AMM-R2R - Roll-to-Roll Manufacturing Science and Applications: Accelerate R2R Materials Manufacture for Energy Storage and Generation

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AMO Peer Review
Poster Presentation
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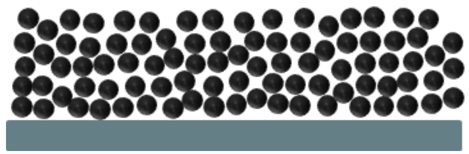
Project Objectives and Technical Innovation

1. Implement high-speed, low-cost R2R manufacturing methods for reaching ultimate lithium ion cell cost targets
2. Link electrode slurry processing parameters to cell performance
3. Develop optimized electrode architecture layering approaches common to many existing and emerging applications
4. Develop in-line metrology and non-destructive evaluation (NDE) for determining effect of coating defects on cell performance

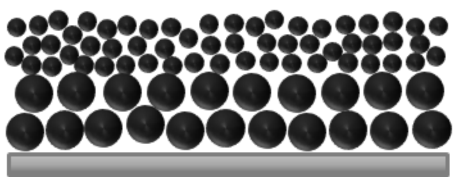
- Combination of graded electrode lithium-ion battery architectures with novel processing, process modeling and novel in-line process modeling to solve known problem of thick electrode mass-transport limitations.
- Understanding the rheological properties of electrode slurries is highly desirable for optimizing and reducing the cost of lithium ion battery manufacturing and achieving bilayer/multilayer electrode architectures.

Technical Approach
Pouch Cell Testing Matrix

Cathodes



Cathode #1:
All Small Particles

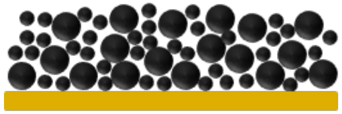


Cathode #3:
Dual-Pass: Large Bottom/Small Top

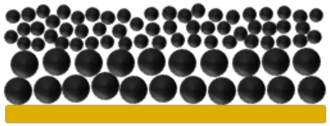
- Fabricate and test all combinations of 2 cathodes and 6 anodes

Anodes

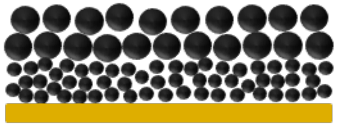
Anode #1:
All Small Particles



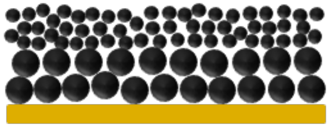
Anode #2: Mixed Particles



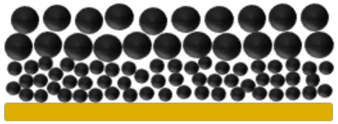
Anode #3:
Dual-Pass Large Bottom/Small Top



Anode #4:
Dual-Pass Small Bottom/Large Top



Anode #5:
Single-Pass: Large Bottom/Small Top



Anode #6:
Single-Pass Small Bottom/Large Top

Anode #7:
All Large Particles

Accomplishments and Progress

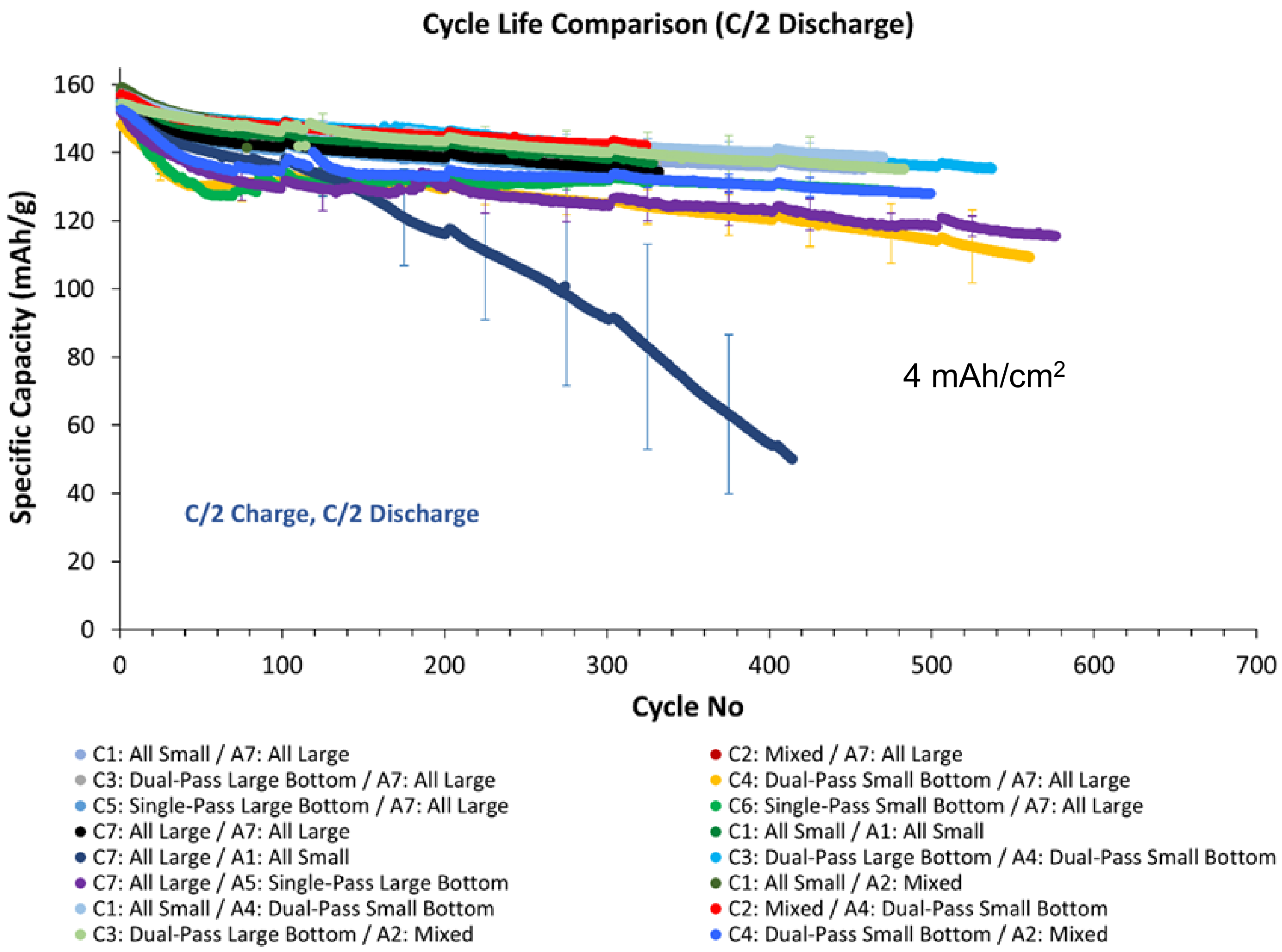
Dual-Pass Electrodes Generally Outperform Single-Pass (Dual Slot-Die)

