Formulation Strategies for the Large-Scale Manufacturing of Crack-Free Electrodes

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HFTO Postdoctoral Recognition Awards – May 11th, 2022.

U.S. DEPARTMENT OF
ENERGY

Acknowledgements

NREL

- Bertrand Tremolet de Villers
- James Young
- Jason Pfeilsticker
- KC Neyerlin
- Tim Van Cleve

ANL

- Debbie Myers
- Firat Cetinbas
- Jaehyung Park
- Nancy Kariuki

ORNL

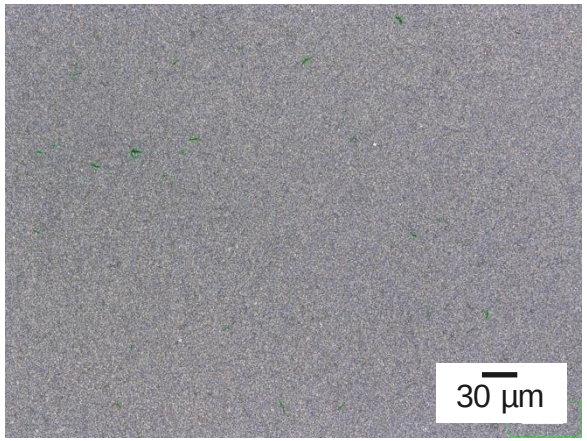
- David Cullen
- Haoran Yu
- Kimberly Reeves

Cathode Catalyst Layers in PEMFCs: Scalability Challenges

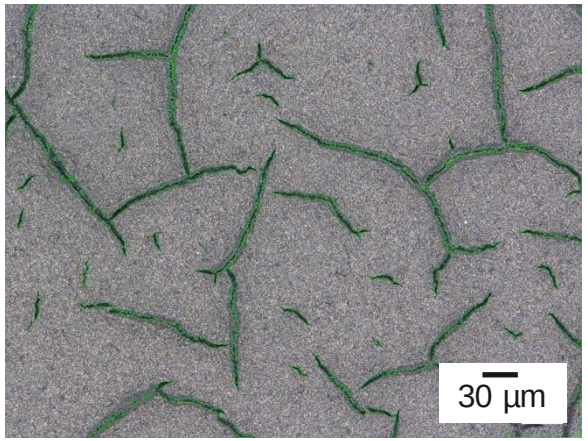
Scalability Challenges

Light-Duty

Heavy-Duty



0.1 mg Pt/cm^2



0.3 mg Pt/cm^2

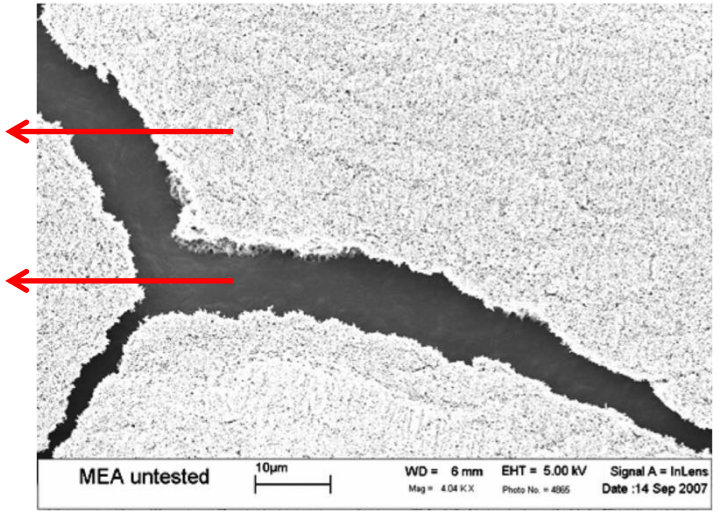
If cracking is detrimental for fuel cell durability, why not mitigate it?

Catalyst Layer

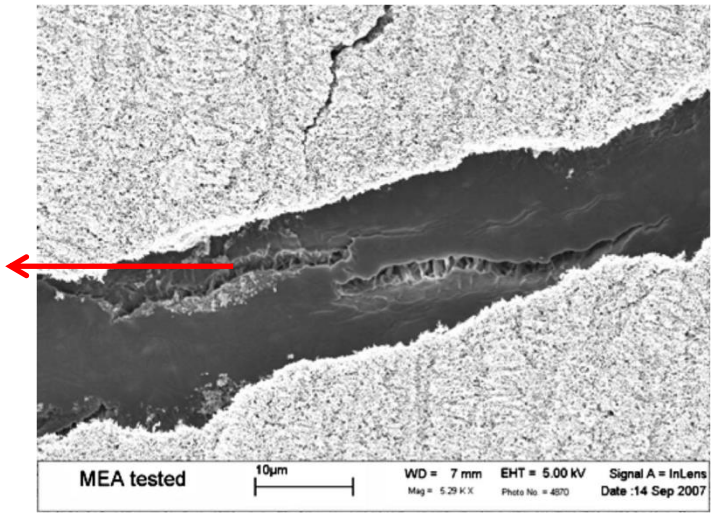
Membrane

Pre-existing electrode cracks
↓
Membrane cracking
↓
Leakage
↓
Shorter fuel cell lifespan

Untested MEA



Tested MEA – 7 min cycling



Pestrak et al. J Fuel Cell Sci. Technol. 2010, (7)
https://global.toyota/en https://wha-international.com/

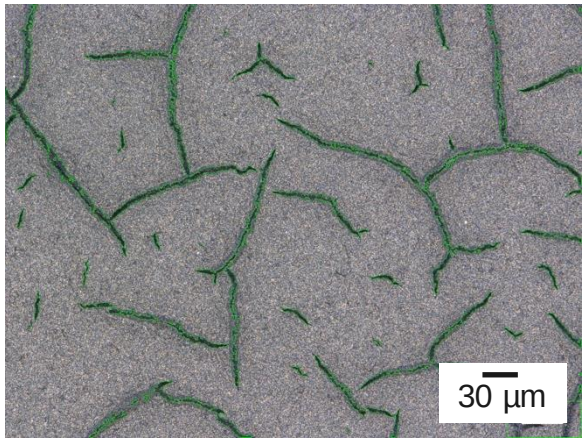
Cathode Catalyst Layers in PEMFCs: Scalability Challenges

Scalability Challenges

Roll-to-roll (R2R) manufacturing

Scalable manufacturing strategies (rod coating, R2R) may contain defects in the electrode

Heavy-Duty



0.3 mg Pt/cm^2

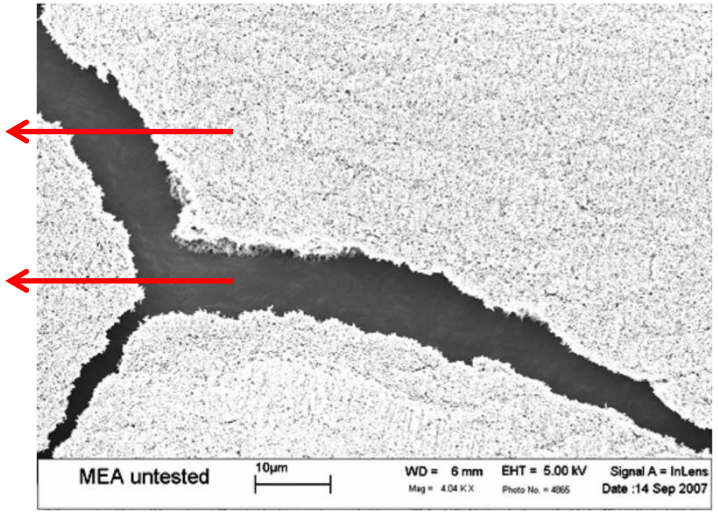
It is critical to understand how to mitigate electrode cracking in the manufacturing stage

