typical wet based thick electrodes has CBD migration problem



- PVDF based wet electrode shows microcrack induced from CBD migration to the surface
- Dry electrodes with PTFE and paraffin have uniformly integrated electrode structure

**Robust, flexible and well-wetted to liquid electrolyte**  
without wet based primer coating

A:B:C = 96:2:2, 40 mg cm<sup>-2</sup>, 3.5~3.7 g cc<sup>-1</sup>

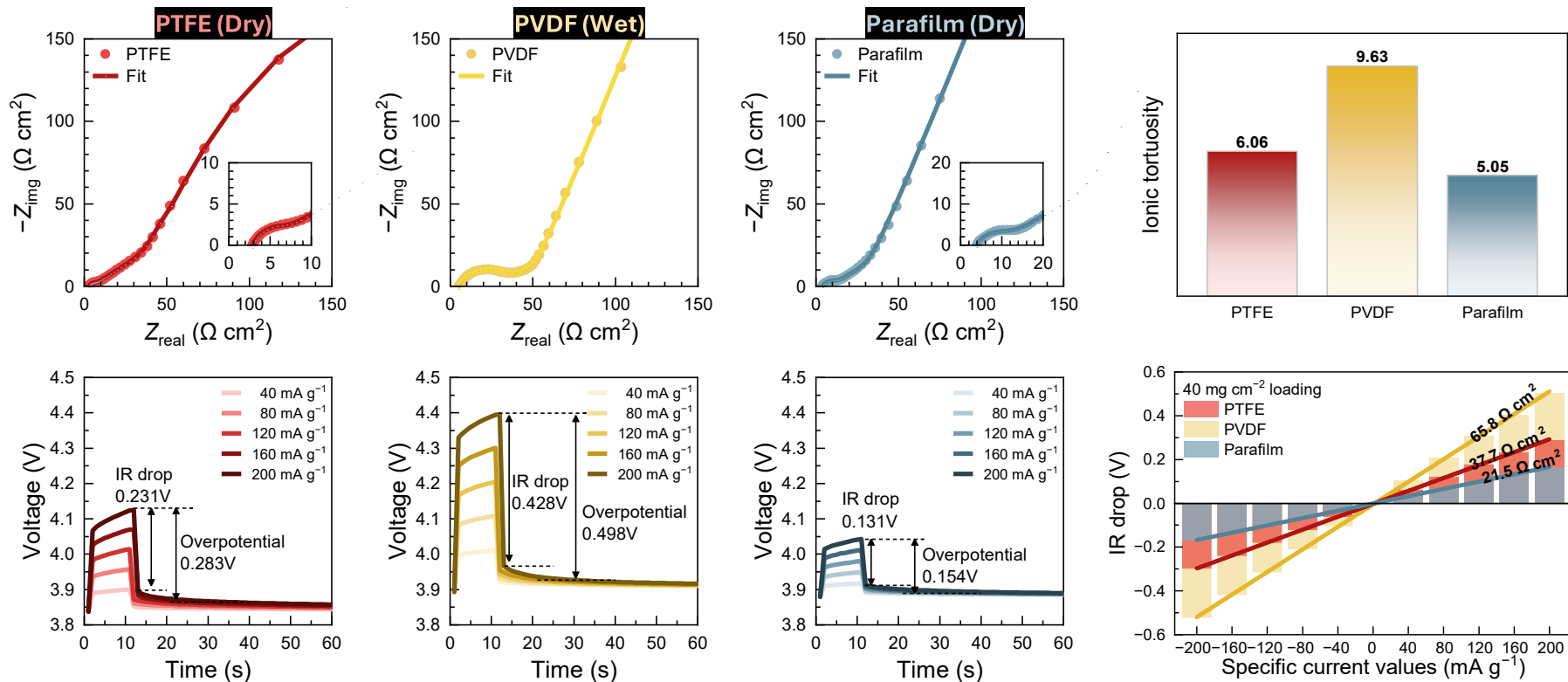


- Parafilm based DBE shows better adhesion/cohesion even without primer coating
- Liquid electrolyte wettability was also better with Parafilm based DBE