Cycle Life (2C Discharge)			Rate Performance (2C Discharge)	
Cell Combination	**Final Capacity (Avg of Last 50 Cycles) (mAh/g)**	**Final Capacity Retention (Avg of Last 50 Cycles)**	**Cell Combination**	**Capacity Retention at 2C**
C2 / A4	35	35%	C3 / A4	59%
C1 / A4	35	34%	C1 / A7	55%
C1 / A2	31	34%	C1 / A4	54%
C1 / A1	31	36%	C3 / A2	53%
C3 / A4	31	30%	C1 / A2	53%
C2 / A7	30	33%	C3 / A7	47%
C5 / A7	29	32%	C2 / A4	46%
C1 / A7	29	29%	C2 / A7	41%
C3 / A7	23	22%	C1 / A1	40%
C6 / A7	22	31%	C5 / A7	40%
C3 / A2	21	23%	C4 / A2	30%
C4 / A2	21	26%	C7 / A7	30%
C4 / A7	20	28%	C6 / A7	29%
C7 / A1	15	23%	C4 / A7	28%
C7 / A7	15	21%	C7 / A1	28%
C7 / A5	12	22%	C7 / A5	25%

- SEM cross-sections verified that electrode structures were similar for single-pass and dual-pass coatings.
- Two graded configurations outperformed the all-small-particle cathode baseline.
- All-large-particle cathode baseline was one of the worst performers.
- Generally good agreement between the rate capacity results and the cycle-life results.

Accomplishments and Progress

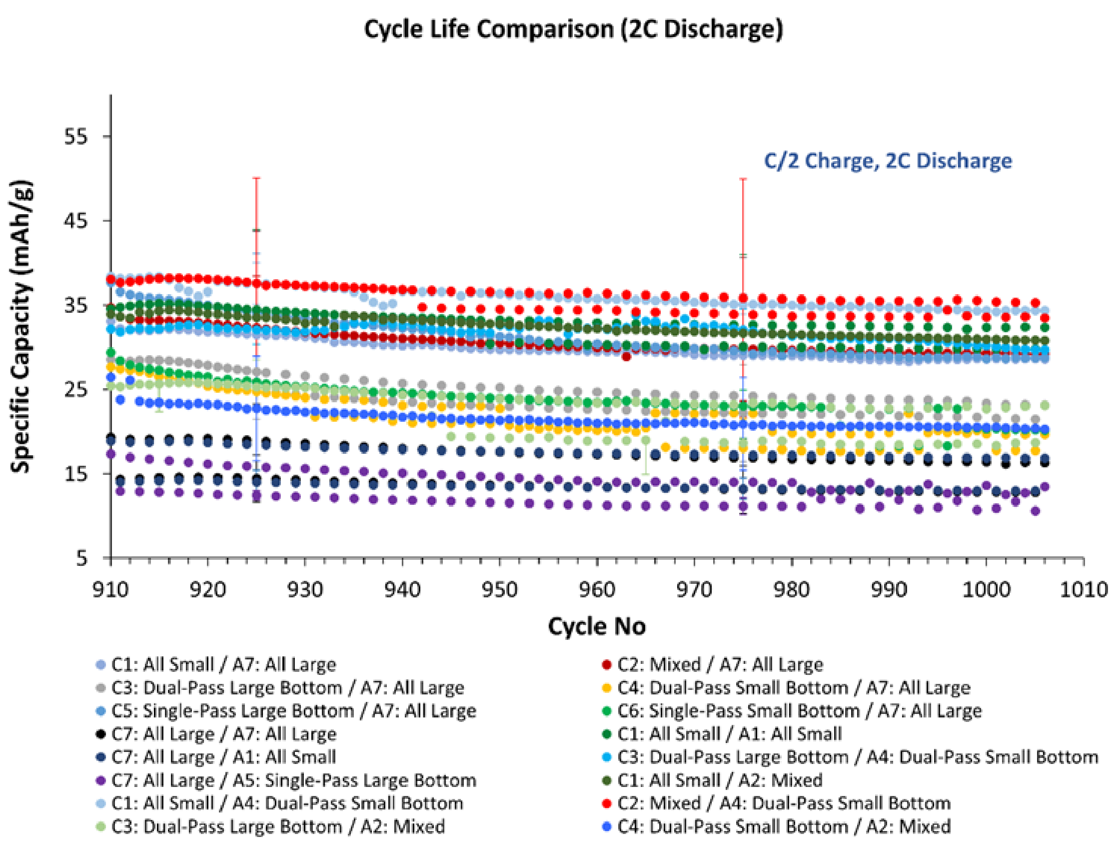
Excellent Capacity Retention Under Extended USABC Cycling at 0.33C/-0.33C Charge/Discharge Rates



