NREL
NATIONAL RENEWABLE ENERGY LABORATORY

# Material-Process-Performance Relationships for Roll-to-Roll Coated PEM Electrodes

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Presenter: Scott Mauger

Hydrogen and Fuel Cells Annual Merit Review and Peer Evaluation Meeting
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# Overview

## Timeline and Budget

- Project start date: 10/1/2016
- FY16 DOE funding: $ 350,000
- FY17 planned DOE funding: $15,000
- Total DOE funds received to date: $ 350,000

## Barriers

| Barrier | Target |
|---|---|
| A. Lack of high-volume MEA processes | $20/kW (2020) at 500,000 stacks/yr |
| H. Low levels of quality control | |

# Relevance: Objective

**Project**

Study material-process-performance relationships to understand the effects of ink formulation, coating physics, and drying dynamics on morphology, electrochemistry, proton conduction, and mass transport for roll-to-roll (R2R) coated PEMFC/EC cell materials. Provide a proof-of-scalability pathway for industry, lab and academic partners, e.g. ElectroCat, FC-PAD, HydroGen, L'Innovator

**FY 2017**

Establish baselines for spray-coated and R2R-coated catalyst-coated diffusion media, and R2R-cast membranes

# Relevance – Project Addresses MYRD&D Plan Milestones

| Task 1: Membrane Electrode Assemblies | |
|---|---|
| 1.2 | Develop processes for direct coating of electrodes on membranes or gas diffusion media. (4Q, 2017) |
| 1.3 | Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017) |

| Task 5: Quality Control and Modeling and Simulation | |
|---|---|
| 5.5 | Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018) |

- Roll-to-roll (R2R) processes represent the lowest cost/highest throughput method for production of FC materials
- R2R coating techniques require different formulation of catalyst and ionomer dispersions and have different intrinsic physics than lab-scale processes which may affect morphology, uniformity, performance, and durability
- Many companies/universities/labs do not have or have access to the infrastructure to understand how the conditions and processes of R2R will impact their materials
- Results directly relevant to fuel cell producers – small and large – and academic/national laboratory researchers

# Collaborations

| Institution | Role |
|---|---|
| National Renewable Energy Laboratory<br>• Mike Ulsh, Scott Mauger, K.C. Neyerlin<br>• Jonathan Stickel | • Prime; Electrode production, coating, rheology, MEA performance testing, advanced diagnostics<br>• Unfunded, rheology advisor. High quality collaboration that enables rheological measurement of catalyst and membrane inks; not in DOE Hydrogen and Fuel Cells Program |
| Oak Ridge National Laboratory<br>• Karren More | • Unfunded; Electron microscopy of electrode materials; Crucial to understanding morphology of electrode materials; In DOE Hydrogen and Fuel Cells Program |
| AMO Roll-to-Roll Consortium<br>• David Wood | • Collaborating on roll-to-roll coating |

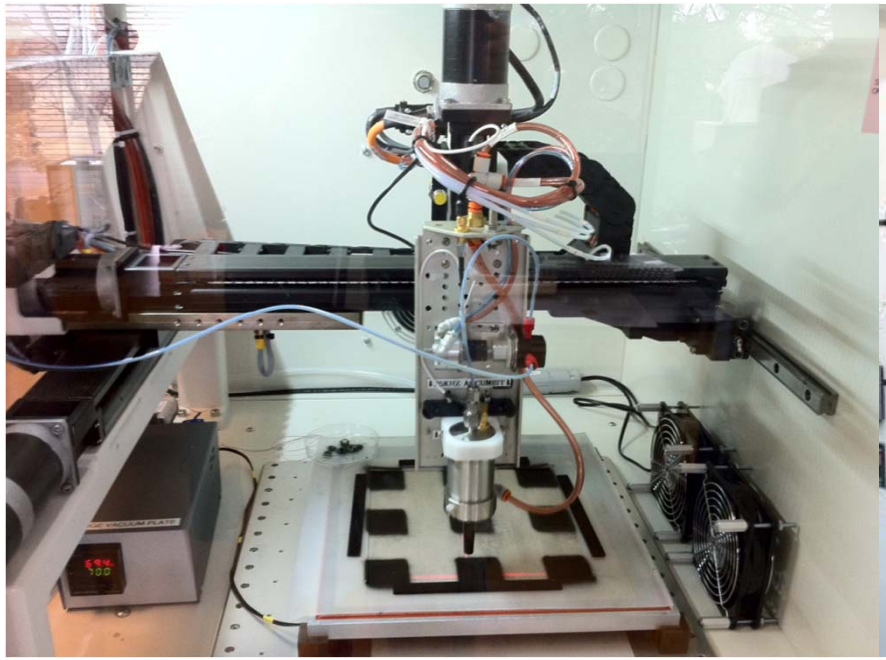
# Approach

- Understand foundational relationships between ink rheology, interparticle interactions, coating and drying physics, and film microstructure in R2R-coated electrodes and membranes
- Leverage advanced diagnostic techniques and electron microscopy developed through FC-PAD to correlate microstructure to electrochemical performance, proton transport, and mass transport.
- Utilize this fundamental understanding to develop innovative ink formulations and coating processes to optimize membrane, catalyst, and MEA properties and performance

| Date | Milestone/Deliverable (as of 4/10/2017) | Complete |
|---|---|---|
| 12/2016 | Fabricate and characterize baseline ultrasonic-sprayed electrodes for process study. | 100 % |
| 6/2017 | Fabricate and characterize baseline slot-die and micro-gravure roll coated electrodes on R2R coating station. | 70 % |
| 9/2017 | Fabricate and characterize baseline cast membranes on R2R coating station. | 0 % |

# Approach (Background) – Electrode Production

## Lab Scale – Ultrasonic Spray



Used to demonstrate new materials and for fundamental studies

**Conditions**

- Dilute ink (~0.6 wt% solids)
- Ultrasonic mixing
- Sequential build up of layers
- Heated substrate
- Vacuum substrate

## Large Scale – Roll-to-Roll (R2R)

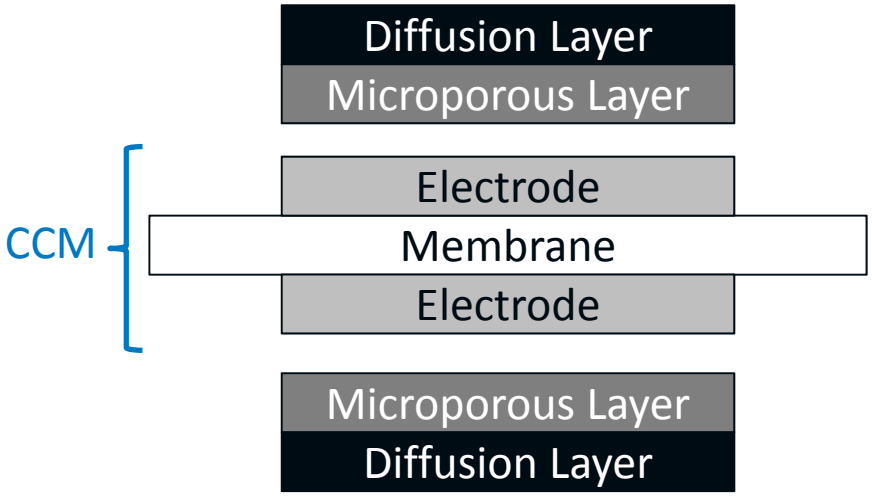
Needed to demonstrate industrial relevance and scalability of materials and MEA/cell designs

**Conditions**

- Concentrated ink (~4.5 wt% solids)
- Shear mixing
- Single layer
- Room temp. substrate
- Convective drying