# Ionic Transport Kinetics within Thick Electrodes

## Comparable ionic tortuosity and diffusivity

facile Li ion transport within the thick electrode structure

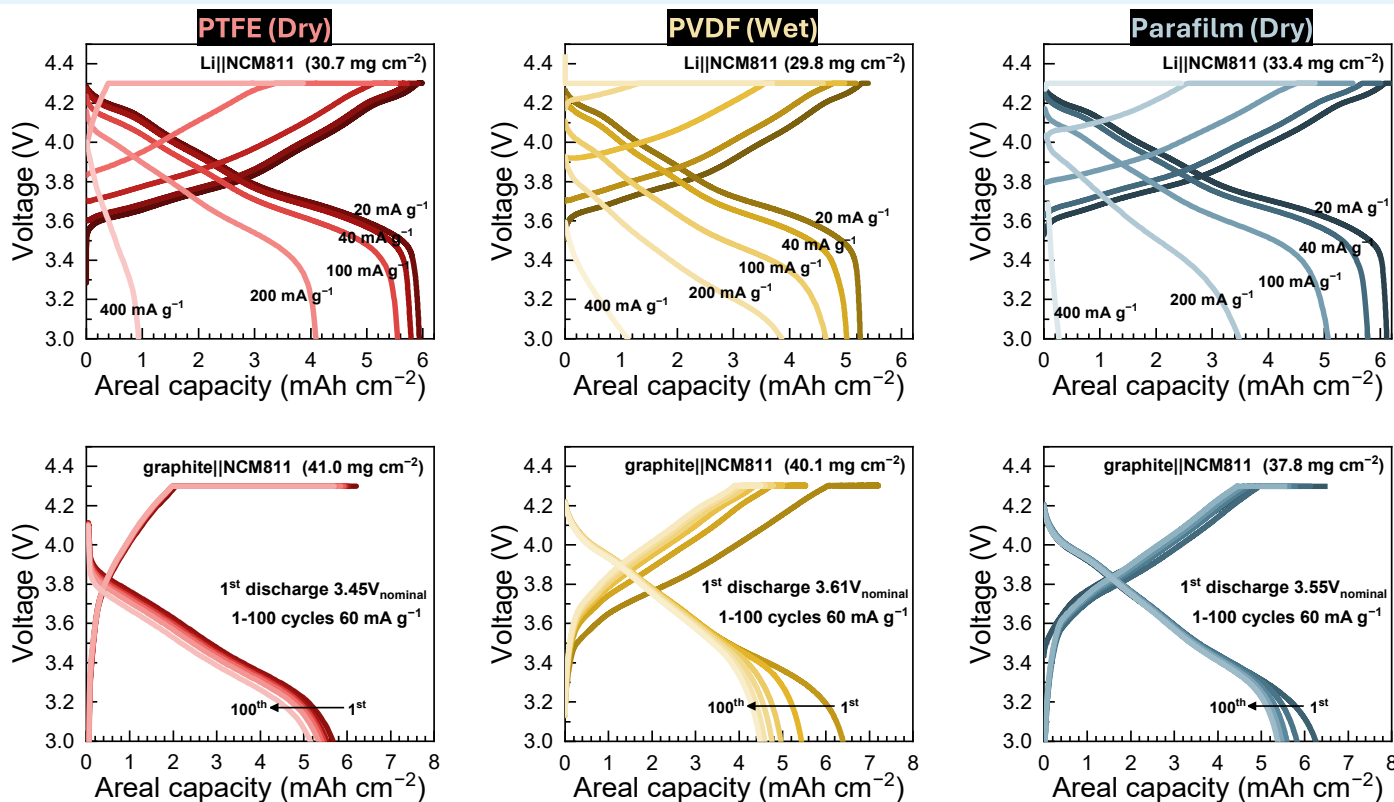


- Paraffin binder is also facile to transport Li ions though the dry thick electrode

# Electrochemical Cycle Characteristics of Thick Electrodes

## Paraffin based dry electrode shows similar performance

facile Li ion and electron transport within the thick electrode structure

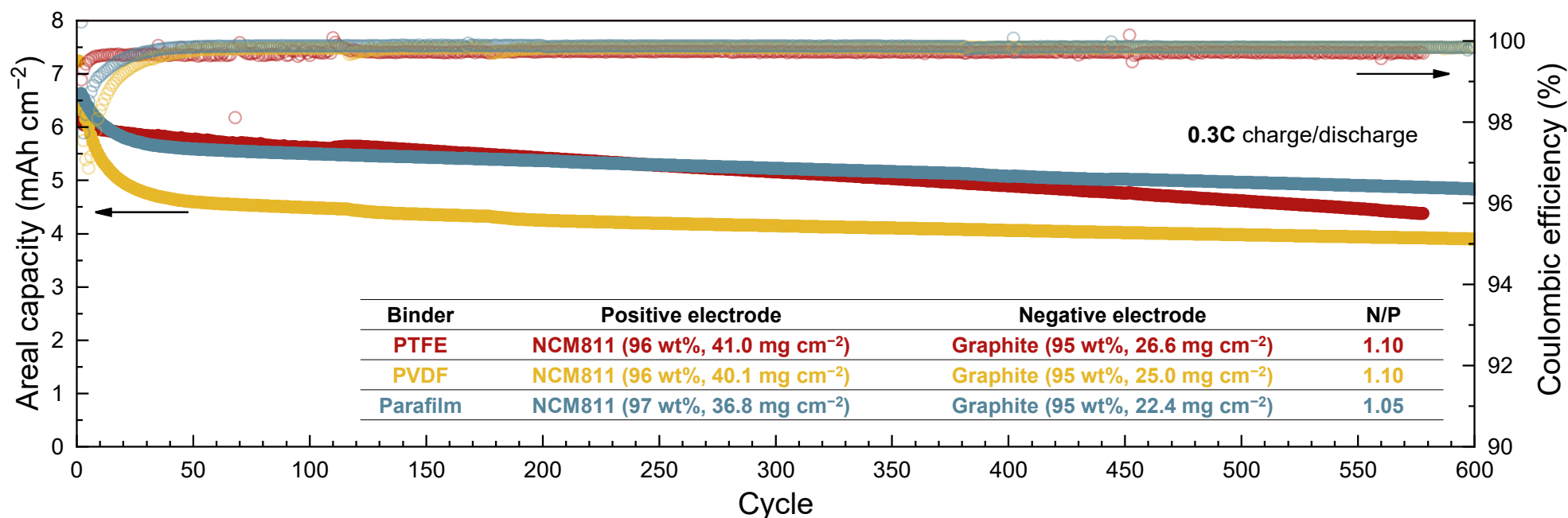


- Full cell: graphite anode (wet) + paraffin based NCM811 SC cathode (dry)
- Paraffin based dry electrode shows superior cycle performance (600 cycle)

# Electrochemical Cycle Characteristics of Thick Electrodes

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facile Li ion and electron transport within the thick electrode structure