Accomplishments and Progress

Particle Size and Porosity Grading Both Make a Substantial Difference in Capacity Retention at 2C Discharge Rates (Accelerated Durability Testing)

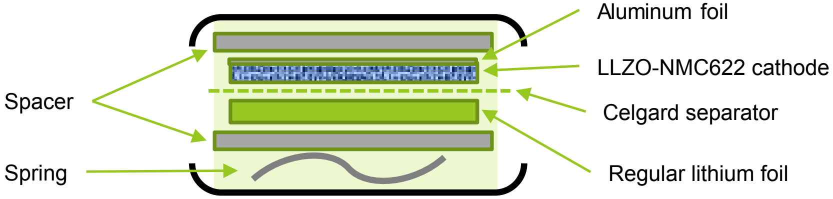
b)

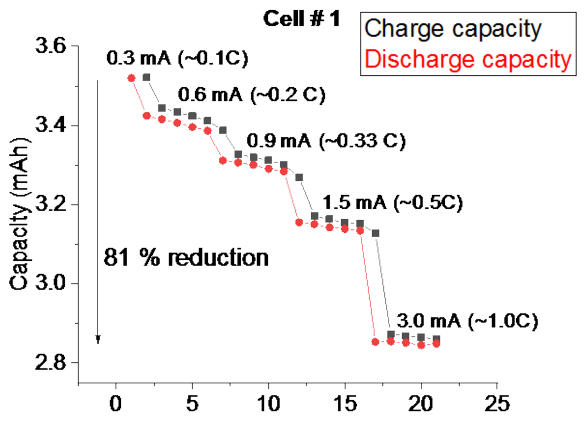


- Best long-term performer was a mixed particle cathode with a dual-pass, small-particle bottom layer.
- Worst performer was the all-large particle cathode paired with a single-pass, large-particle bottom layer.
- Worse performance for single-pass (dual slot-die coating) cases is likely due to unoptimized drying protocol.

Fisker/LBNL/ORNL CRADA project: Freeze Tape Casting of LLZO Electrodes

- Purpose: Development of novel high-energy-density solid-state lithium batteries based on $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte and high-capacity cathode active materials.
- Technical Innovation: Application of freeze tape casting to make thin dense LLZO electrolyte layers and vertically porous cathode scaffolds with LLZO.
- Technical Approach
  - Freeze tape casting of LLZO electrolyte bilayers
  - Novel freeze drying and sintering protocols to obtain LLZO cubic phase
  - Infiltration of cathode active material into LLZO scaffold pores
  - Evaluation of hybrid coin cells with liquid electrolyte added to cathode
- Accomplishments and Progress
  - Developed a novel formulation protocol for LLZO slurries
  - Successful freeze tape casting of LLZO bilayers
  - High ionic conductivity obtained after sintering to LLZO cubic phase
  - Successful assembly of hybrid coin cells and rate capability testing
- Next steps
  - Increase freeze tape casting coating length
  - Apply Li anode to LLZO/cathode bilayer via evaporation
  - Assemble full pouch cell and test for rate capability and cycle life

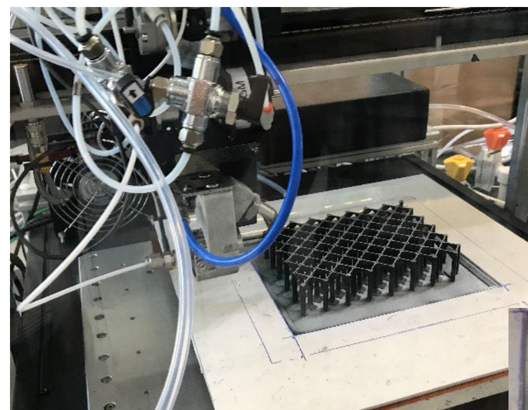


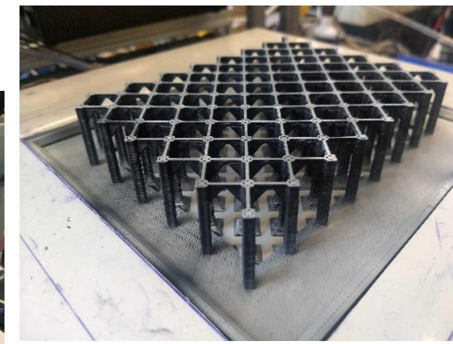


Hybrid coin cell rate capability results with Gen 2 electrolyte addition to cathode

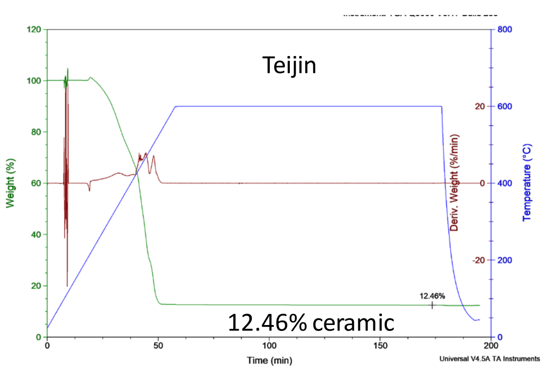
Navitas Systems/ORNL/NREL CRADA project: LIB Separator Coatings