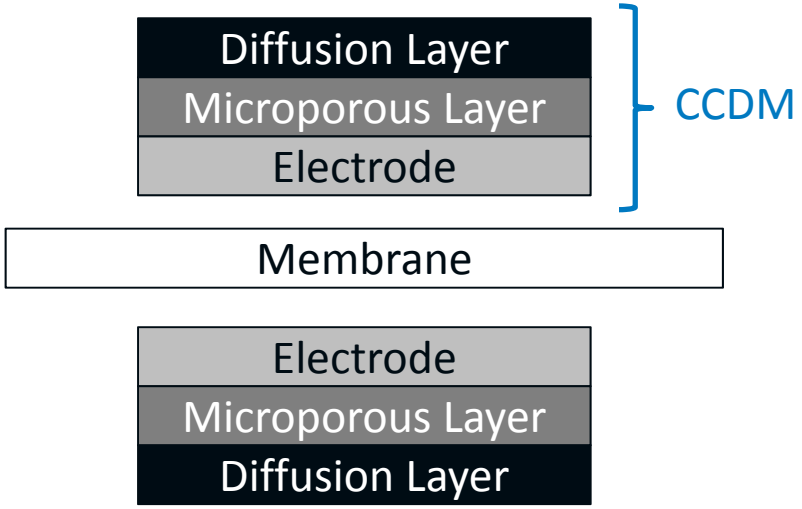
# Approach (Background) – Electrode Types

## Catalyst-Coated Membrane (CCM)




- Electrode applied to membrane
- Extensive knowledge and large body of research at NREL and in literature
- Difficult for manufacturing due to swelling of membrane

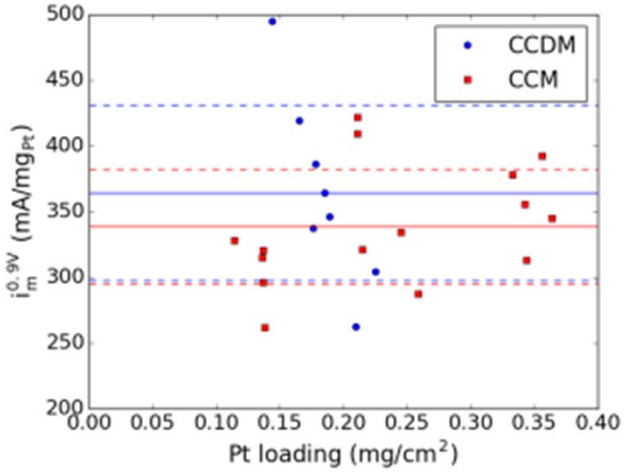
## Catalyst-Coated Diffusion Media (CCDM aka GDE)

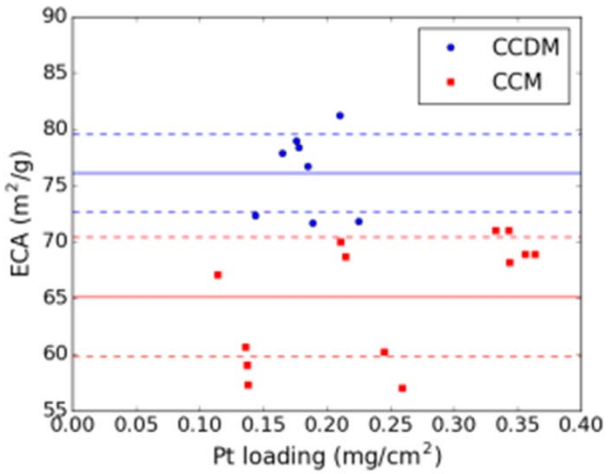



- Electrode applied to microporous layer, over coated with thin layer of ionomer, then hot pressed to membrane
- Less experience at NREL and fewer studies in literature
- Easier for manufacturing and preferred by industry

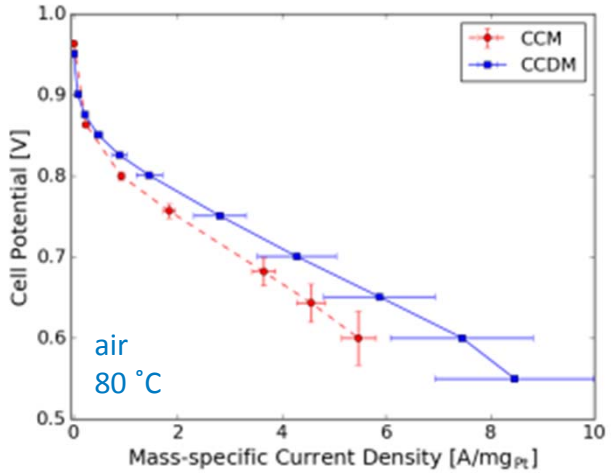
# Accomplishments and Progress:

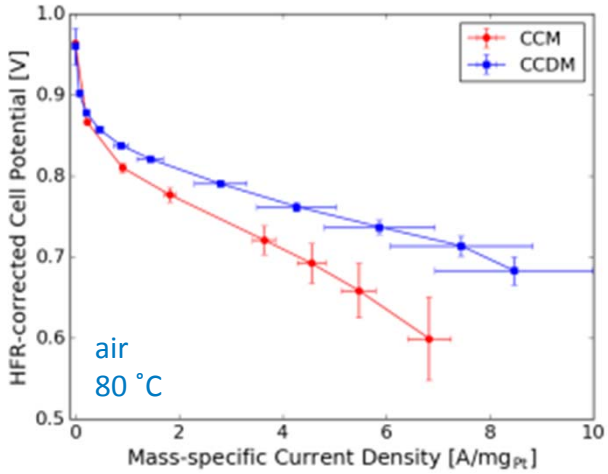
## Achieved Comparable Performance between Spray-Coated CCM and CCDM