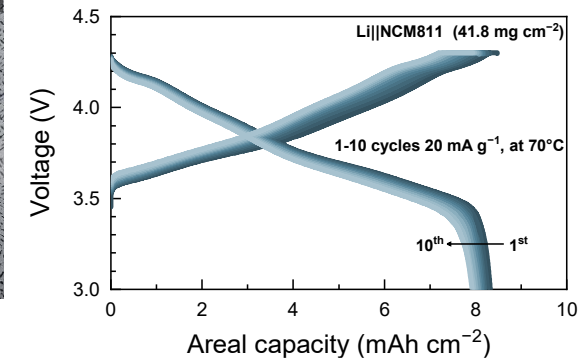
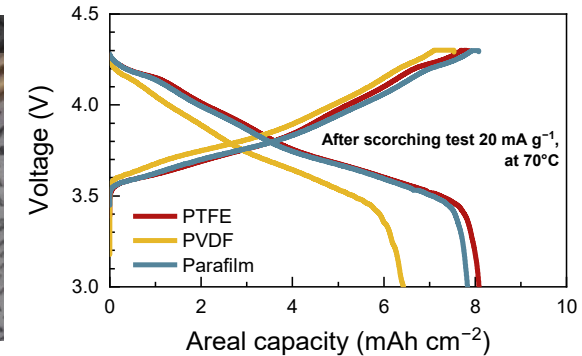
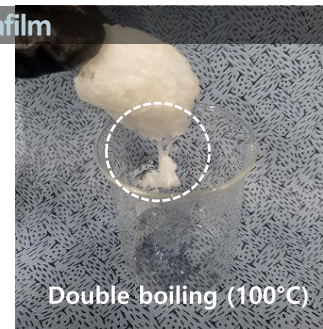
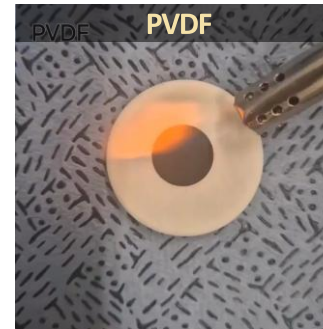
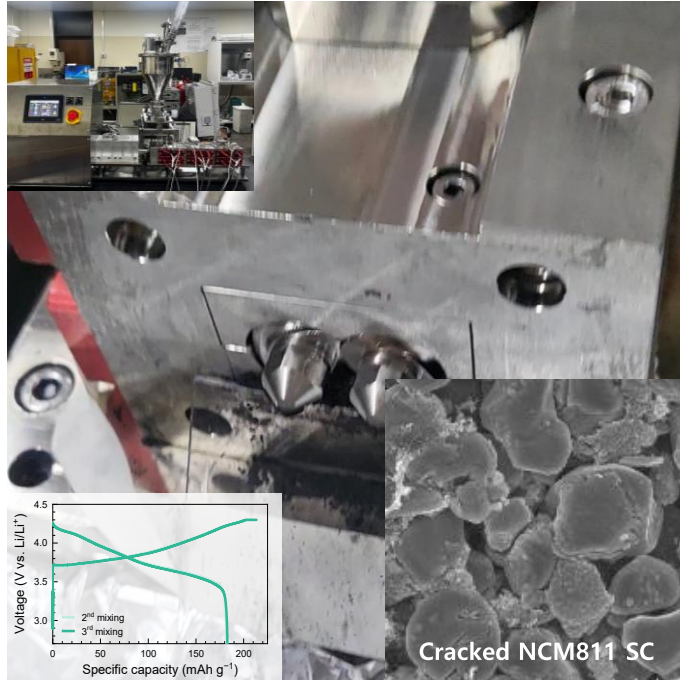


- Full cell: graphite anode (wet) + paraffin based NCM811 SC cathode (dry)
- Paraffin based dry electrode shows superior cycle performance (600 cycle)

# Twin-Screw Dry Mixing and High Temperature Stability

## Favorable large-scale dry mixing without equipment stress

facile output which governs the processing speed



- A:B:C = 96:2:2 (w/w) → Significant cohesion & granulation → NCM811 SC was pulverized
- Cheesy and sticky nature of Parafilm → upto  $70 \sim 100^\circ\text{C}$  (upper threshold of battery system)

## F-Free Pressure-Sensitive Adhesive (PSA) as Dry Process Binder for Graphite Anodes

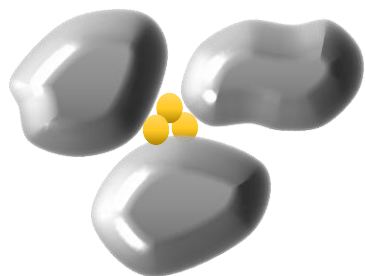
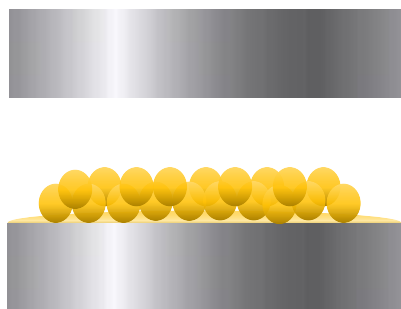
S. Choi<sup>\*</sup> et al. *ACS Energy Lett.* 10 (2025) 2670-2678

## Elastic-based Pressure-Sensitive Adhesives (PSAs)

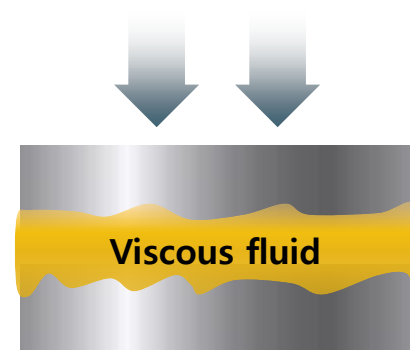
Unique properties that differentiate the PSA binder from other dry-process binders