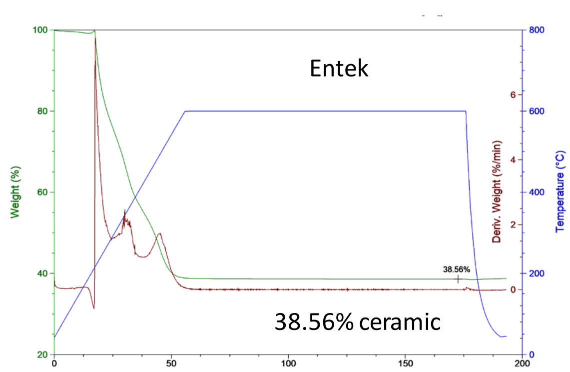
- Purpose: Improve the stability and lifetime of LIB separators
- Technical Innovation: Explore ceramic separator coatings to improve properties
- Technical Approach
  - Identify ceramic materials to provide improved thermal and mechanical stability
  - Develop ceramic slurries and characterize properties
  - Perform uniform and patterned coatings
  - Test cells to understand improvements
- Accomplishments and Progress
  - Characterized slurries by TGA, SEM, XRD
  - Performed uniform coatings
  - Performed patterned spray coatings
- Next steps
  - Make interdigitated spray coatings
  - Test cells
  - Demonstrate R2R pattern-coating





Patterned spray coating





TGA to determine ceramic content

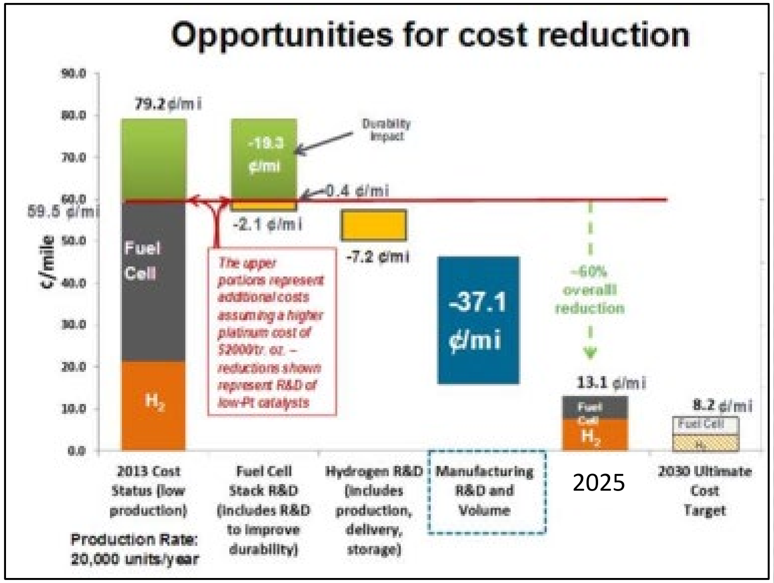
Project Objectives

Relevance

- R2R is the only manufacturing process platform that will meet cost and volume targets for MEAs
- All DOE-sponsored cost analyses for high volume production of MEAs/cells assume R2R processing
- Cost reduction need: 60 cents/mile in 2013 to 13 cents/mile in 2025

Objective

- Develop single-step coating process for direct coating of electrodes



FCTO MYRDD Plan

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

Technical Innovation

- Current standard manufacturing practice for most PEM MEAs is by fabricating catalyst-coated membranes (CCM)
  - The electrodes are coated onto separate transfer liners and then hot-pressed onto the membrane, or
  - The electrodes are directly coated onto the membrane
- Limitations to CCM production
  - The former method entails multiple additional steps and materials, due to the use of a transfer liner
  - The latter is very difficult due to swelling of the membrane during solvent- or aqueous-coating of the electrodes

Production Volume (sys/yr)	1000	10,000	20,000	50,000	100,000	500,000
m^2 active area/yr	7,470	74,702	149,404	373,511	747,022	3,735,111
Slot die coating process ($/m^2) - Direct or Decal	$52.59	$9.14	$4.92	$4.00	$2.93	**$1.30**
Total Additional Cost for Decal Transfer ($/m^2)	$9.19	$4.03	$3.63	$3.51	$2.26	**$2.17**
Total Cost of Catalyst Application with Decal Transfer ($/m2)	$61.77	$13.17	$8.55	$7.51	$5.19	$3.47
Additional Decal Transfer Cost (% of Coating Cost)	17%	44%	74%	88%	77%	**167%**

At high volumes, direct electrode coating would provide significant cost reduction for electrode production

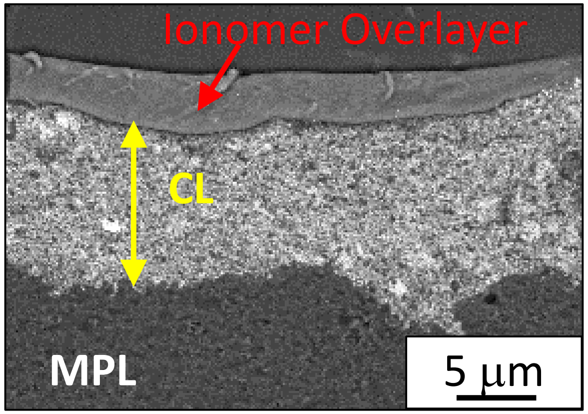
Technical Innovation

The goal of this project is to explore, understand and optimize material and process parameters for single-process (no extra ionomer over-layer) R2R manufacturing of direct-coated GDEs with comparable performance to CCMs