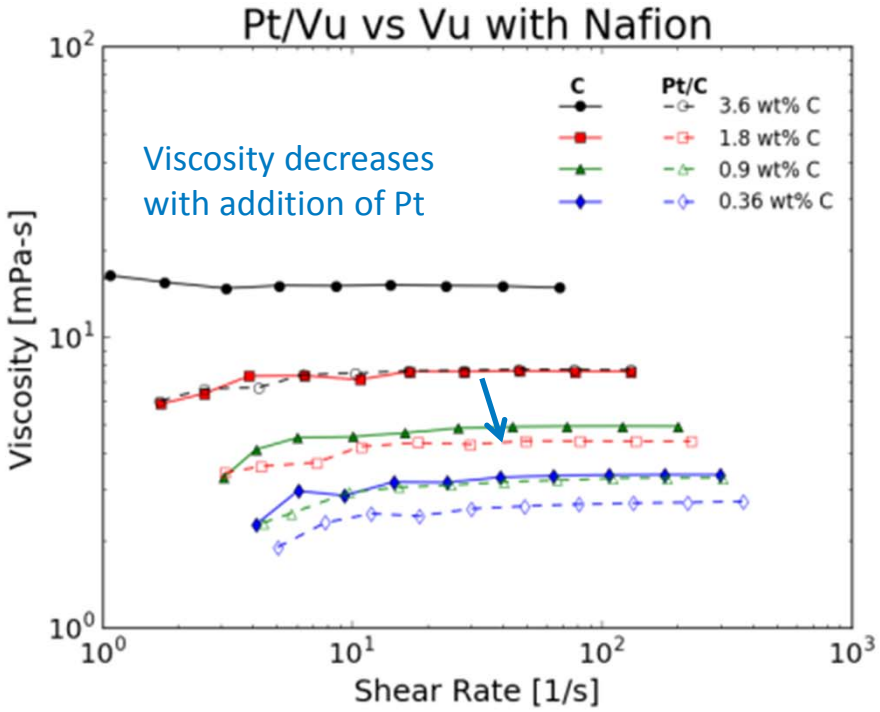

Pt/HSC, 50 wt% Pt
100 %RH
150 kPa

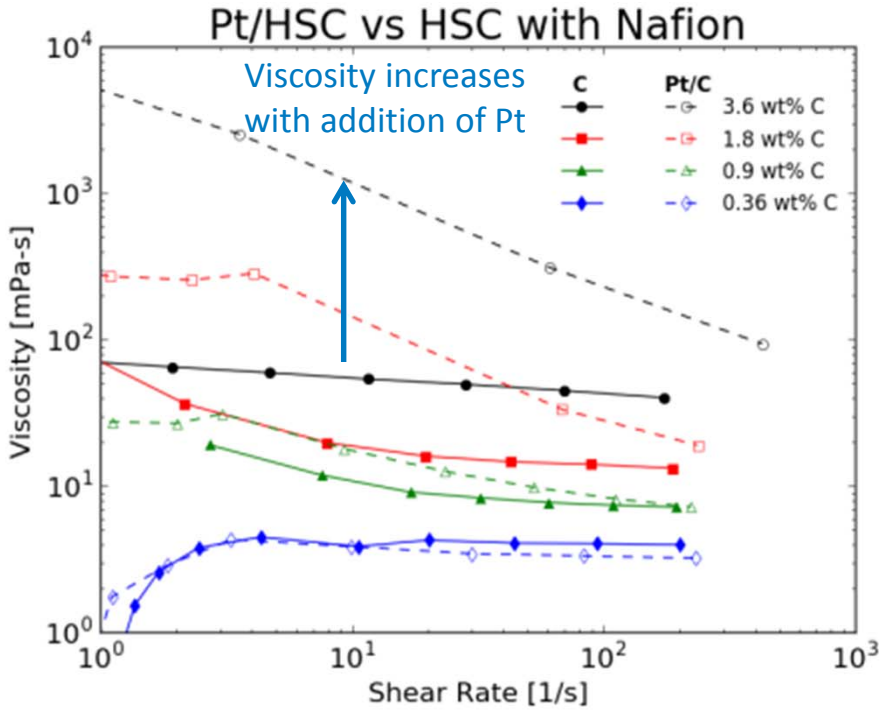



- This project leverages NREL's expertise, data, and experience in MEA testing from FC-PAD and our MEA Integration core competency
- Also utilizes advanced diagnostics techniques such as impedance spectroscopy and limiting current measurements

# Accomplishments and Progress:
# Determined Catalyst Ink Viscosity Dependent on Carbon Type and Pt



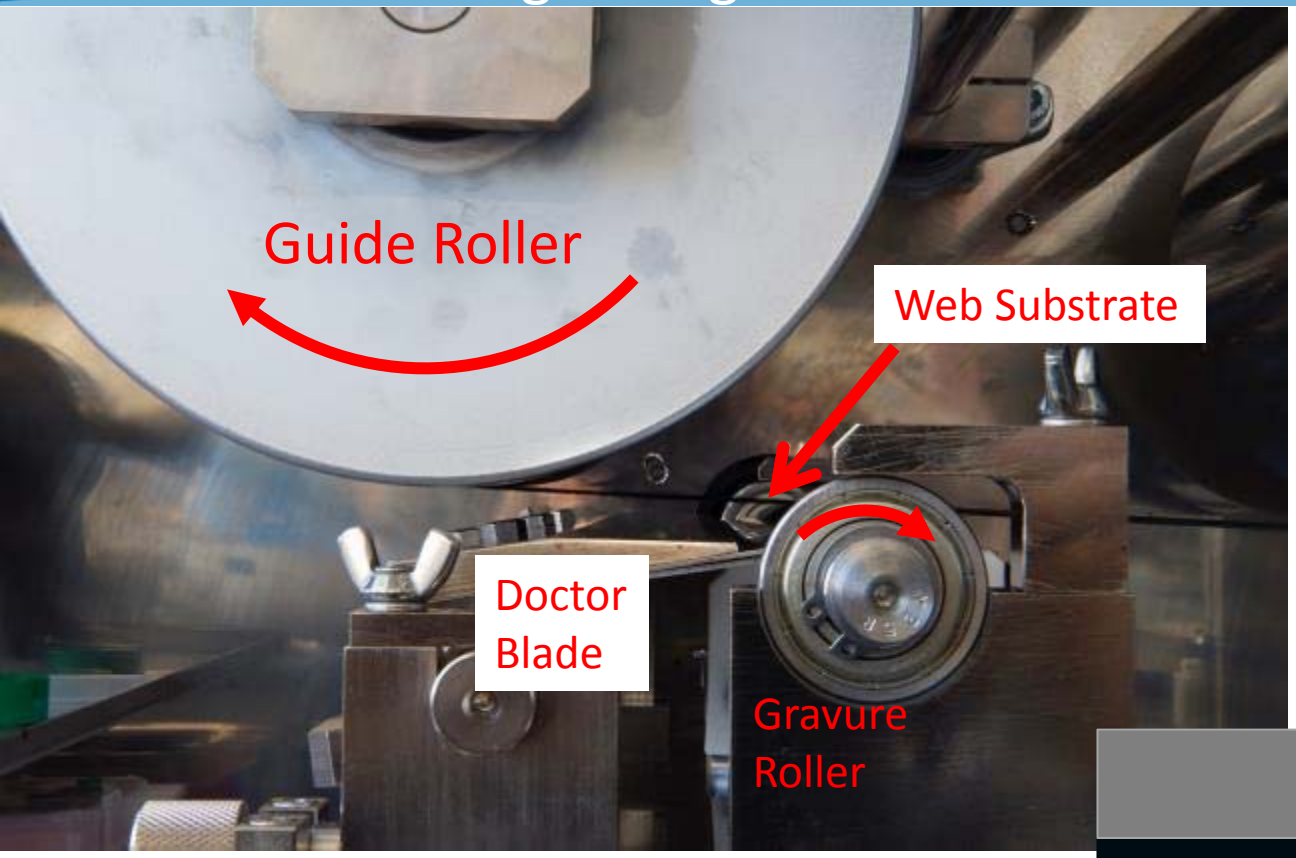



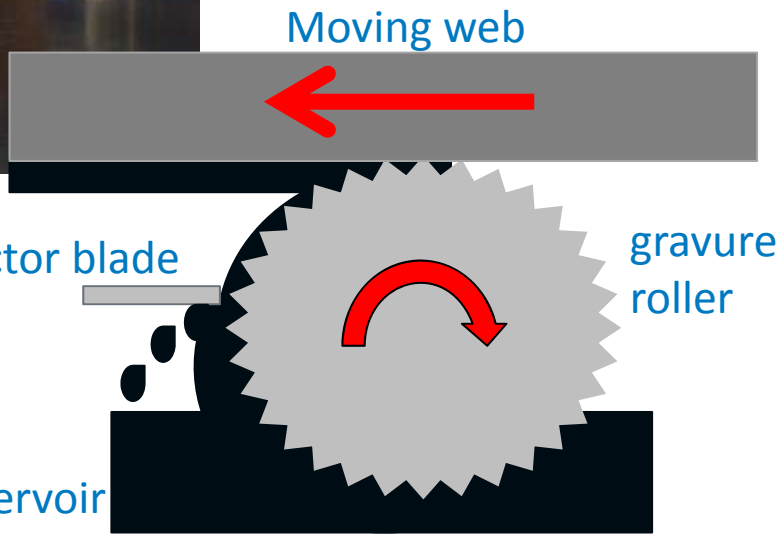

| Material | BET Surface Area [$m^2/g_C$] | Pore Volume [$cm^3/g_C$] |
|---|---|---|
| Vulcan XC-72 | 237 | 0.62 |
| Pt/Vulcan (TEC10V50E) | 166 | 0.52 |
| HSC (TKK E-type carbon) | 802 | 1.33 |
| Pt/HSC (TEC10E50E) | 554 | 0.89 |

Vulcan – Newtonian HSC – Shear thinning

- HSC more viscous than Vulcan due to larger pore volume
- Addition of Pt changes viscosity in opposite directions for Vulcan (decrease) and HSC (increase)
- Hypothesis: different ionomer interactions between carbon types

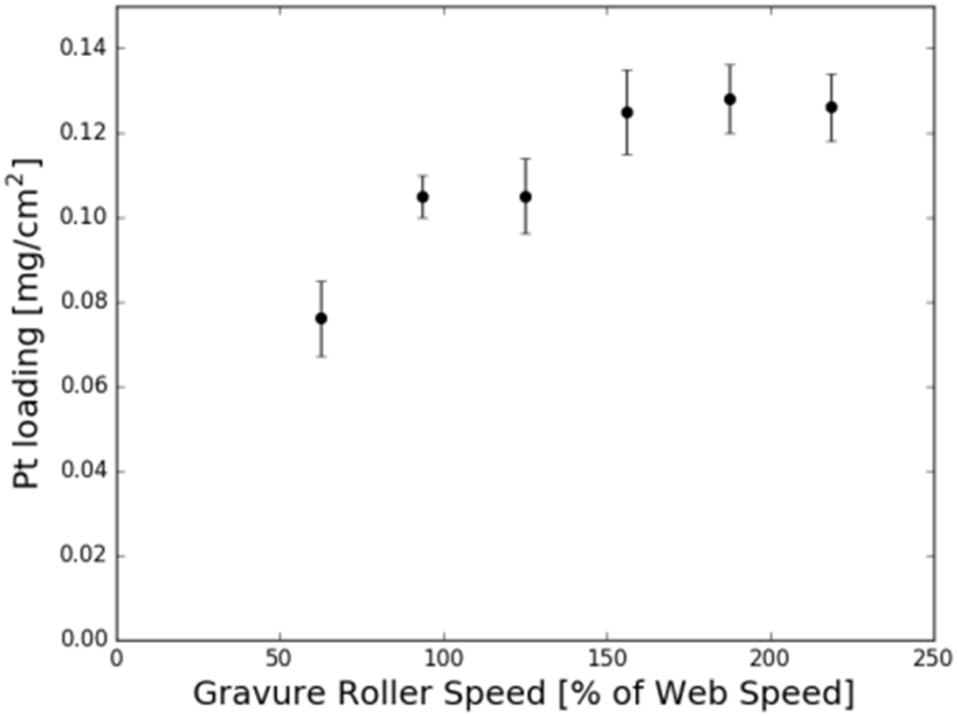
# Accomplishments and Progress: Gravure Coating Configuration