PSA-SBR

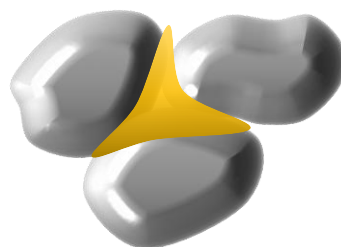
Ambient Pressure



High Pressure



Wetting of the substrate



Ambient Pressure



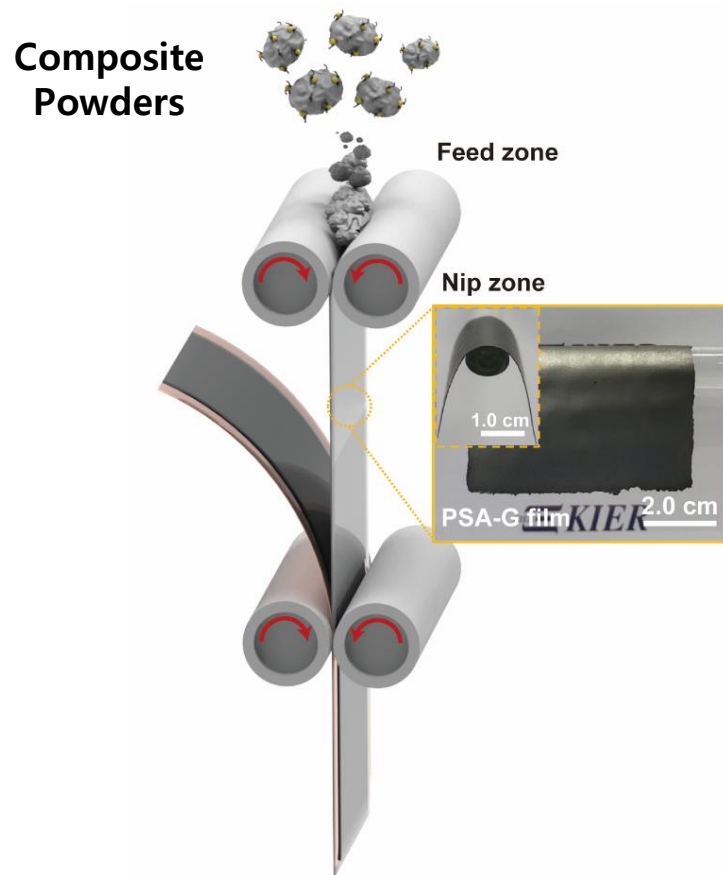
Elastic Bridge



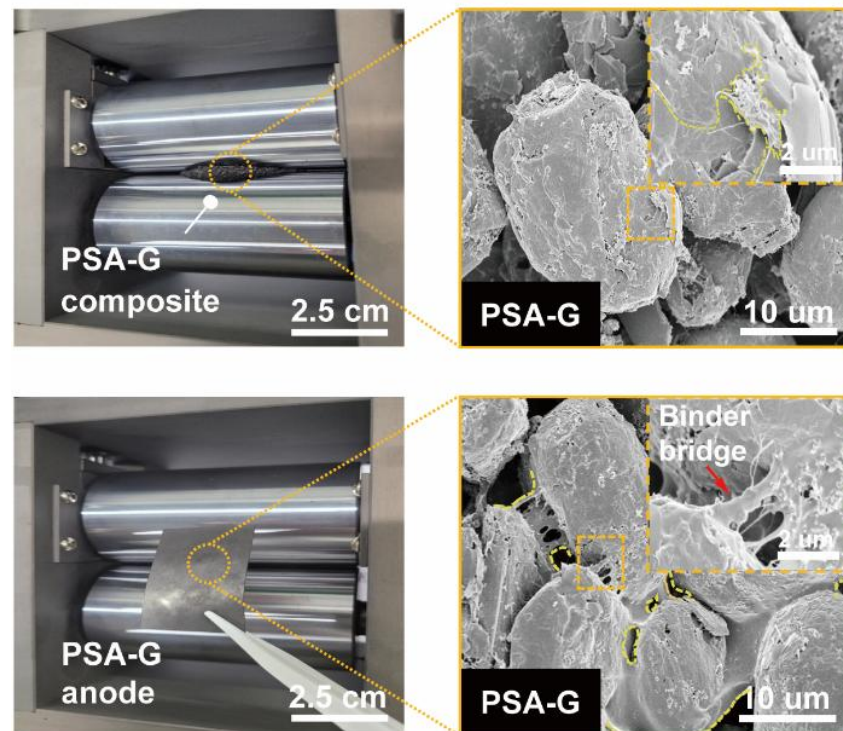
- PSA; Viscoelastic property change under applied pressure
- Normal pressure; Elastic property / High pressure; Sticky & viscous Properties

## Elastic-based Pressure-Sensitive Adhesives (PSAs)

Powder-to-film electrode fabrication enabled by a roll-to-roll electrode manufacturing process