Catalyst Layer

Membrane

Pre-existing electrode cracks
↓
Membrane cracking
↓
Leakage
↓
Shorter fuel cell lifespan

Untested MEA



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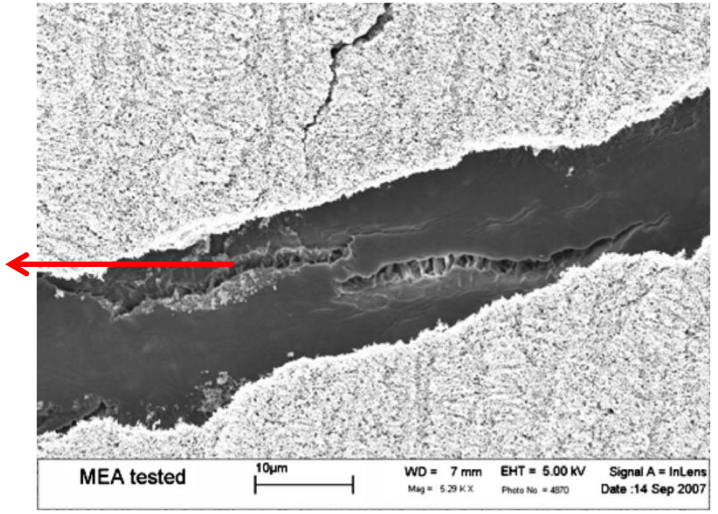

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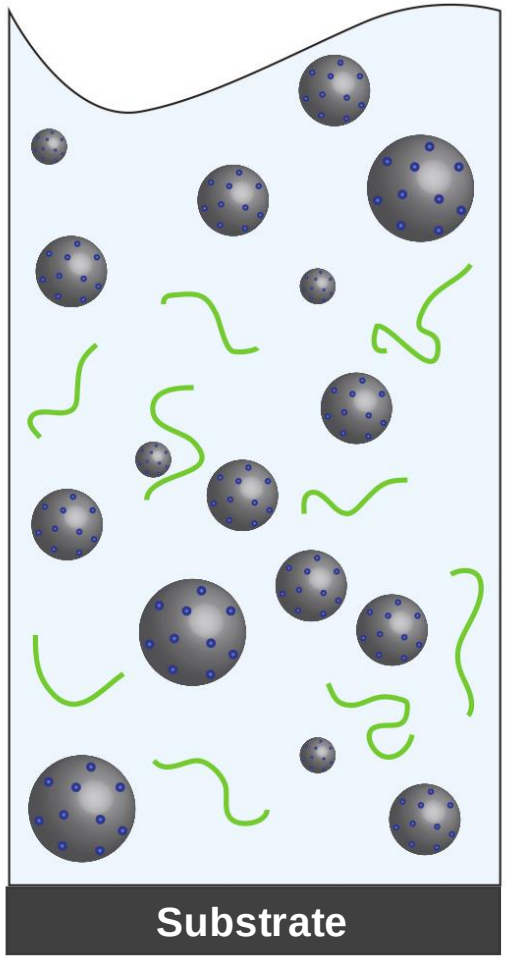
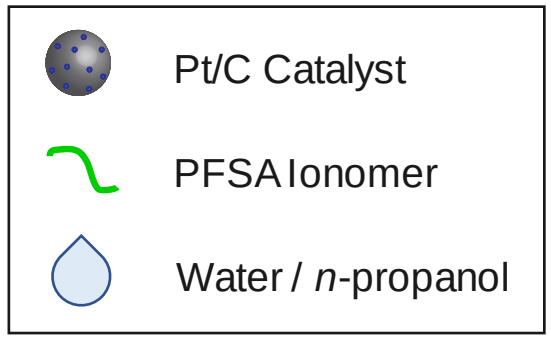
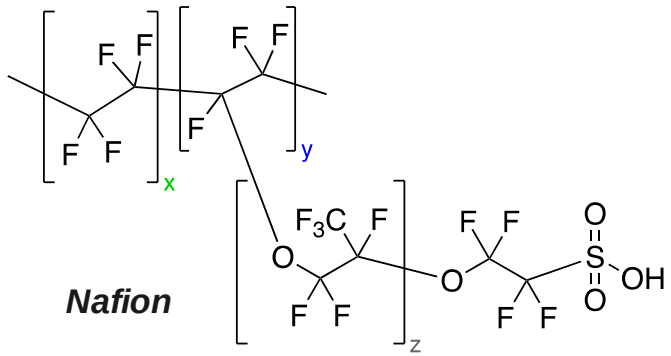
How Ink Formulations Can Dictate Electrode Cracking?







Cracking may result from a combination of ink material properties and coating thickness

1 $$CCT = \left(\frac{K_c}{1.4\sigma}\right)$$

K_c = *Film toughness*

σ = *Stress on the film*

Critical Crack-Free Thickness (CCT) Equation for Aqueous Dispersions

2 $$CCT = 0.64\left[\frac{G\boldsymbol{M}\phi_{rcp}\boldsymbol{R^3}}{2\gamma}\right]^{1/2}\left[\frac{2\gamma}{-(P_{max})\boldsymbol{R}}\right]^{3/2}$$

G = *particle shear modulus*

$\boldsymbol{M}$ = *coordination number*

ϕ_{rcp} = *particle volume fraction at close packing*

$\boldsymbol{R}$ = *particle radius*

γ = *solvent-air interfacial tension*

P_{max} = *capillary pressure*

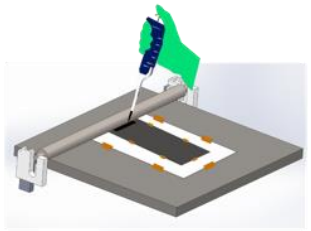
G, γ, P_{max} → *Constant (same materials and processing conditions)*

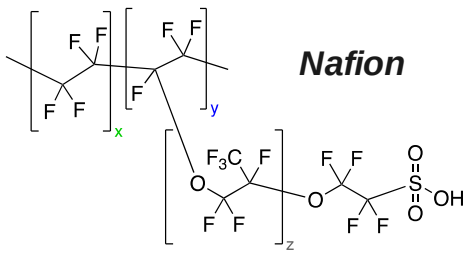
$\boldsymbol{M}, \phi_{rcp}, \boldsymbol{R}$ → *Dictate CCT*

Higher magnitude ↔ Higher fracture resistance

Chiu et al. J. Am. Ceram. Soc., 1992, (76)
Singh et a. Phys. Rev. Lett., 2007, (98)