Gravure Roller

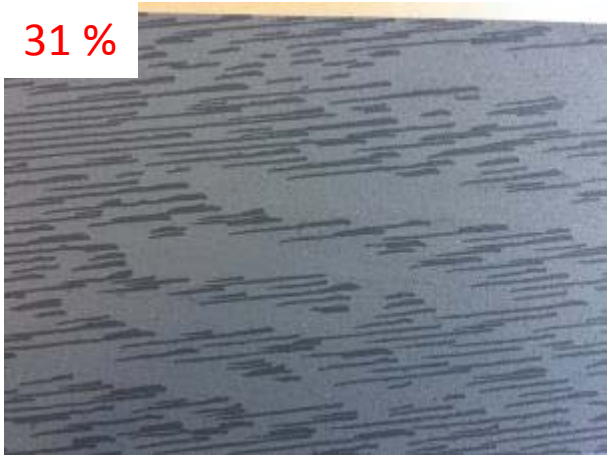
# Accomplishments and Progress: Loading and Coating Quality Dependent on Roller Speed




Pt/HSC, 50 wt% Pt
Nafion 1000 EW
3.2 wt% PtC
0.9 I:C
SGL 29BC

- 7 m coated on SGL 29BC roll (15 cm x 50 m)
- About 1 m long section coated at each condition
- Loading measured by XRF, average of 5 points in 50 cm$^2$ area from 1m section
- Low gravure roller speed (relative to web speed) results in coating defects
- Increasing loading (coat weight) with roller speed follows expected trend

31 %



63 %

94 – 219 %

# Accomplishments and Progress:
# Coating Quality Dependent on Roller Speed and Pattern

## Gravure Roller

## Gravure Roller Pattern

三角形の溝がラセン状に刻られており、高粘度の絞り、転移性の悪い粘着材等のコーティングに適します。

| 線数 (L/inch) | 深度 (μ) | セル容積 ($cm^3/m^2$) |
|---|---|---|
| 36 | 275 | 138 |
| 38 | 255 | 131 |
| 45 | 305 | 149 |
| 50 | 195 | 100 |
| 55 | 165 | 81 |
| 60 | 220 | 105 |
| 65 | 130 | 65 |
| 70 | 150 | 73 |
| 75 | 160 | 82 |
| 80 | 130 | 67 |
| 85 | 150 | 73 |
| 90 | 95 | 49 |
| 95 | 90 | 46 |

| Gravure Roller Wet Film Thickness [μm] | Gravure Roller Speed [%] 100 | 150 | 200 |
|---|---|---|---|
| 12-20 | | | |
| 30-45 | | | |
| 50-80 | | | |

- Thinner films must be coated with higher roller speeds for defect-free coatings
- Relationship between roller pattern, viscosity, and surface tension seems to determine coating quality

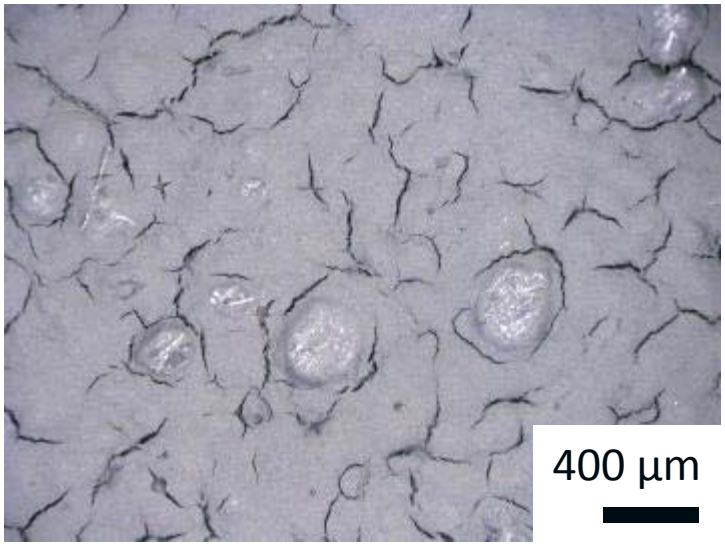
Pt/HSC, 50 wt% Pt
Nafion 1000 EW
3.2 wt% PtC
1.2 I:C
SGL 29BC

# Accomplishments and Progress:
# Achieved High Quality Coating with Gravure Method

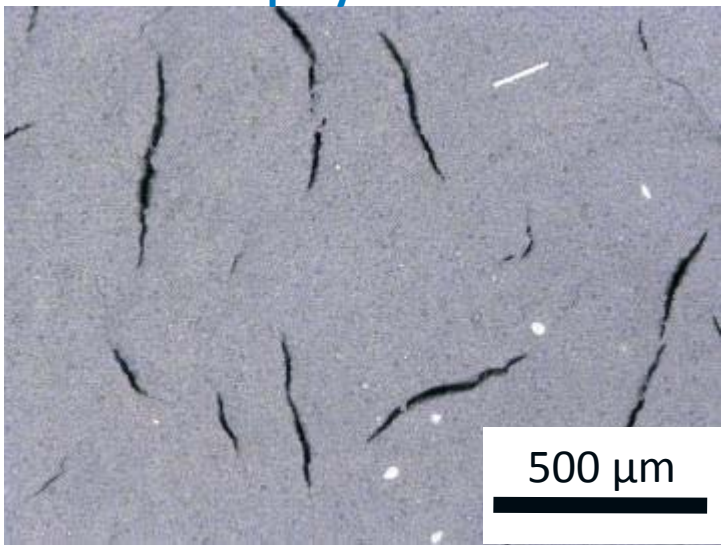
Pt/HSC, 50 wt% Pt
Nafion 1000 EW
3.2 wt% PtC
0.9 I:C
SGL 29BC

- PtHSC/Nafion (0.9 I:C) on SGL 29BC roll (15 cm x 50 m)
- Viscous R2R ink mostly covers cracks in MPL, **no microscale coating defects**
- Less viscous spray-coated ink does not fill cracks