**PSA-G** : Dry-processed electrode by using PSA-SBR

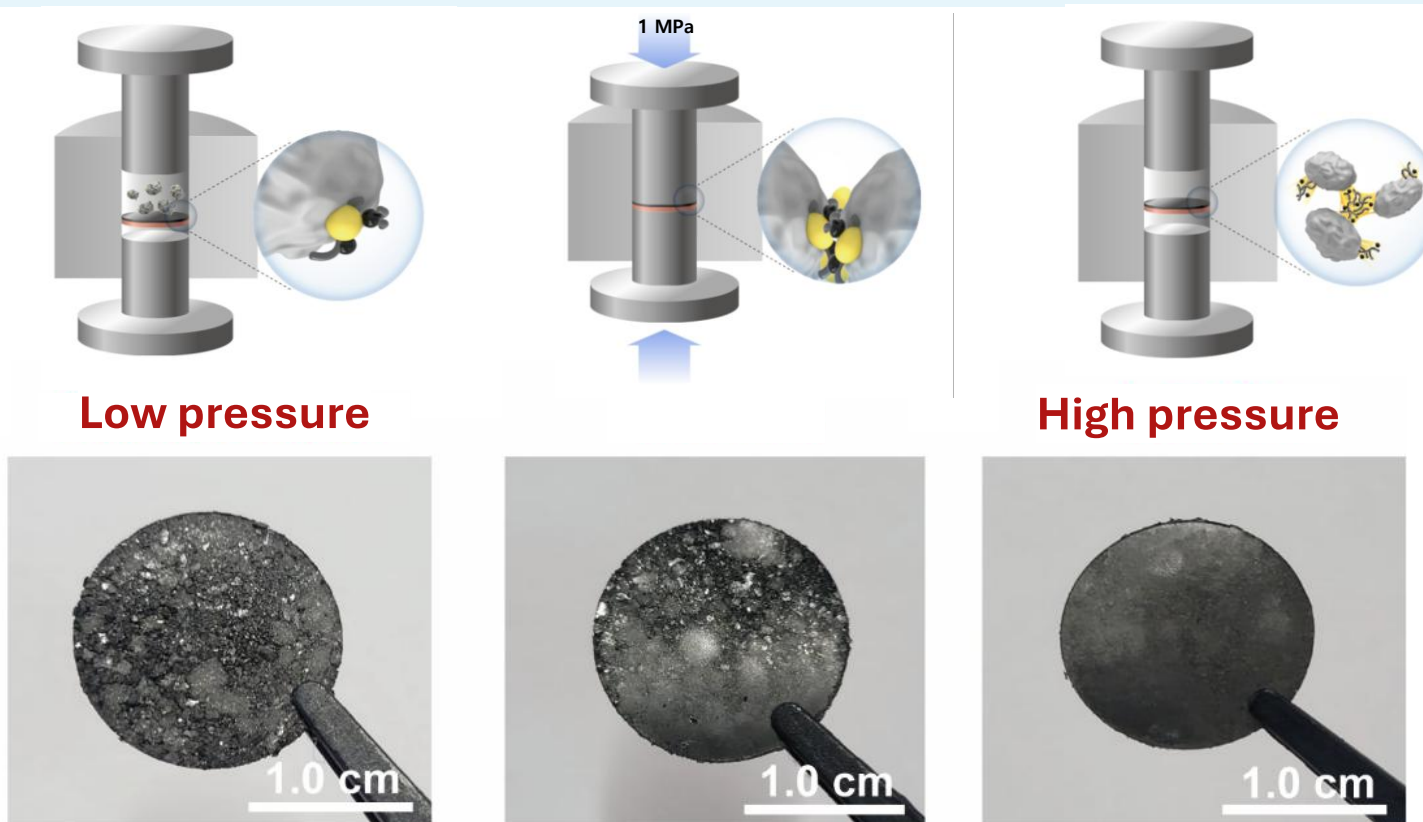


Graphite : Conductive Agents : PSA-SBR = 95:1:4

- Elastic binder bridging network between particles enables a flexible freestanding film

## Elastic-based Pressure-Sensitive Adhesives (PSAs)

Critical pressure required PSA-binder activation



- Low Pressure; PSA not activated → Composite powder morphology partially remained
- High Pressure; PSA fully activated → Smooth & dense electrode layer Formed

## Powder-to-Film Manufacturing Process (25 °C)

Actual fabrication procedure at lab scale



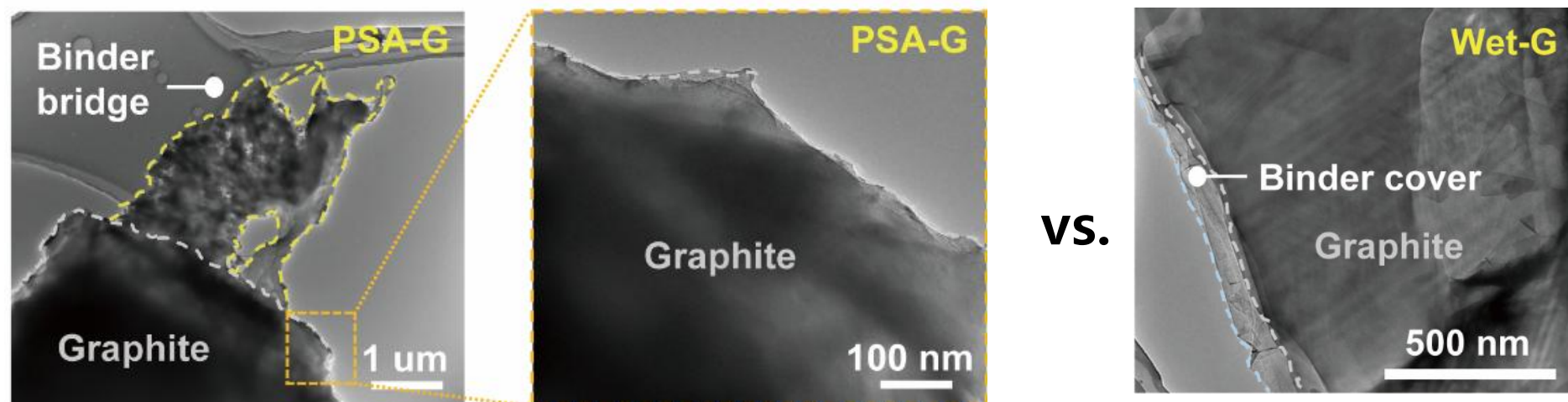
- Evenly distributed PSA composite powders in the gap between rollers
- Roller rotation → Line pressure applied → PSA activation → Freestanding electrode film