Electrode Cracking as a Function of Solvent Ratio

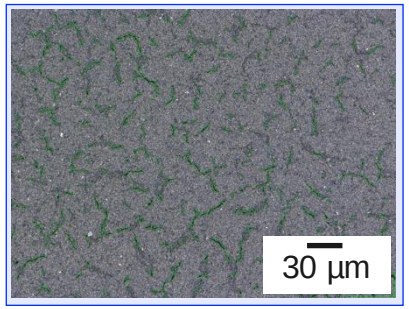




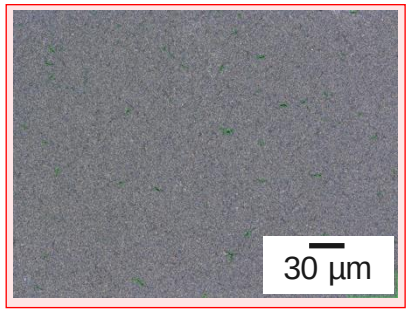
Nafion

Catalyst wt %	I/C	H_2O wt%	Pt loading
3.5	1.00	75-25	~0.3 mg Pt/cm^2

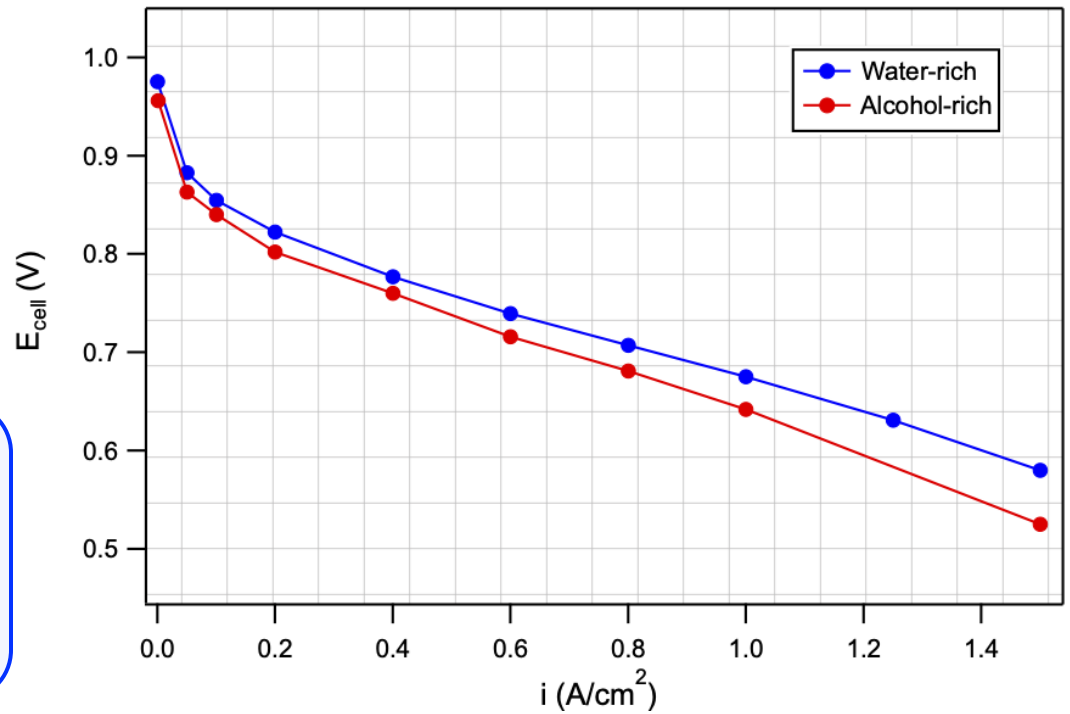
Ink concentration, mixing strategy, and coating tool are relevant for R2R manufacturing.



75 wt. % H_2O
High electrode cracking



25 wt. % H_2O
Low electrode cracking

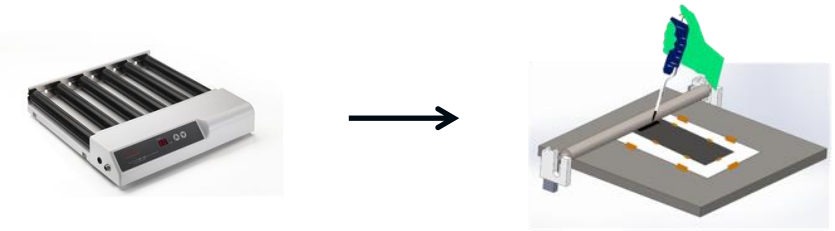


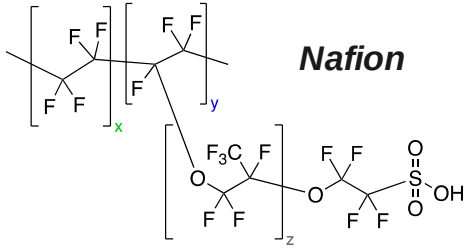
Ball milling for ***large-scale*** ink mixing

Rod coating – Pilot for ***large-scale*** coatings relevant to R2R manufacturing

Van Cleve et al. ACS Appl. Mater. Interfaces, 2019 (11)
https://www.fishersci.com/

Electrode Cracking as a Function of Solvent Ratio





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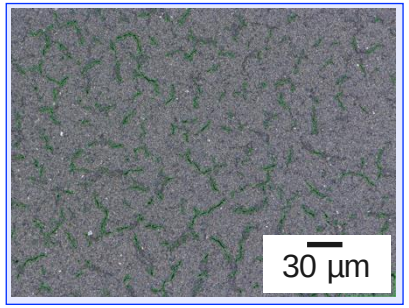

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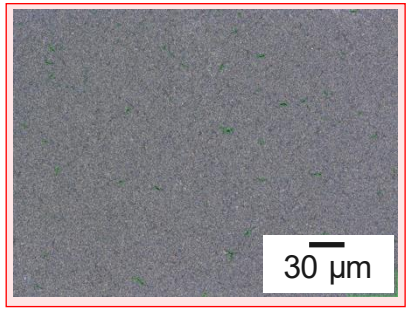
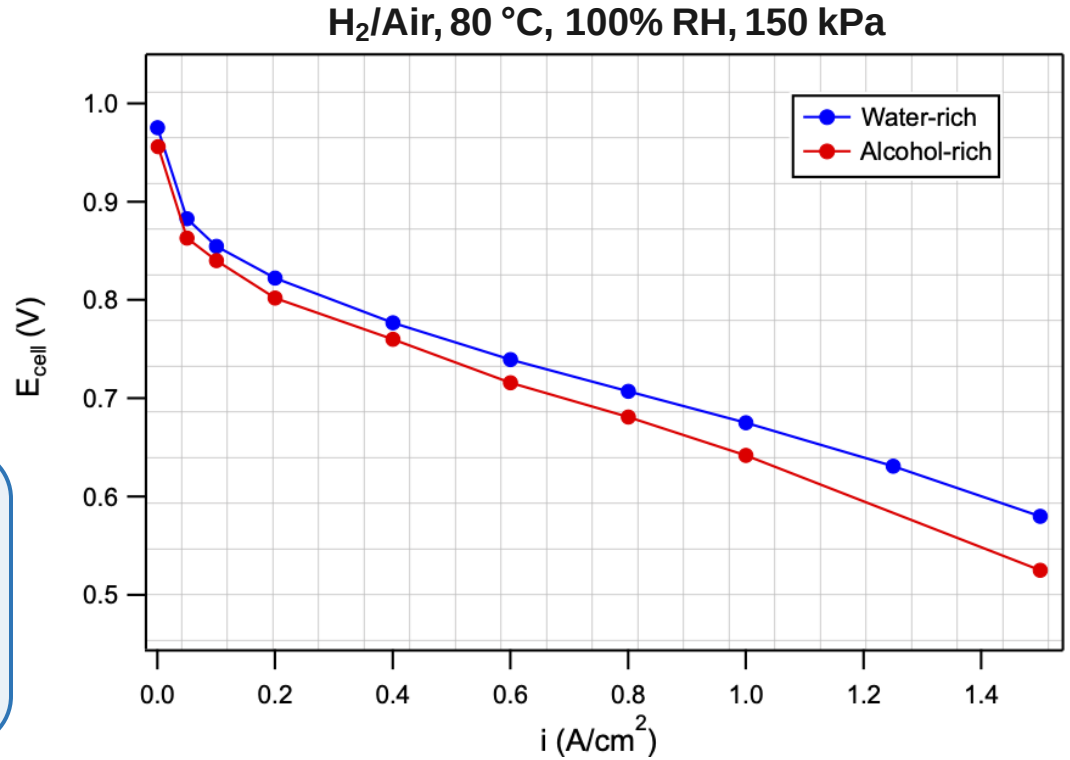