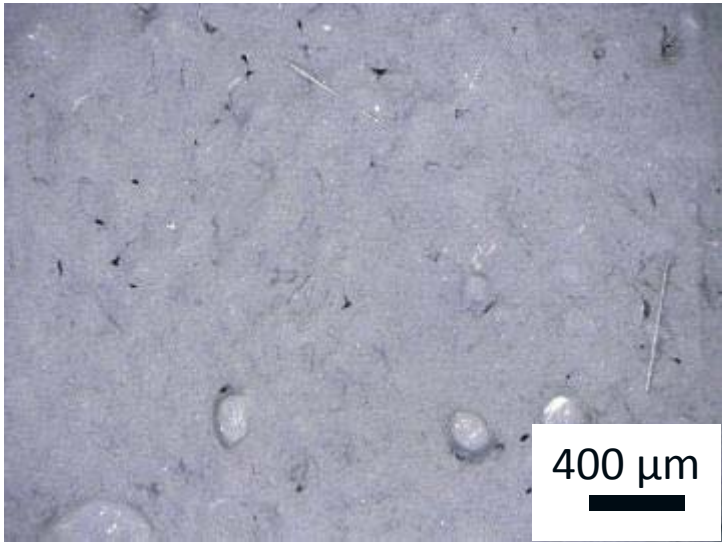
**Uncoated MPL**




**Spray Coated**

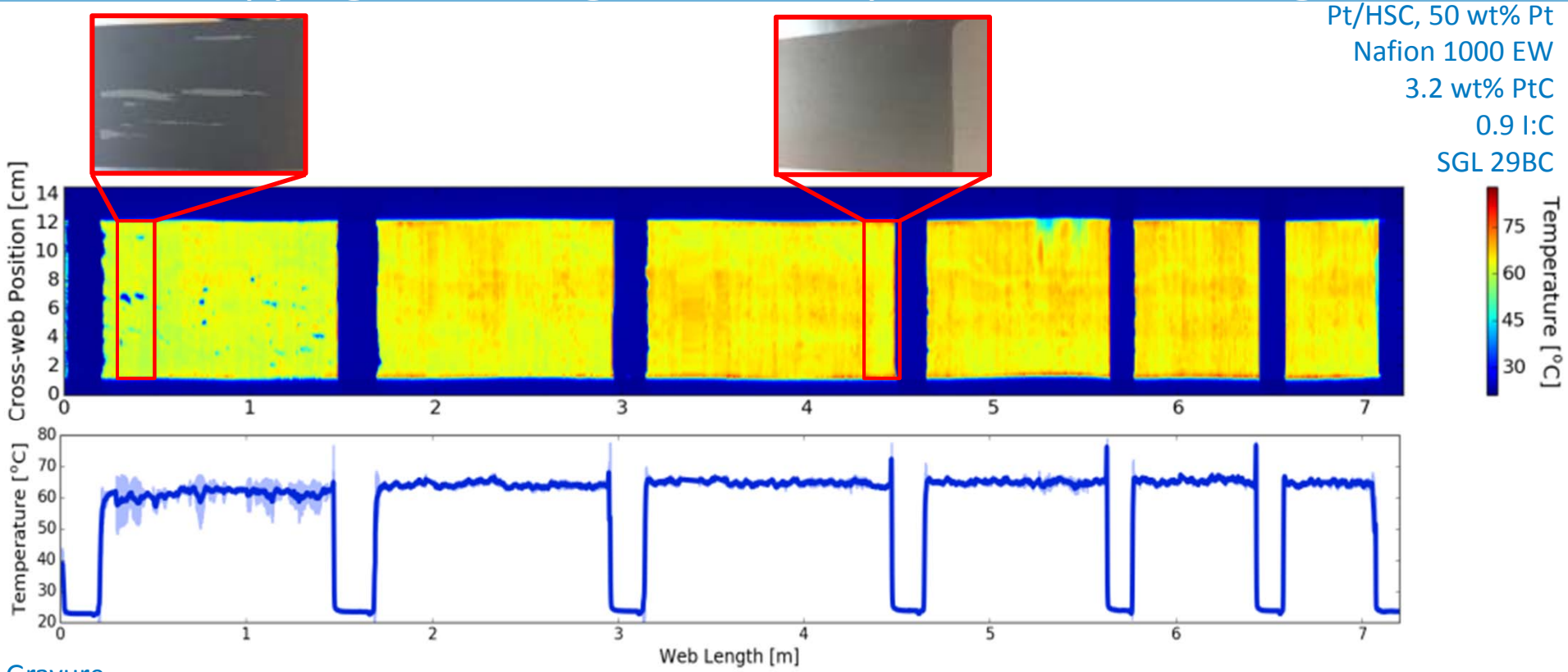



**R2R Gravure Coated**



# Accomplishments and Progress:
# RIF Mapping Shows High Uniformity of Gravure Coating

Pt/HSC, 50 wt% Pt
Nafion 1000 EW
3.2 wt% PtC
0.9 I:C
SGL 29BC



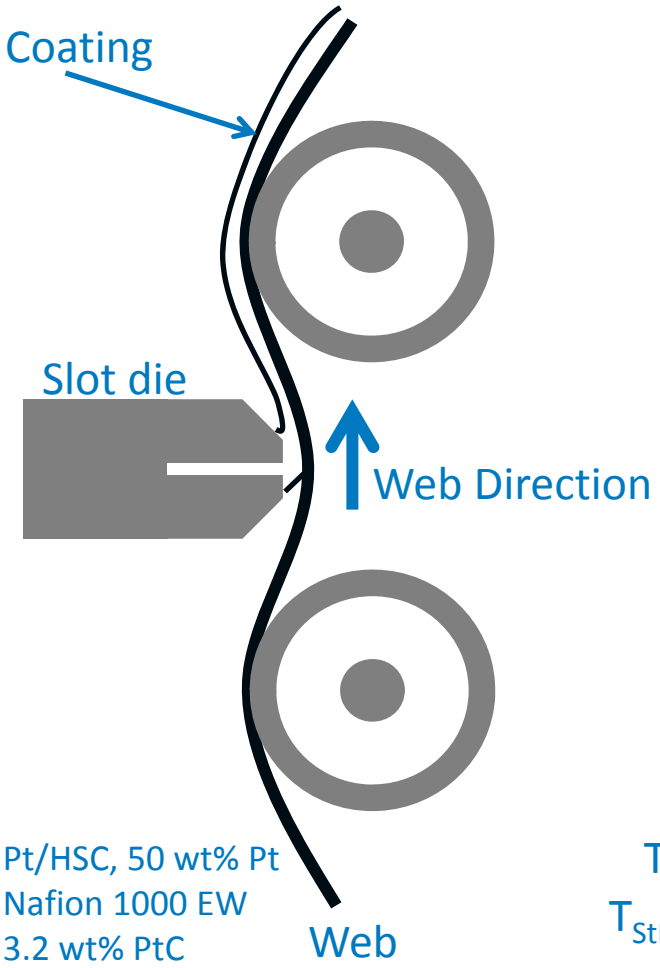

| Gravure Roller Speed | 63 % | 94 % | 125 % | 156 % | 188 % | 219 % |
|---|---|---|---|---|---|---|
| $T_{avg}$ | 61.1 ˚C | 63.9 ˚C | 64.6 ˚C | 64.8 ˚C | 65.2 ˚C | 64.5 ˚C |
| $T_{StDev}$ | 3.9 ˚C | 1.3 ˚C | 1.3 ˚C | 1.4 ˚C | 1.1 ˚C | 1.3 ˚C |
| Loading [$mg_{Pt}/cm^2$] | 0.08 | 0.11 | 0.11 | 0.13 | 0.13 | 0.13 |

**Loading correlates with temperature**

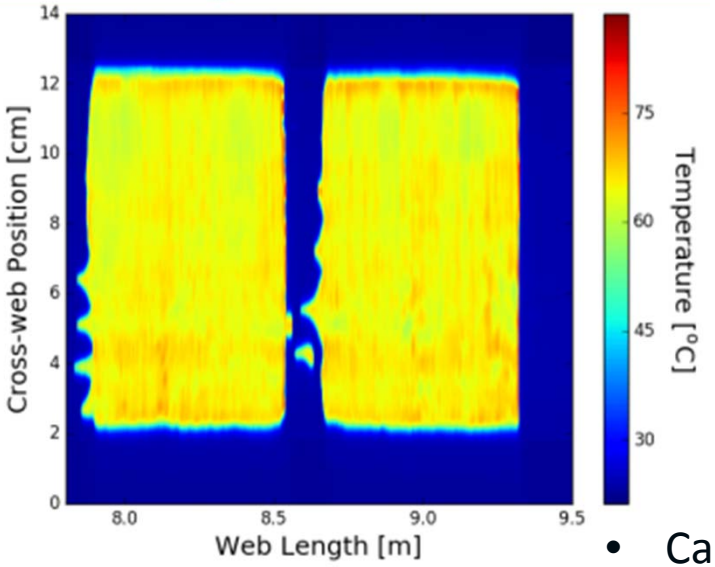

Ulsh, 2017 AMR. MN001, 6/8/17 1:45 pm
Zenyuk, *J. Power Sources* **2016,** 332, 372-382.