# Binder Morphology

## 'Open-channel Interface' vs. 'Closed-channel Interface'

Binder morphology differences depending on the electrode fabrication process

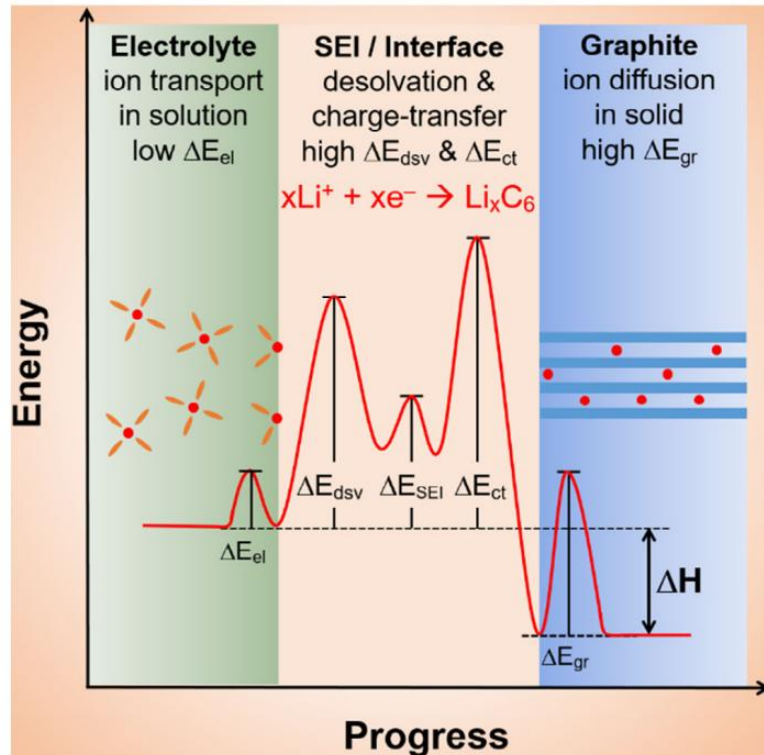
**Wet-G** : Wet-processed electrode by using commercial SBR/CMC



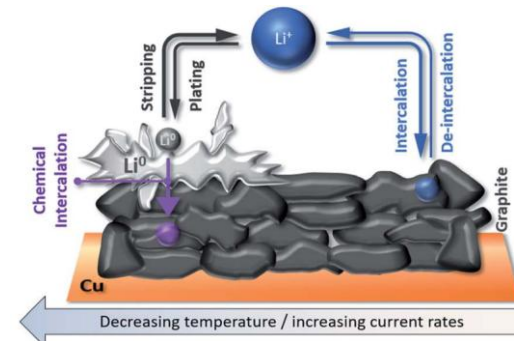
- **Binder**; Intrinsically an ionically and electronically insulating polymer
- **Wet-G (Closed-channel interface)**
  - : **Uniformly covered by binder against graphite particles (surface-to-surface adhesion)**
- **PSA-G (Open-channel interface)**
  - : **Locally covered by binder on the graphite surface (point-to-point adhesion)**

## 'Open-channel Interface' vs. 'Closed-channel Interface'

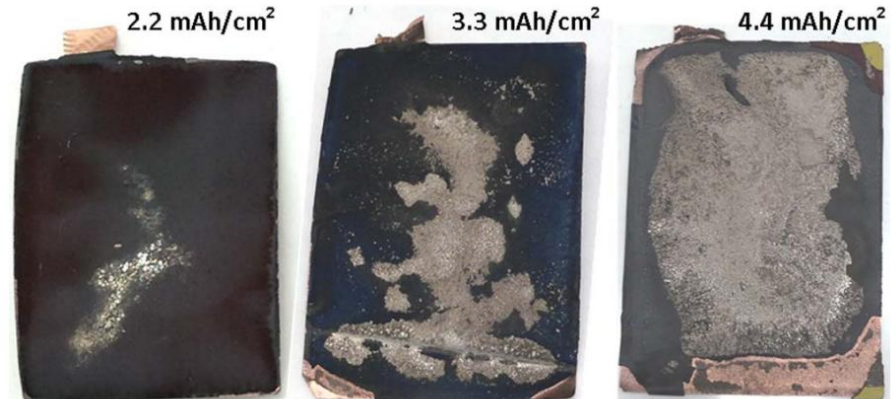
Importance of interfacial resistance in graphite anodes