25 wt. % H_2O
Low electrode cracking

Similar trend for low Pt-loaded (crack-free) spray coated catalyst layers

Performance relates to nanoscale ionomer structure and not cracks



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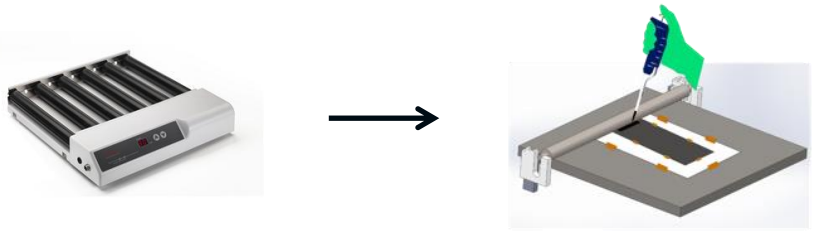

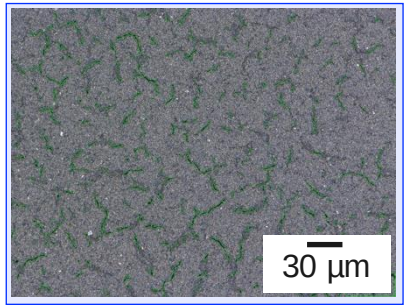

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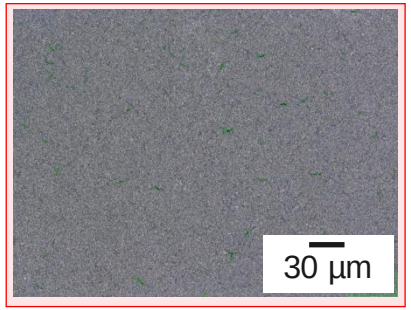

Similar trend for low Pt-loaded (crack-free) spray coated catalyst layers

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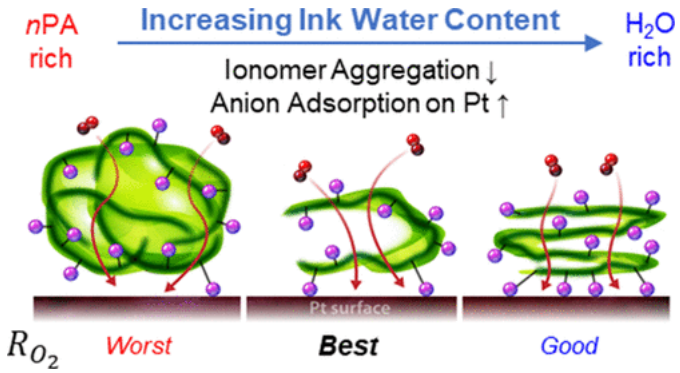
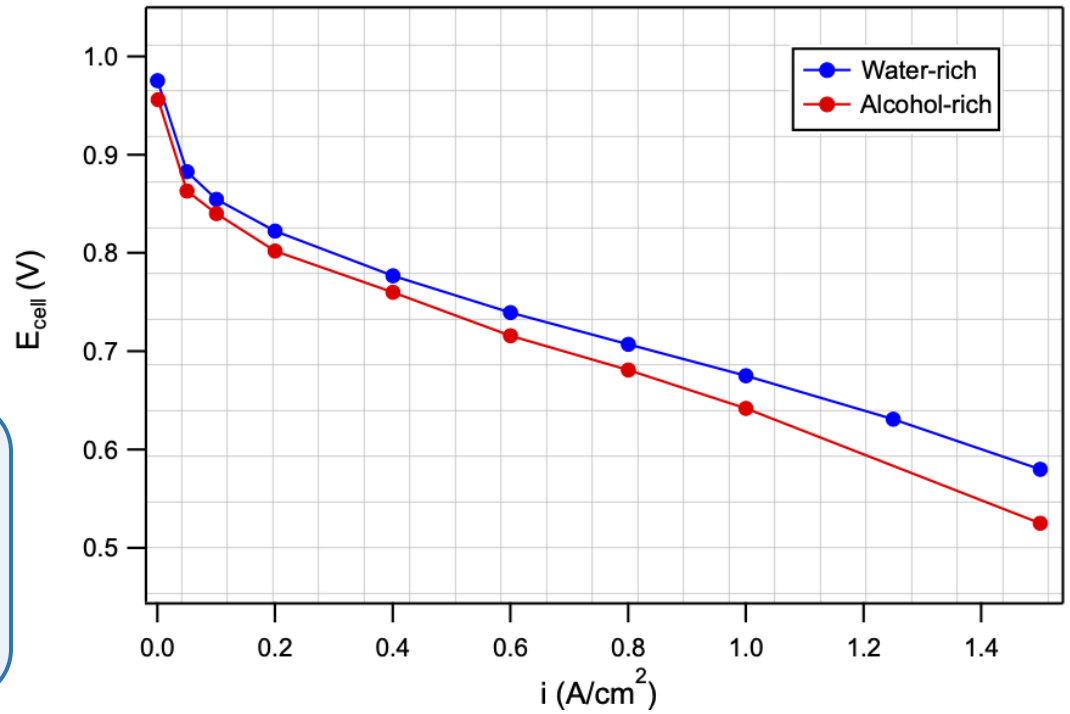
Problem:



Specific solvent ratio is critical to maximize performance

Electrode cracking may reduce durability

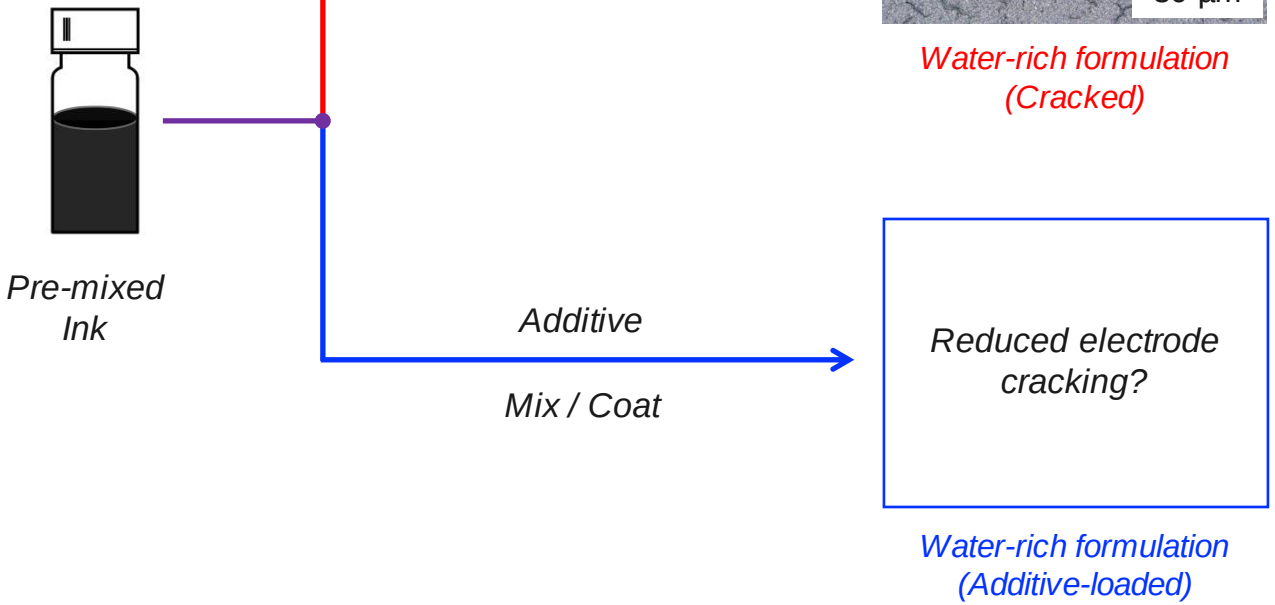
H_2/Air, 80 °C, 100% RH, 150 kPa

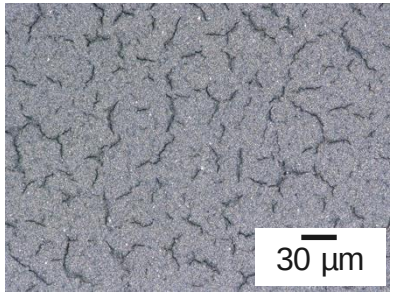


How to reduce electrode cracking while maintaining the electrochemical performance in water-rich systems?

Van Cleve et al. ACS Appl. Mater. Interfaces, 2019 (11)
https://www.fishersci.com/

New Formulation Route: Incorporation of Polymeric Additives





Water-rich formulation (Cracked)

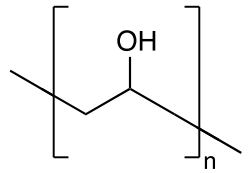
Water-rich formulation (Additive-loaded)

Catalyst wt %	I/C	H_2O wt%	Pt loading
3.5	1.00	75	~0.3 mg Pt/cm^2

1

High-shear mixing and ball milling for ***large-scale*** ink mixing

2

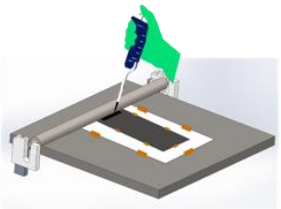


Poly (vinyl alcohol) *(PVA)*

M.W. = 89-98 k

Low-cost, commercially available polymer – ***5 wt.% relative to ionomer mass***

3



Rod coating – Pilot for ***large-scale*** coatings relevant to roll-to-roll manufacturing

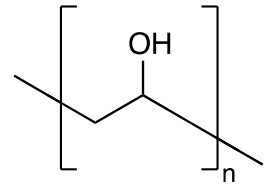
Features

1. *Polymeric additive should aid ionomer in binding particles*
2. *5 wt. % relative to ionomer mass (1.5% of the total electrode mass)*
3. *Small enough not to compete with the ionomer nor reduce performance*

https://www.fishersci.com/ https://www.ika.com/

Electrode Imaging Techniques to Elucidate Microstructure

Thickness Measurements via SEM	
Control	7.6 ± 1 µm
PVA-loaded	6.3 ± 0.5 µm



Poly (vinyl alcohol) *(PVA)*

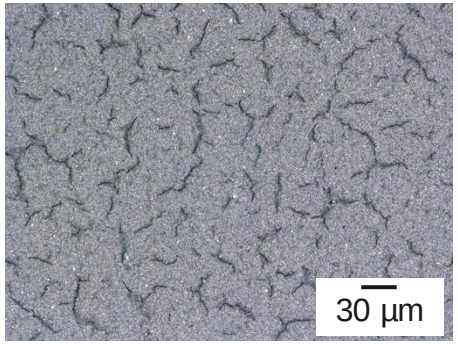
Catalyst wt %	I/C	H_2O wt%	Pt loading
3.5	1.00	75	~0.3 mg Pt/cm^2