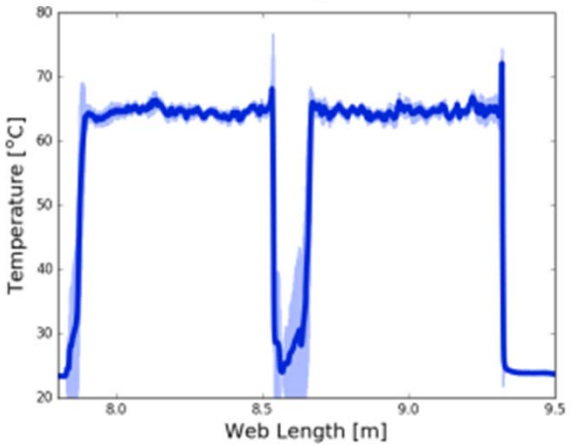
# Accomplishments and Progress
## Demonstrated Higher Loadings with Slot Die Coating

**Tensioned Web Over Slot Die Coating**




Pt/HSC, 50 wt% Pt
Nafion 1000 EW
3.2 wt% PtC
0.9 I:C
SGL 29BC



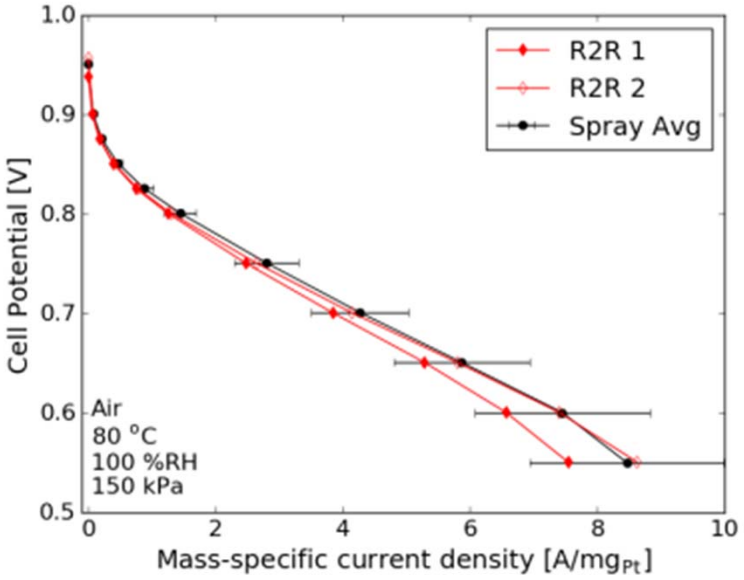
| | | |
|---|---|---|
| $T_{avg}$ | 64.5 ˚C | 64.6 ˚C |
| $T_{StDev}$ | 1.2 ˚C | 1.3 ˚C |
| Avg Loading | 0.215 $mg_{Pt}/cm^2$ | 0.196 $mg_{Pt}/cm^2$ |
| Std Dev. | 0.075 $mg_{Pt}/cm^2$ | 0.066 $mg_{Pt}/cm^2$ |

- Can coat thicker films than with gravure
- Coating less uniform than gravure, thus far
- Variation in temperature does not correlate well with XRF
- Process improvements and more data analysis needed

# Accomplishments and Progress:

## Achieved Comparable High-Current Density Performance between Gravure R2R and Spray

### Pt/HSC CCDM Performance

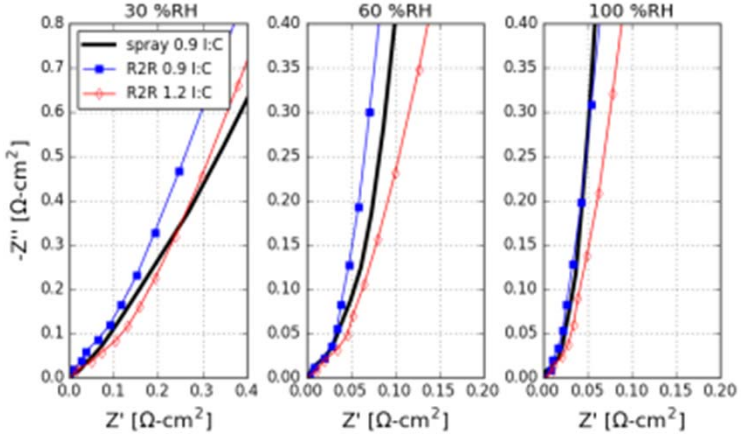



| Coating Method | ECA [m²/g] | $i_m^{0.9V}$ [mA/mg] | $i_s^{0.9V}$ [µA/cm2] |
|---|---|---|---|
| Spray Coated Avg | 76 ± 4 | 364 ± 66 | 460 ± 64 |
| R2R MEA 1 | 74.7 | 255 | 341 |
| R2R MEA 2 | 70.1 | 268 | 383 |

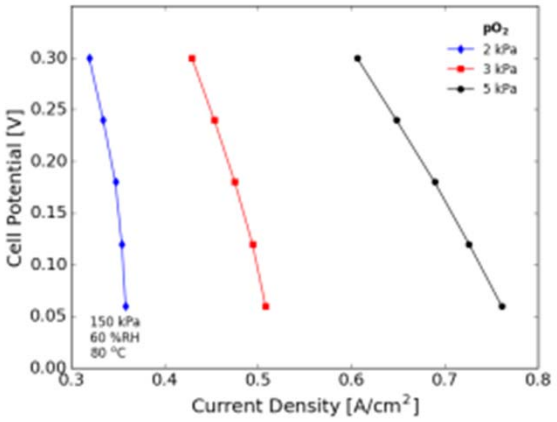
- Gravure-coated MEAs have inferior activity to spray-coated MEAs
- Comparable performance at high current density
- Similar proton resistance for spray and R2R
- Exploring diffusion limited current measurements to understand mass transport

### Advanced Diagnostics

*Electrochemical Impedance Spectroscopy*




*Diffusion Limited Current*





K. C. Neyerlin, et al., *ECS Meeting Abstracts,* **MA2016-02** (38), 2492 (2016).

A. Weber, AMR 2017 **FC137**: FC-PAD: Electrode Layers and Optimization

# Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year.

# Remaining Challenges and Barriers

- Improve R2R-coated electrode performance to match spray-coated electrode performance
  - Barriers: Understanding of R2R-coated electrode morphology, penetration of catalyst and/or ionomer into microporous layer, impact of ink formulation, polymer-catalyst interactions, and coating physics on electrode morphology and performance
- Improve uniformity of slot coated electrodes
  - Barriers: understand sources of variation
- Coat membranes with performance equivalent to commercially available products
  - Barriers: determination of optimal coating parameters, understand influence of environmental conditions

# Proposed Future Work

"Any proposed future work is subject to change based on funding levels"

**FY2017**

- Improvement in R2R-coated electrode performance through improved understanding of materials-property-performance relationships
  - Influence of coating physics, rheology, interparticle forces on electrode morphology
  - Effects of electrode morphology on electrochemical properties, proton resistance, and oxygen transport
  - Utilize TEM (K. More, ORNL) to characterize morphology, thickness-dependent composition
- Low Pt loaded electrodes
- Coat electrodes onto transfer liner
- Coating and qualification of R2R-coated membranes (9/2017)
  - Influence of coating and drying physics on membrane properties
- Rheology of catalyst layer inks
  - Understand difference between Vulcan and high surface carbon catalyst supports
  - Examine ionomer to carbon ratio

**FY2018**

- Optimize electrode performance, more detailed parametric studies, durability

# Technology Transfer Activities

**Current Funding**

- Small Business Voucher with Altergy
  - High-speed spray coating of PEMFC electrodes
  - Leverages knowledge of concentrated inks
  - Increased throughput by 100x over NREL's standard spray coating procedure

**Potential Future Funding for R2R research**

- SBV
- AMO R2R FOA
- AMO R2R Consortium

# Summary

**Objective:** Study material-process-performance relationships for R2R PEMFC/EC cell materials to understand relationships between process science and material properties and performance