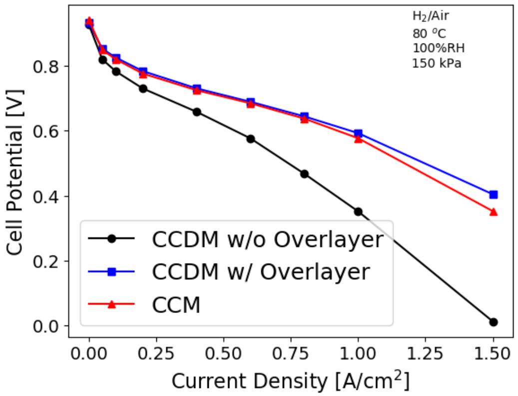
- Gas diffusion electrodes (GDE) are recently becoming of more interest in the industry as a pathway for MEAs
  - The different structure of GDEs may provide improved performance and lifetime under some operating conditions
  - GDEs may also be easier to fabricate
    - Deposition onto the low-strength, highly liquid sensitive (hygroscopic) membrane is eliminated
    - Use of transfer liners is eliminated (liner + hot pressing process = 63% of process cost for decal-based CCM)
- However, it appears that an over-layer of ionomer is required for GDEs to achieve performance comparable to CCMs

Impact

- ***Developing a direct-coating pathway will enable faster, simpler, cheaper manufacturing of fuel cell electrodes***



TEM of spray-coated GDE with ionomer over-layer (left); Performance comparison between lab-scale spray-coated CCM baseline and GDEs with and without over-layer (right)



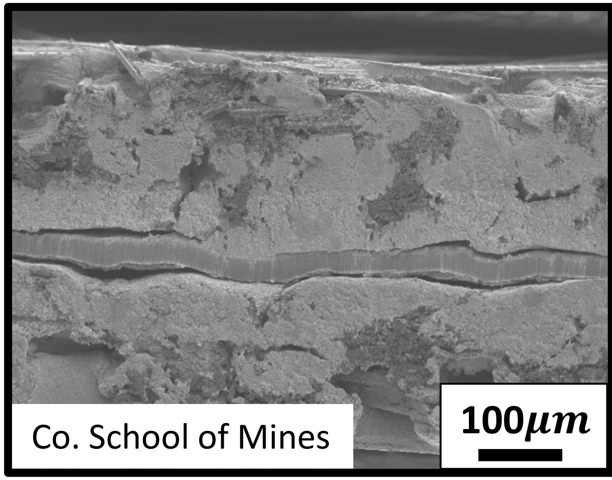
Technical Approach

- Through exploring a combination of ink formulation, cell materials, and processing, develop a method for fabricating high-performance GDEs

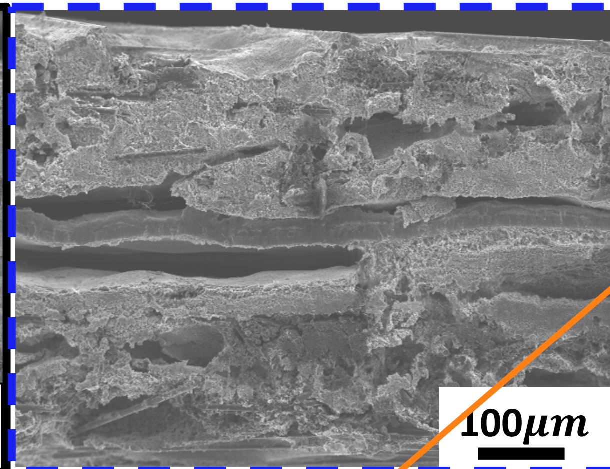
- Gas diffusion electrode studies
  - Gravure, slot die, and dual-slot coating (NREL, ORNL)
  - Coating consolidation modeling (LBNL)
  - XCT, Electron Microscopy, Kelvin Probe and XRF characterization (ANL, ORNL, NREL)
- Ink studies
  - Formulation, mixing and rheology (NREL, ORNL)
  - USAXS characterization (ANL)
  - Rheological modeling (LBNL)
- MEA fabrication and testing (NREL)
- QC development (NREL, ORNL)