*InfoMat*, 2021, 3, 125-130



*Sustain. Energy Fuels*, 2020, 4, 5387-5416



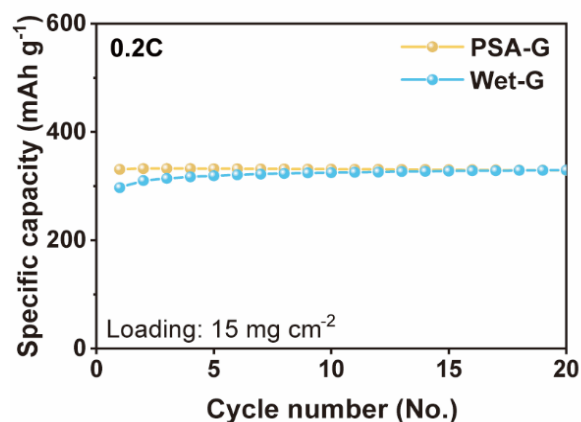
- SEI/Interface; Major contributor to total cell resistance
- Electrode thickening → Increasing interfacial resistance → Li metal plating

# Electrochemical Performance

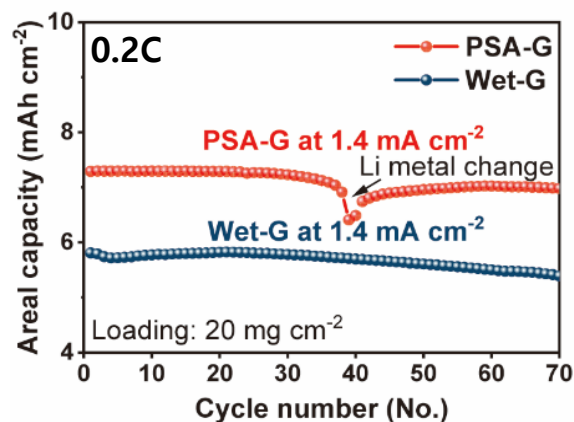
## Electrochemical Test with Varying Areal Loading

Elucidation of the correlation between binder morphology and cell performance

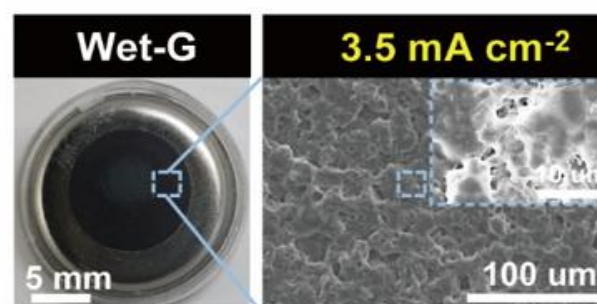
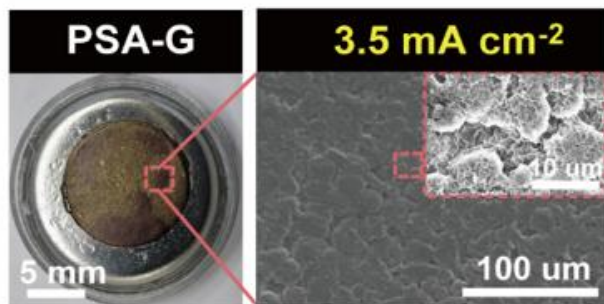
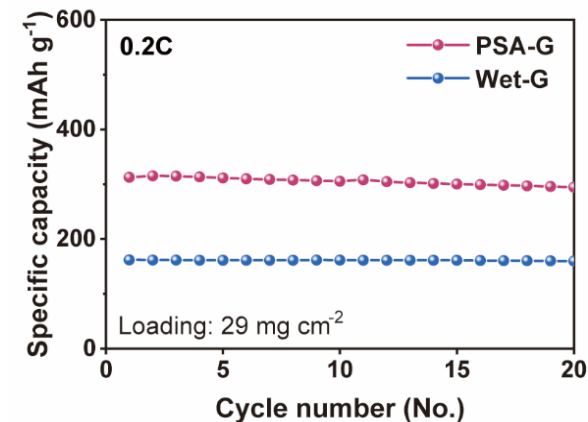
### ► Areal capacity of $\sim 5 \text{ mAh cm}^{-2}$