**Relevance:** Addressing MYRD&D milestones with lowest cost/highest throughput methods for production of FC materials.

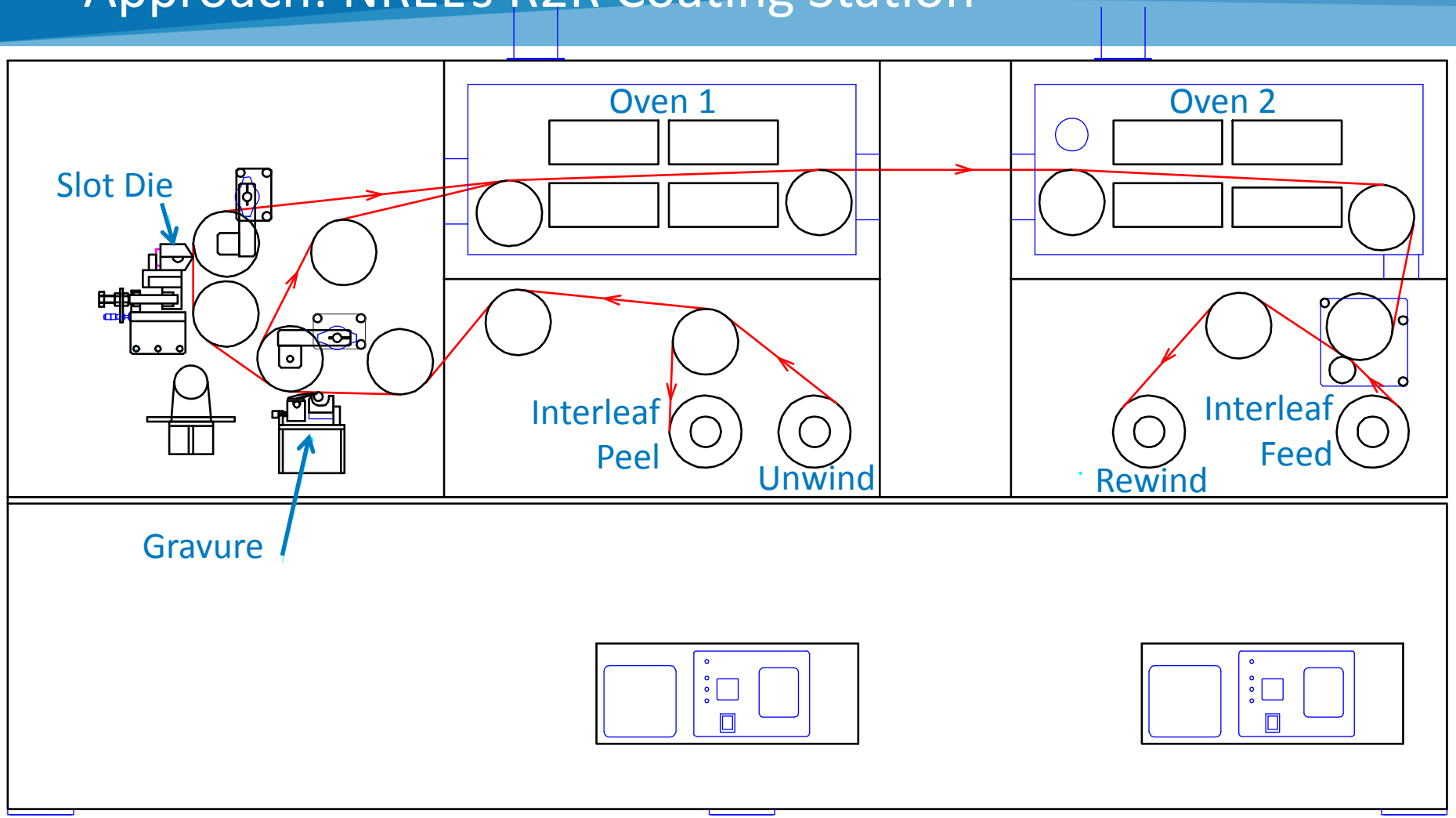
**Approach:** Understand impacts of substrate, ink formulation, coating and drying physics on film morphology, electrochemistry, proton conduction and mass transport

**Accomplishments:**

- Translated lab-scale electrode fabrication to R2R fabrication using two coating techniques
- Coated electrodes with 72% the mass activity of spray coated electrodes and equivalent high-current density performance.
- Leveraged FC-PAD-developed capabilities to determine correlations between process science, electrode morphology, and performance
- Discovered differences in rheological properties of supported catalyst inks suggesting differences in polymer-particle and/or particle-particle interactions