Accomplishments and Progress
Determined Function of Ionomer Overlayer

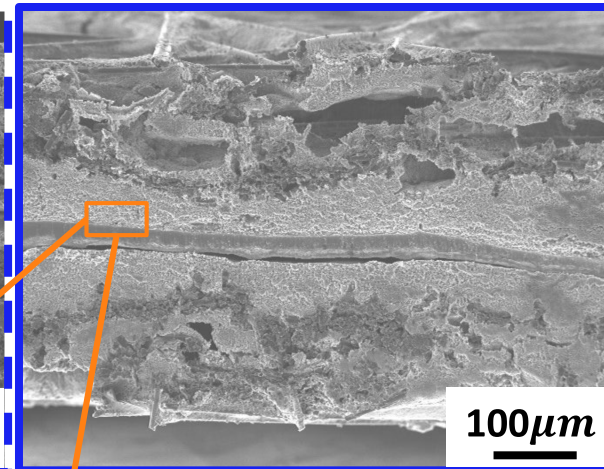
Without Overlayer
Hot Pressed

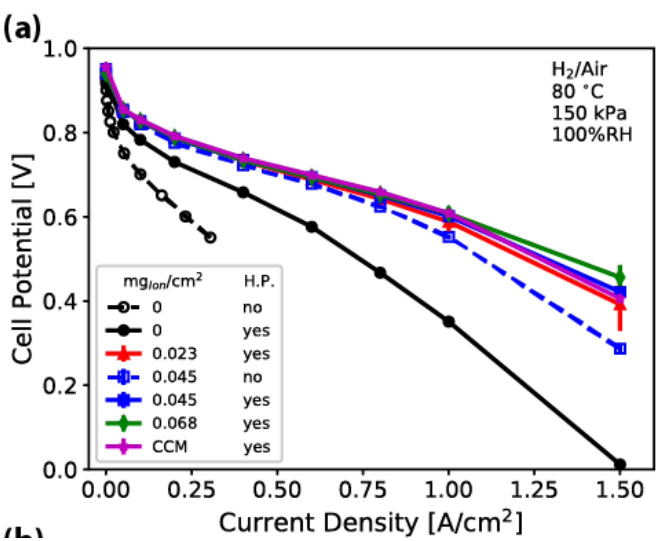


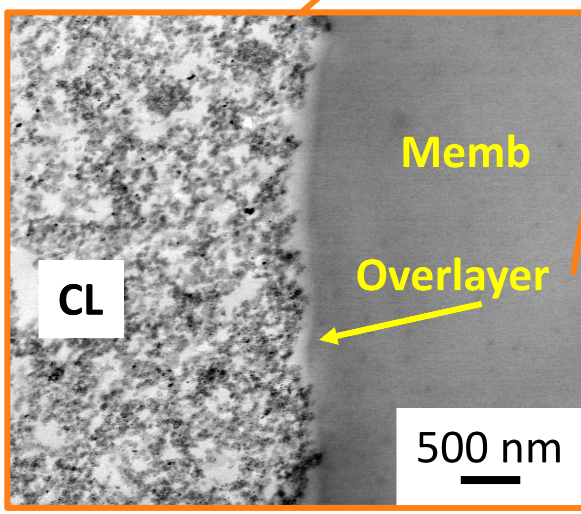
With Overlayer
Not Hot Pressed



With Overlayer
Hot Pressed



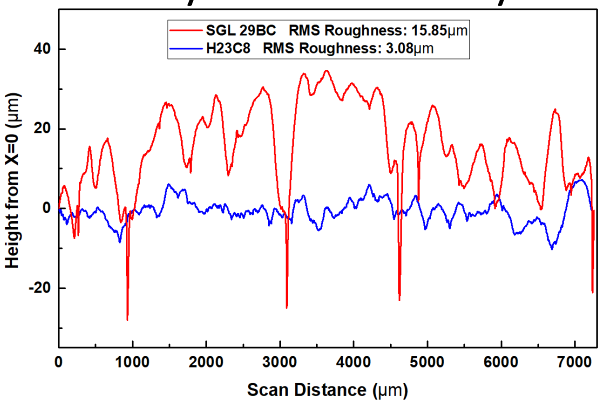




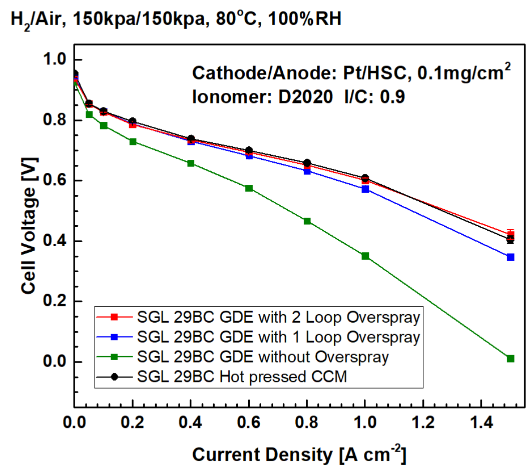
- ***Function:** Ionomer overlayer AND hot pressing* needed to adhere GDE and membrane and create good interface
- Ionomer overlayer is thin: approx. 100-200 nm
- Good interface needed for best performance