Optical Microscopy

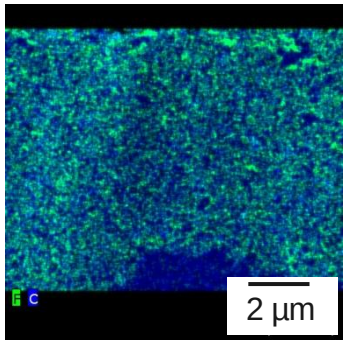
TEM *(ORNL)*

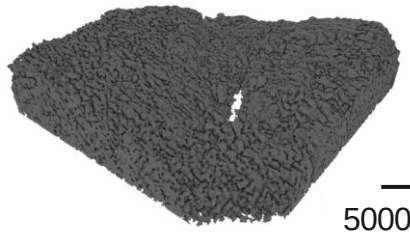
X-ray Computed Tomography *(ANL)*

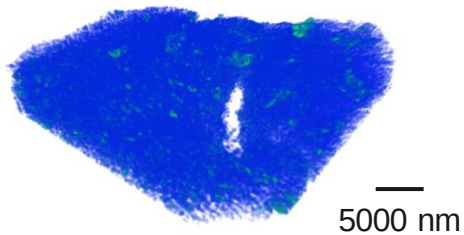
Control

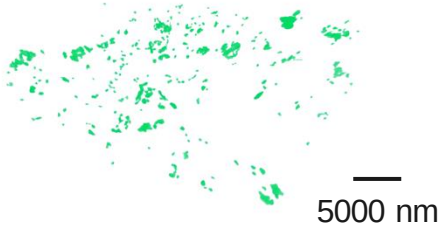


Crack %: 6.895

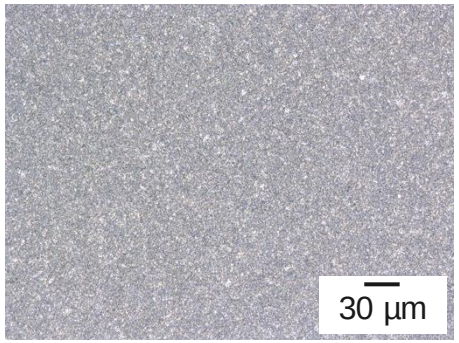


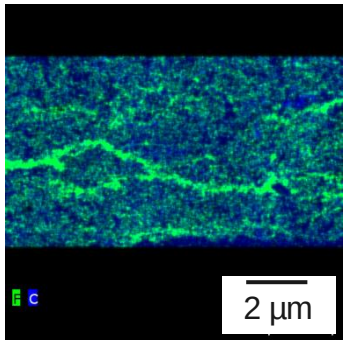


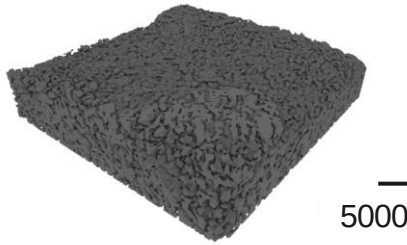


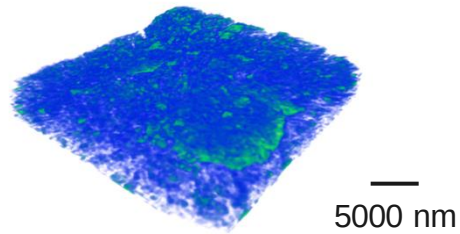


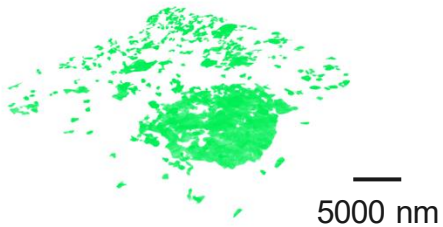
PVA-loaded









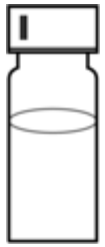


Is PVA changing the ionomer distribution? What interactions trigger this effect?

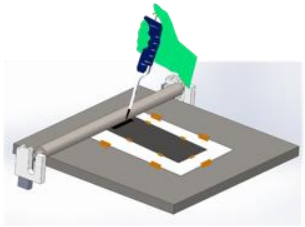
OAK RIDGE National Laboratory

Argonne NATIONAL LABORATORY

Mechanism of Interaction in Additive-Loaded Inks



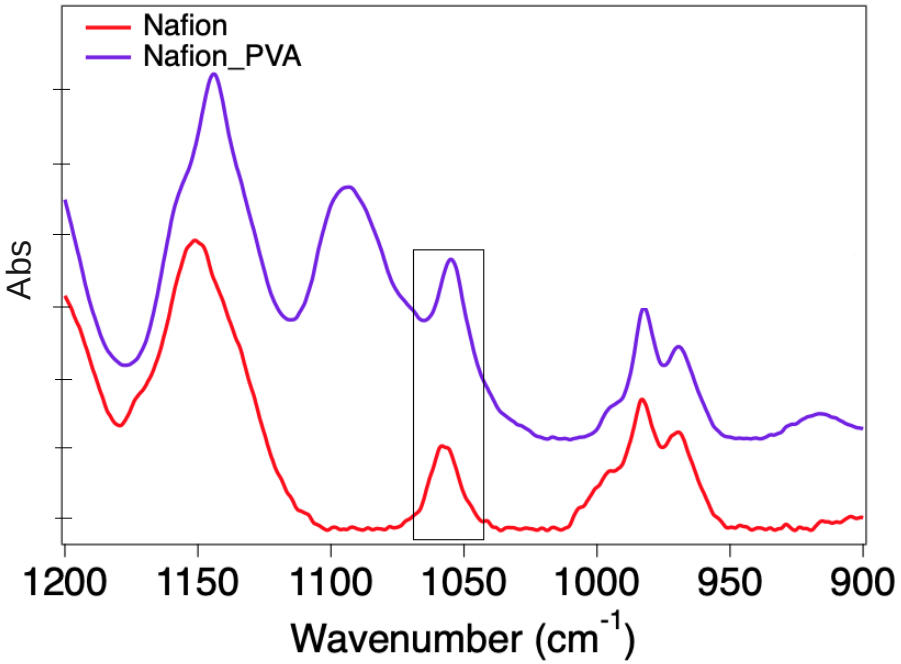
Polymer in H_2O/nPA

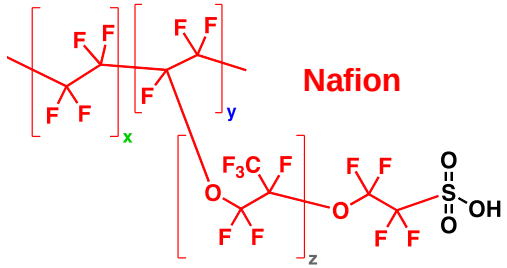


Cast on a heated plate

*IR Spectroscopy (**NREL**)*

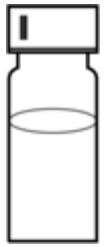
Goal: Elucidate specific interactions between Nafion and PVA





Nafion

Mechanism of Interaction in Additive-Loaded Inks



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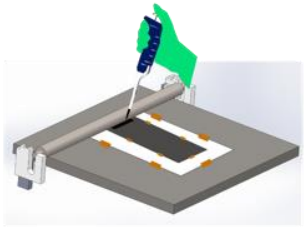

Cast on a heated plate

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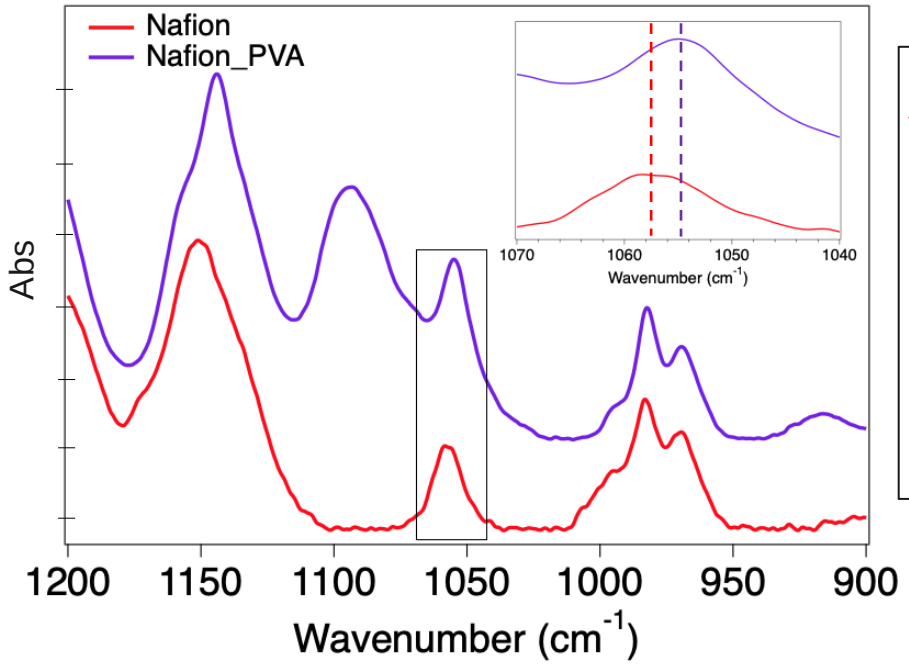
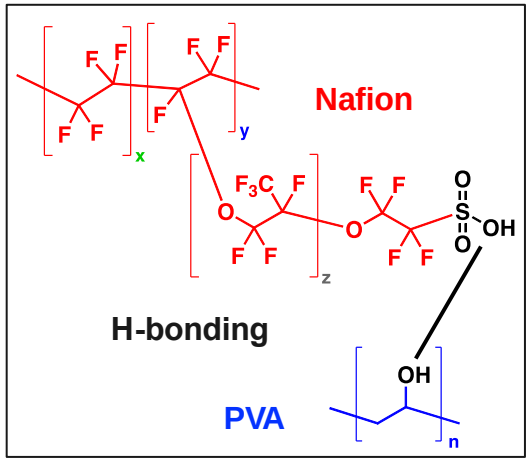
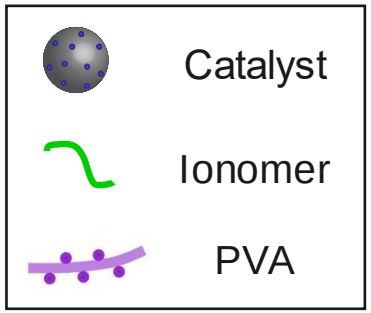
H-bonds may lead to a densely packed electrode