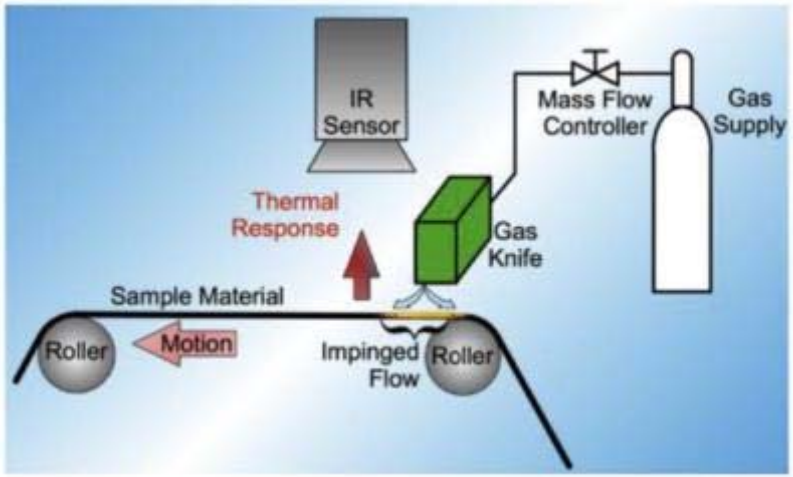
# Technical Backup Slides

# Approach: NREL's R2R Coating Station

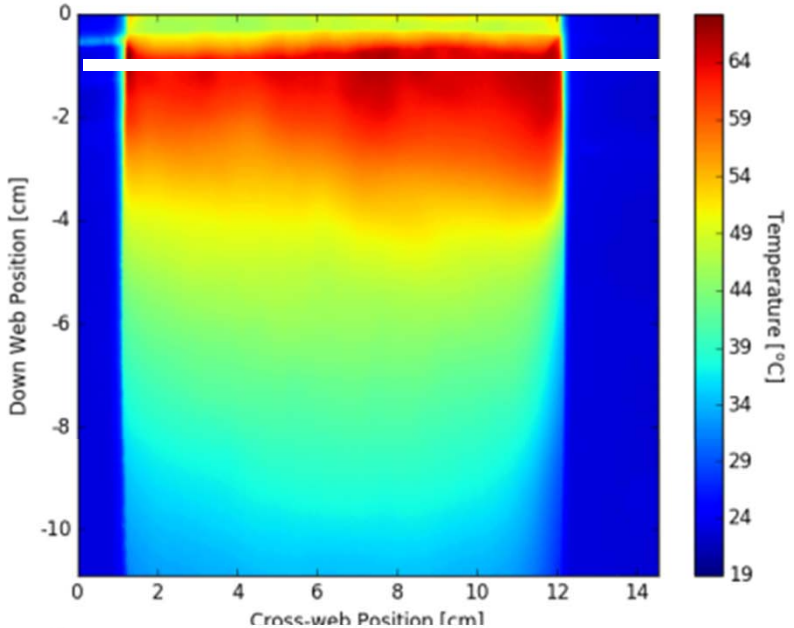


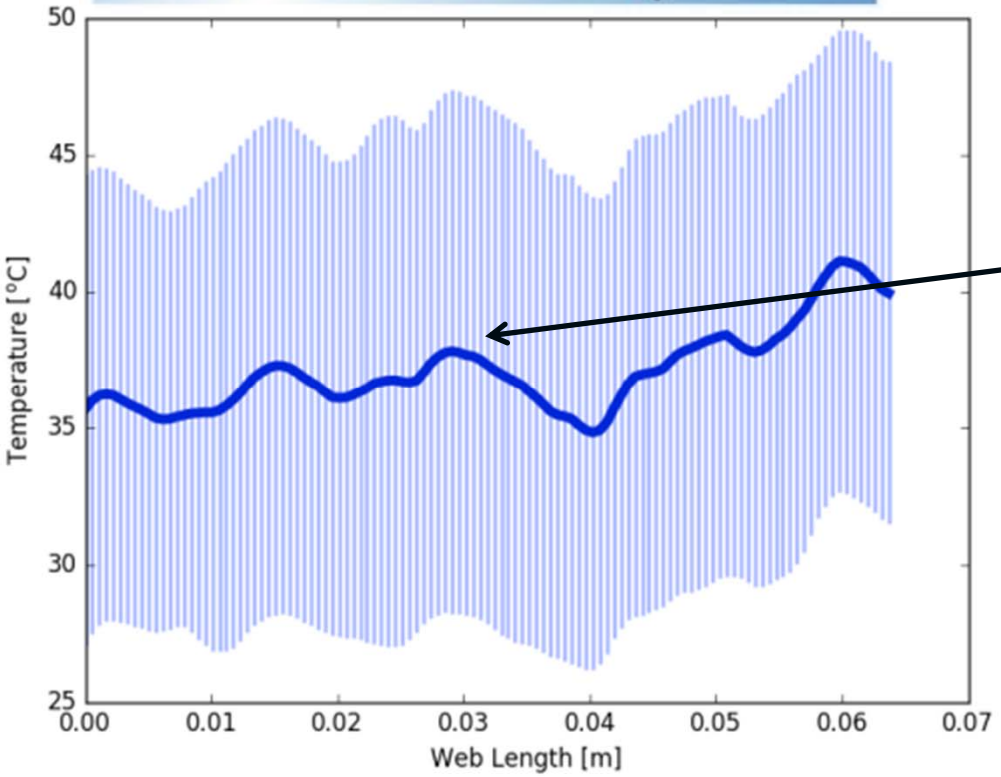

Web speed: 0.1 – 10 m/min
Oven temperature: up to 220 ˚C
Web width: up to 300 mm

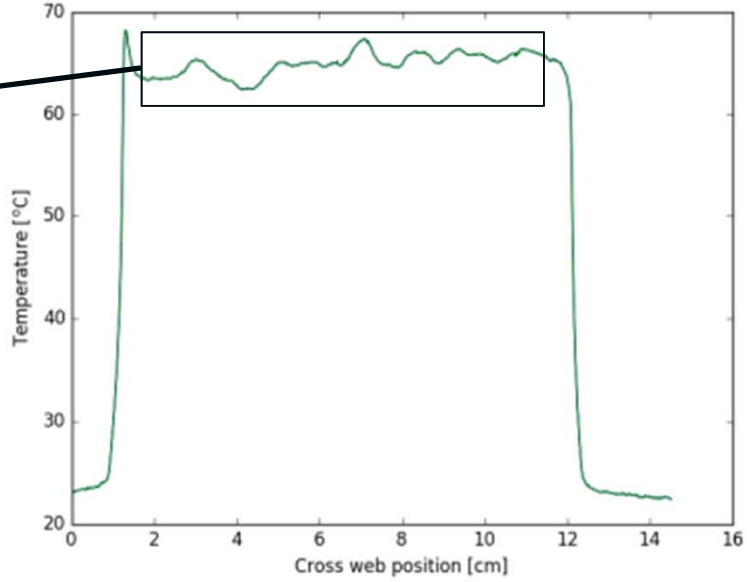
# Approach:
# Reactive Impinging Flow (RIF) of R2R Coated Materials



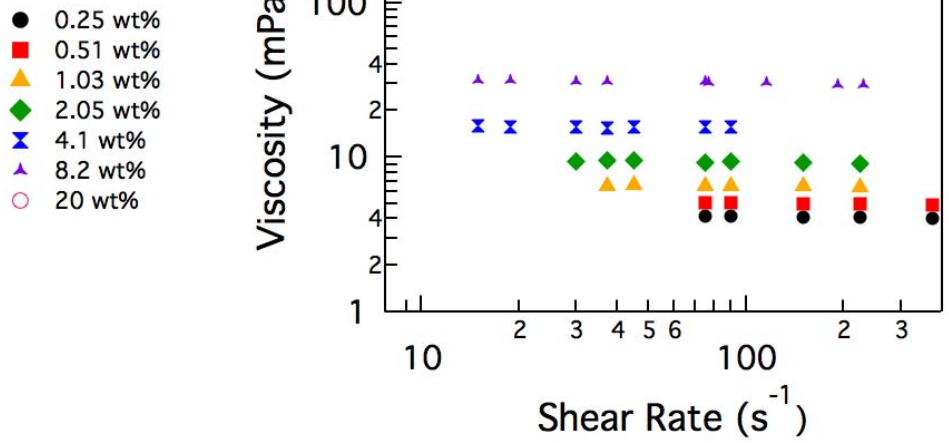

Zenyuk, *J. Power Sources* **2016**, 332, 372-382.

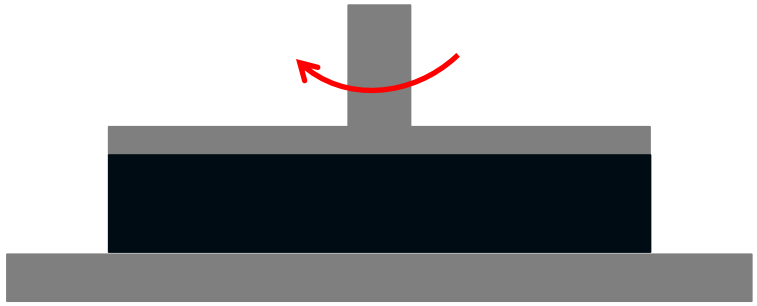
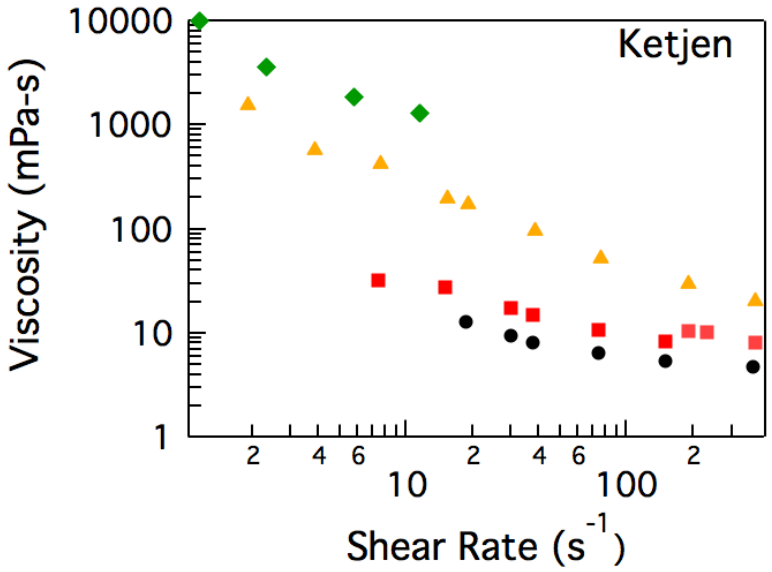
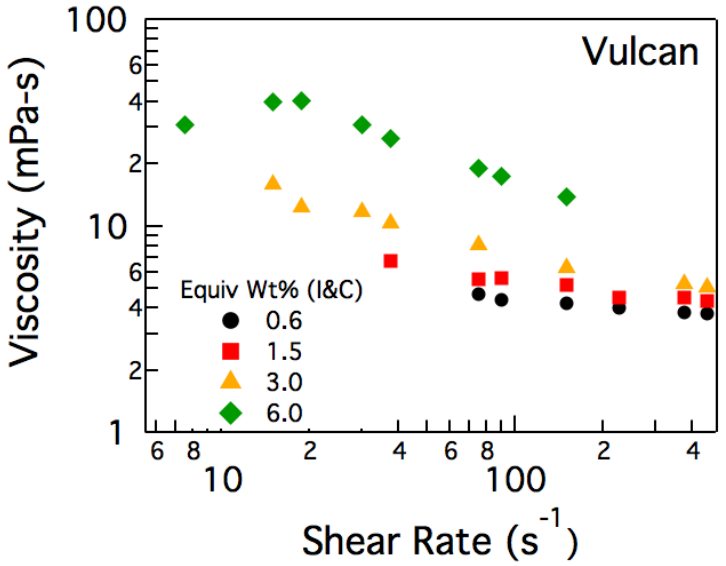


# Accomplishments and Progress: Measured Rheology of Individual Components






- Nafion: Newtonian, even at 20 wt%!
- Carbon blacks are shear thinning
- Higher viscosity of Ketjen due to ~4x higher void volume