Accomplishments and Progress
Determined Influence of MPL Roughness

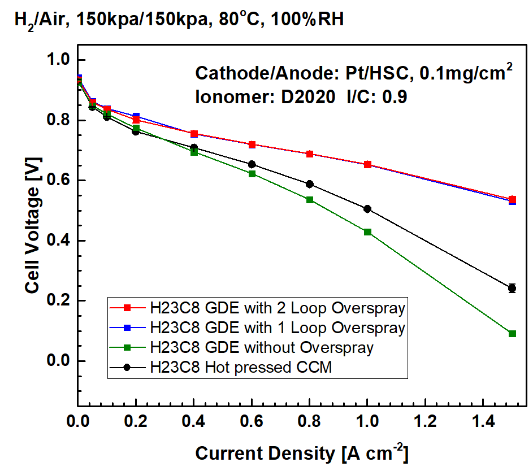
Stylus Profilometry



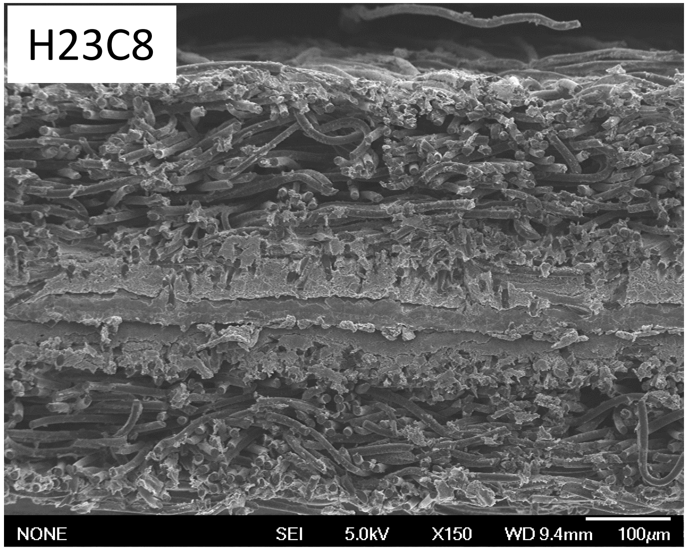
SGL 29BC - Rough



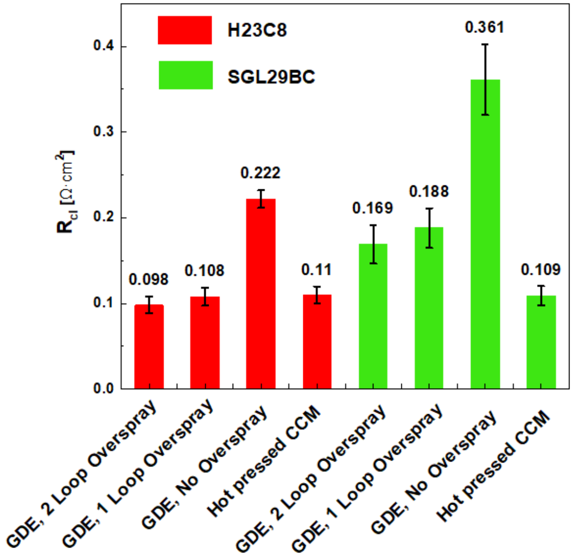
H23C8 - Smooth



MEA Cross-Section



EIS Modeling

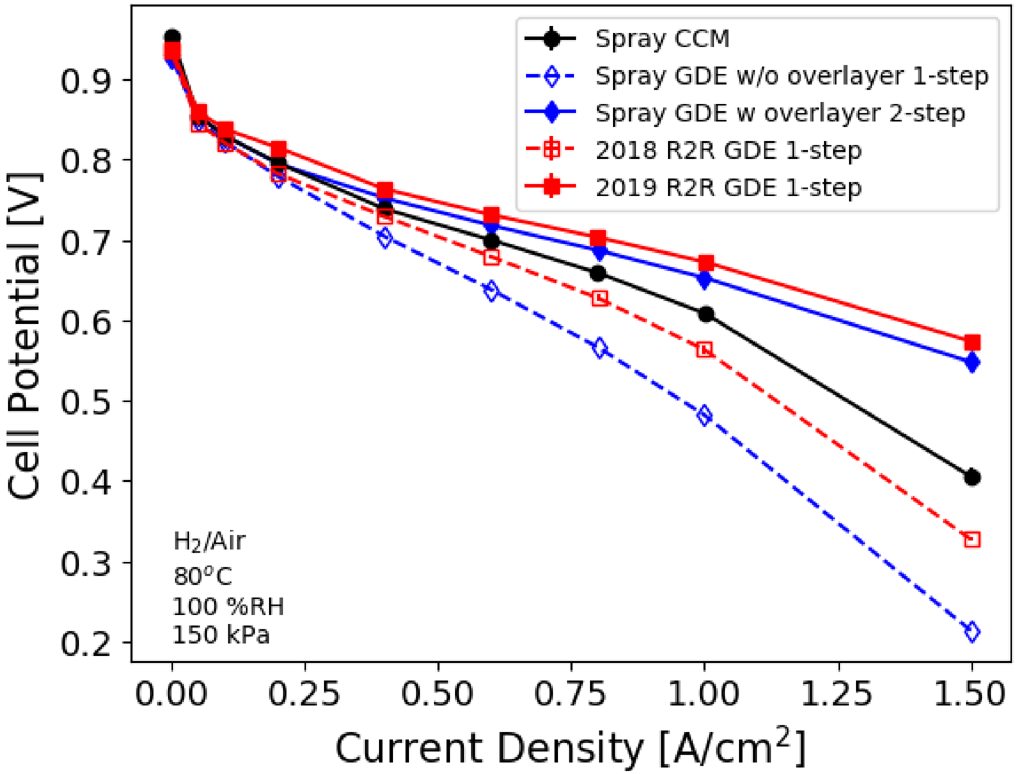


Smoother MPL leads to:

- Less ionomer needed in overlayer
- Lower catalyst layer proton resistance (R_{CL})
- Expected to be better for R2R GDEs

Accomplishments and Progress
Single-Process R2R GDE Surpasses Project Goal

We achieved single-process (no extra ionomer over-layer) R2R manufacturing of GDEs with comparable performance to CCMs



<u>R2R Coated GDEs</u>

Slot die (2019), Gravure (2018)

1 m/min x 9 cm

Cathode loading: 0.12 mg_{Pt}/cm^2

Pt/HSC – Nafion (0.9 I/C)

Coating speed: 1 m/min

<u>2018 vs 2019</u>

- Switch to smooth MPL
- Switched from gravure to slot-die coating (see TA008)
- Reduced I:C (1.6 → 0.9)

<u>Keys to High Performance R2R GDEs</u>

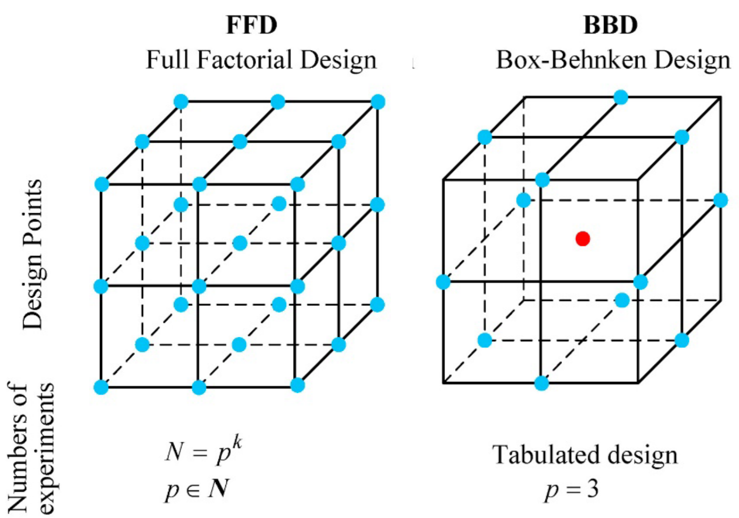
- **Water-rich catalyst ink**
- **GDL with smooth MPL**
- **Slot die coating vs ultrasonic spray**