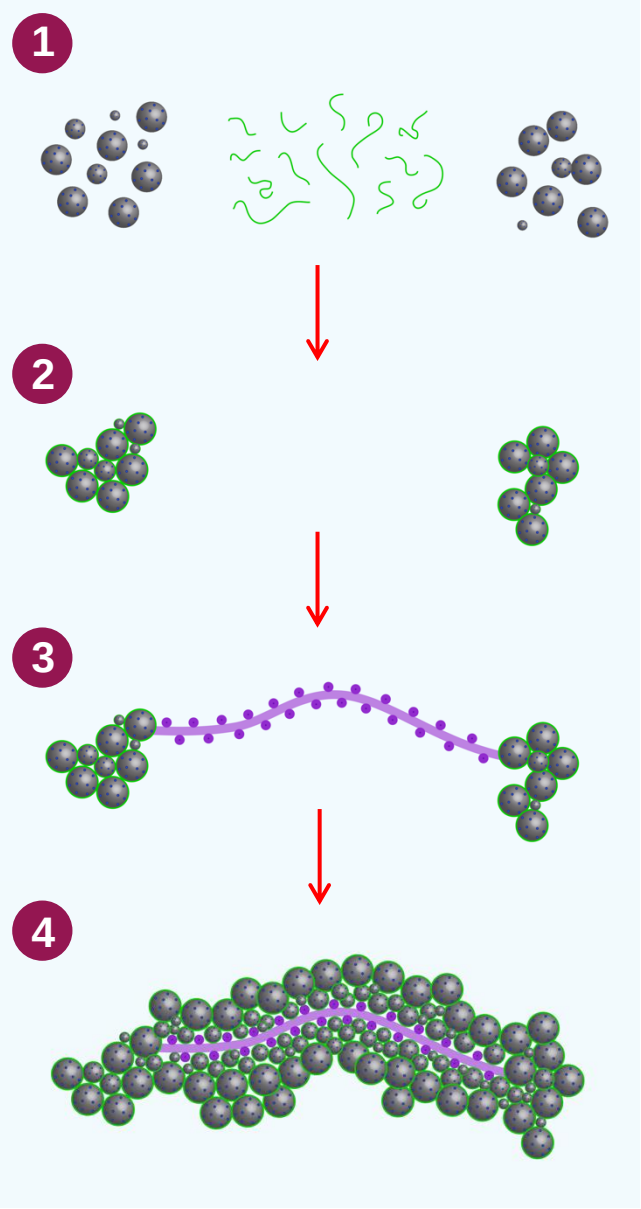




Ionomer holds **catalyst** particles together

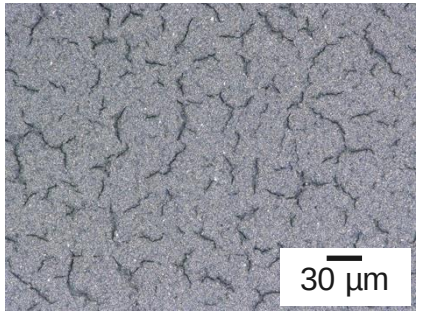
PVA inserts between **catalyst** clusters

PVA holds **ionomer**-covered **catalyst** particles together

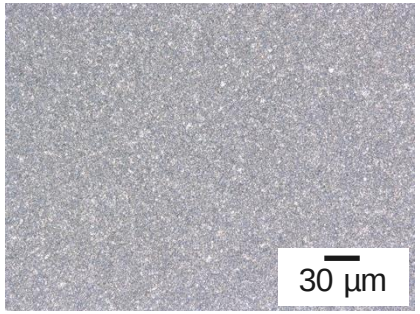


Electrochemical Performance of Additive-Loaded Electrodes

Control



PVA-loaded

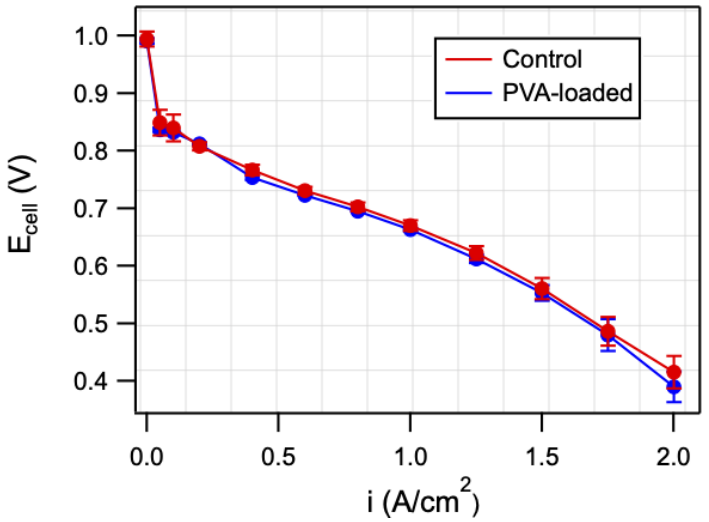


1 This work leads efforts in electrode cracking mitigation in fuel cells

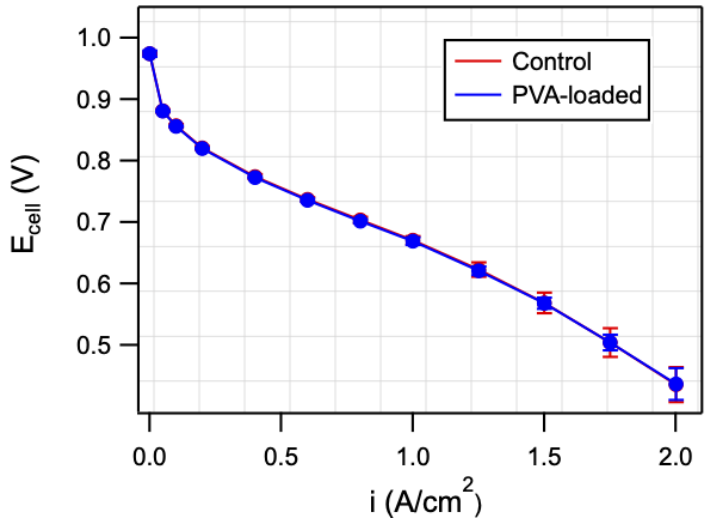
2 This approach targets specific molecular interactions in the ink formulation that translate into cracking-free electrodes with no negative impact on electrochemical performance