### ► Areal capacity of $\sim 7 \text{ mAh cm}^{-2}$



### ► Areal capacity of $\sim 10 \text{ mAh cm}^{-2}$



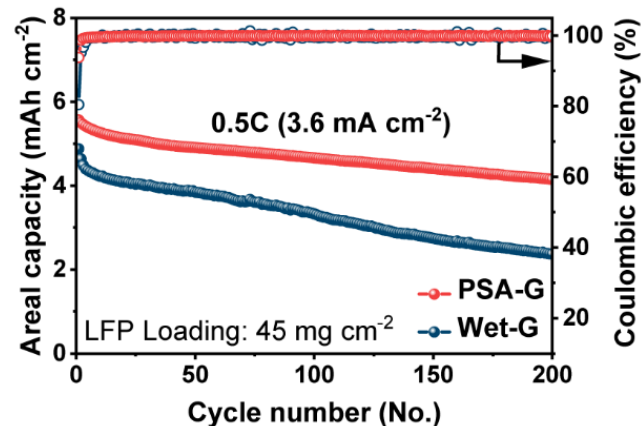
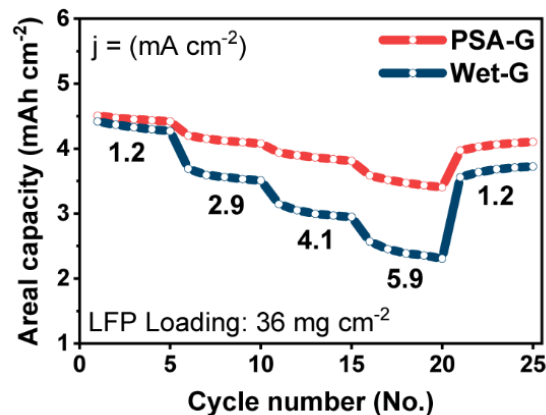
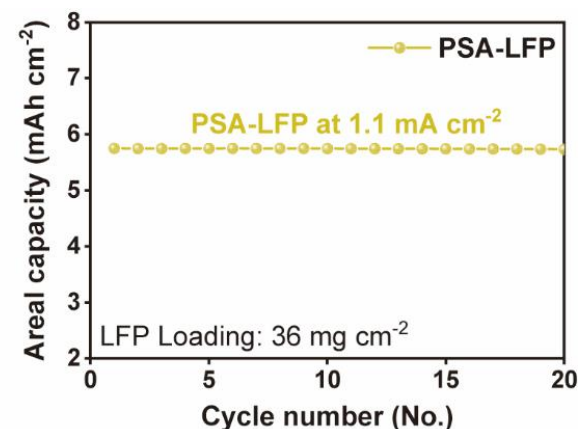
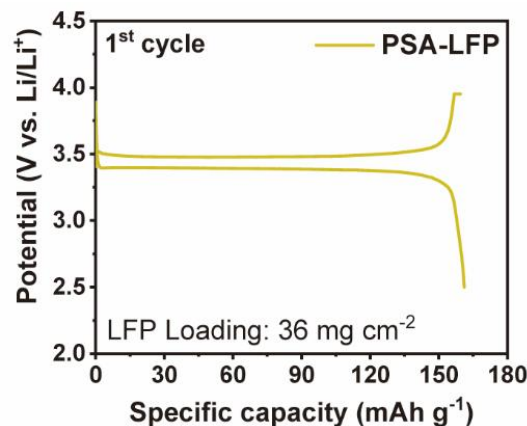
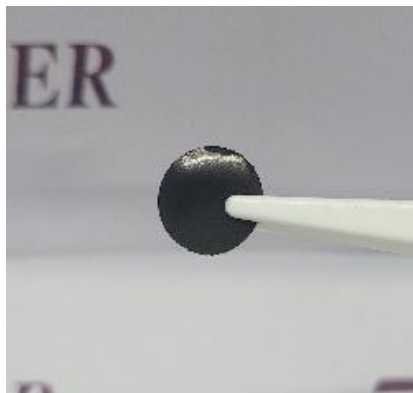
- PSA-G with low interfacial resistance

→ Maintains capacity at high areal loading & suppresses Li metal plating

# Electrochemical Performance

## Full-Cell Test

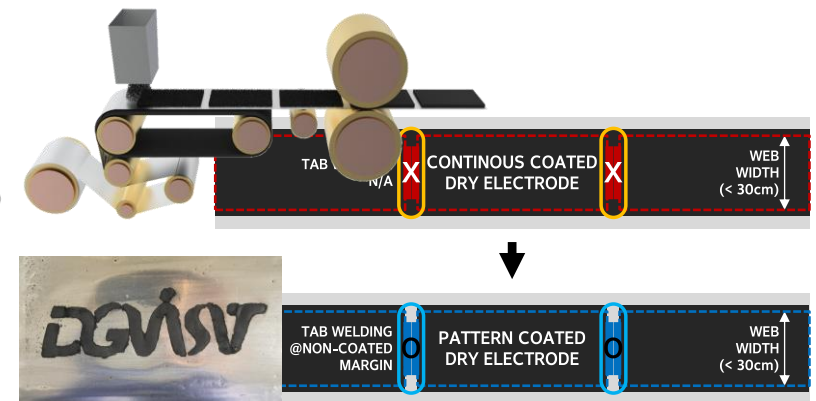
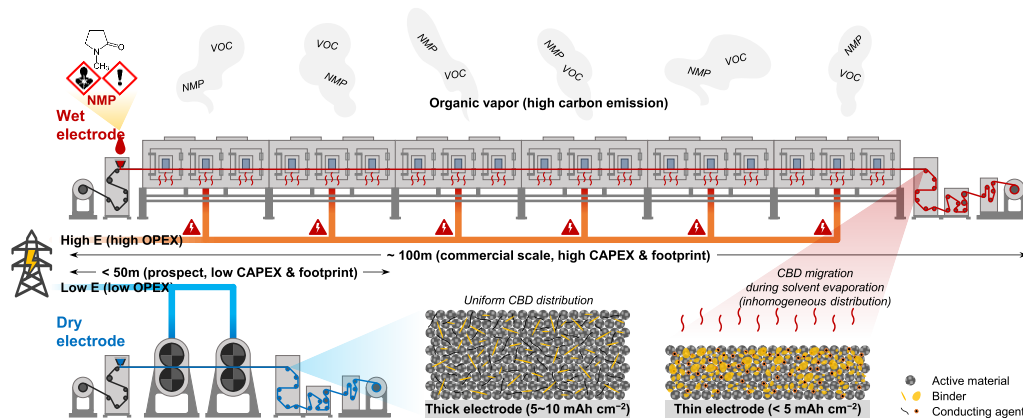
PSA-binder-enabled thick-electrode full cells



- PSA-LFP; PSA binder-based dry processed LFP cathode
- Full-Cell; Graphite anode (dry-PSA) + LFP cathode (dry-PSA)

## Concluding Remarks

- PTFE is not only a binder suitable for the DBE process
- Universal thermoplastics can have a chance to be implemented in DBE
- **Parafilm** and **PSA SBR** were feasible to be applied in an alternative DBE
- Alternative binders also need an alternative processing concept
- Those proof-of-concept should be scaled up through engineering optimizations
- DBE materials development must be coupled with process development



**Thanks for your attention**