3 Fuel cells with longer lifetimes

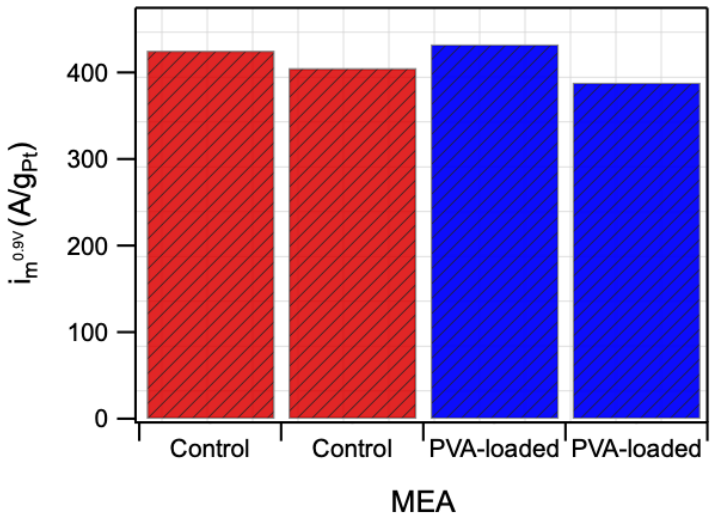
H_2/Air, 90 °C, 40% RH, 250 kPa



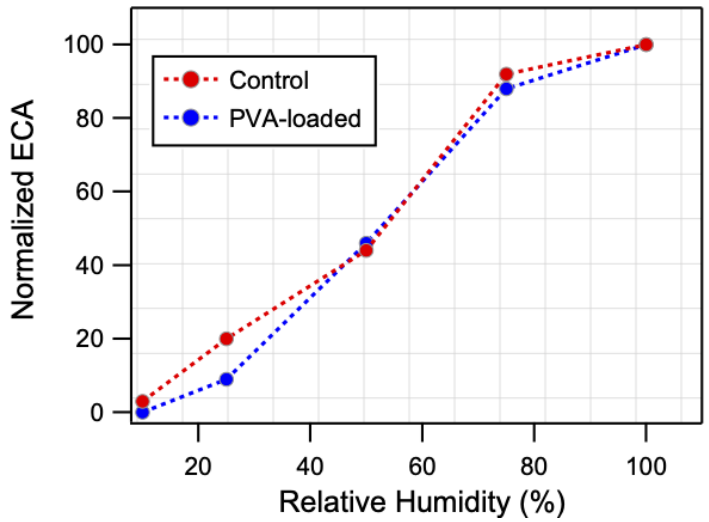
H_2/Air, 80 °C, 100% RH, 150 kPa



Mass Activity after 3 VRs

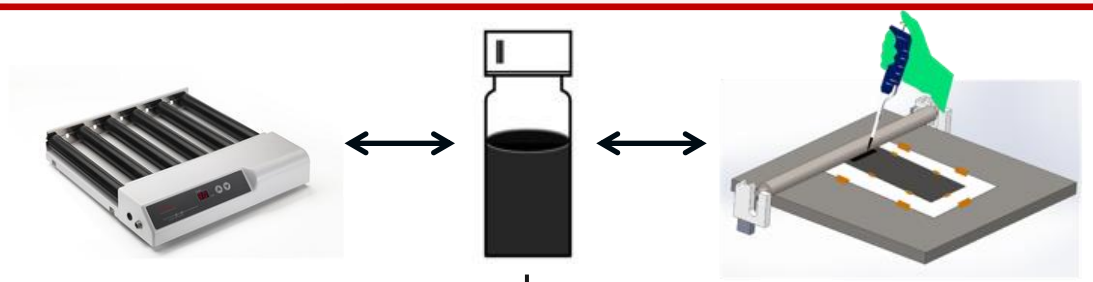


ECA from CO stripping



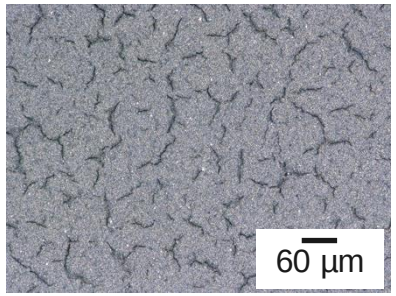
Summary of Relevant Formulation Approaches

1. Processing

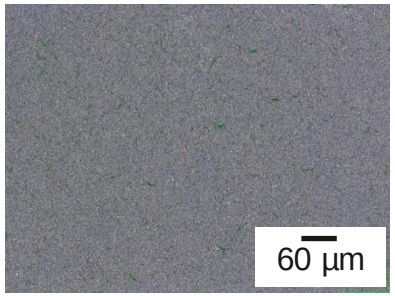


2. Solvent Ratio

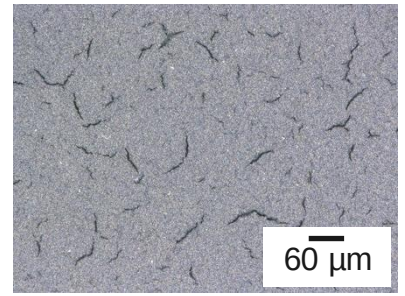
75% H_2O



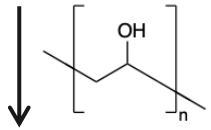
25% H_2O

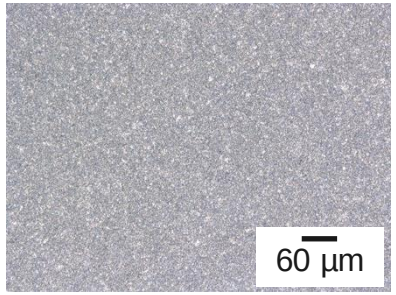


15% H_2O



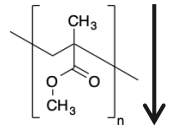
3. Additives

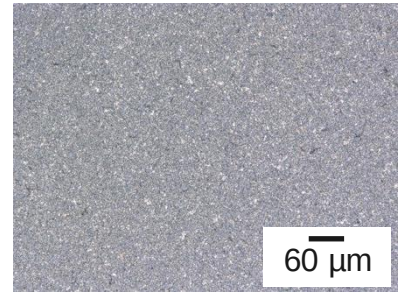




Approaches applicable to fuel cells, electrolyzers, and batteries

Easily translated to other coating technologies (roll-to-roll, core-shell nanostructures)





MILLION MILE FUEL CELL TRUCK

U.S. DEPARTMENT OF ENERGY

Formulation Strategies for the Large-Scale Manufacturing of Crack-Free Electrodes

Carlos Baez-Cotto

Process Science and Engineering Group – NREL
Scott Mauger and Michael Ulsh

HFTO Postdoctoral Awards– May 11th, 2022.

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