- Many technologies (e.g. water filtration membranes, fuel cell and electrolyzers, photovoltaics, batteries, and barrier films) are multilayer constructions that are coated through a series of coating and drying steps
- Multilayer coating processes enable the co-deposition of multiple layers, reducing capital and process costs and increasing throughput
- Multilayer coating presents a challenges as the properties of each layer must be tuned relative to the adjacent layers to enable stable flows and coatings while simultaneously achieving the requisite thickness and functional properties
- Multilayer coating may also enable new device constructions or manufacturing pathways that are not currently accessible with sequential, single layer coatings

Technical Approach – Ink Formulation

- Slide coating requires ink properties to be tuned to enable stable flows
- Many aspect of an ink can be adjusted to affect a specific property
- Design of Experiments (DOE) methods being used to determine correlations between ink formulation and properties and reduce number of experiments
- Future work will couple flow modeling with ink formulation and coating to validate models and produce high-quality coatings

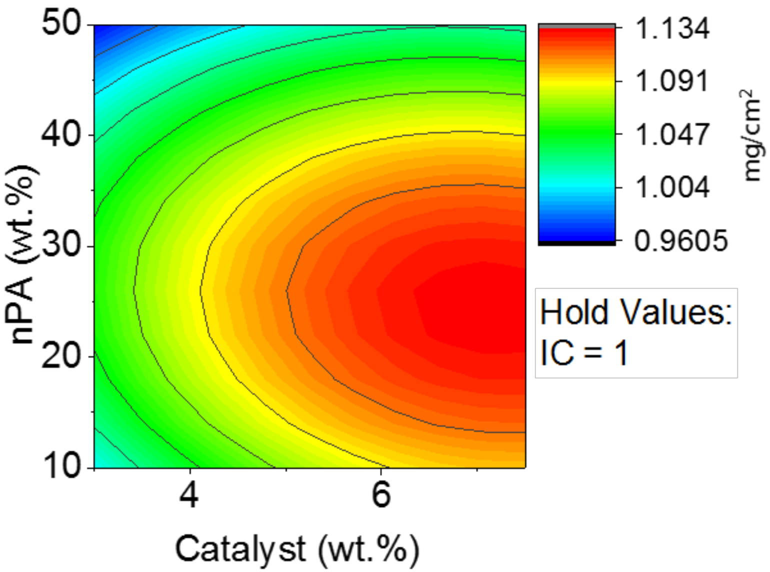
DOE Experimental Matrix



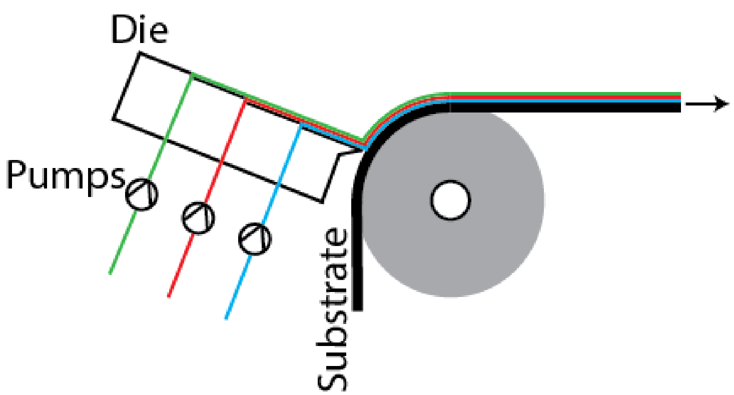
27 cases (FFD) → 15 cases (BBD)

Lian, Binbin, Tao Sun, and Yimin Song. *Robotics and Computer-Integrated Manufacturing* 46 (2017): 1-14.

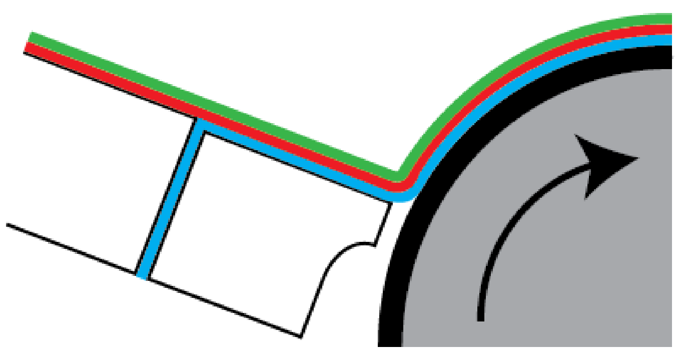
Contour Plot of Catalyst Ink Density



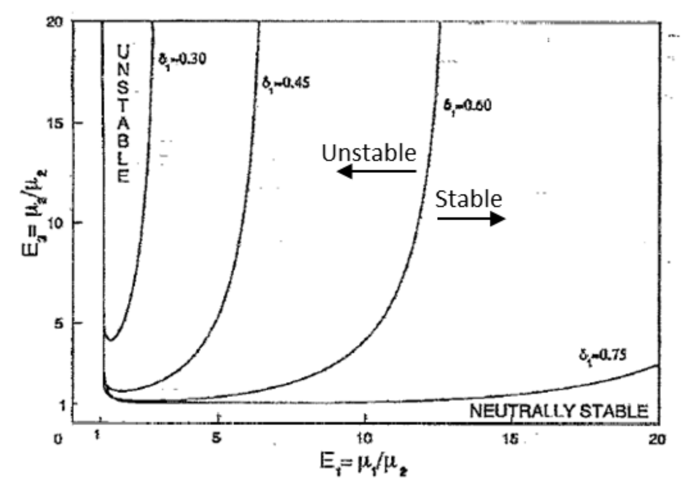
Technical Approach - Multilayer Slide Coating



- Technology developed by photographic film industry but there are few reports in technical literature and it has not been applied to DOE-funded technologies
- The properties of each layer (density, viscosity, surface tension) must be tuned to prevent flow instabilities
- Flow modeling provides guidance on stable flow regimes and can guide ink formulation



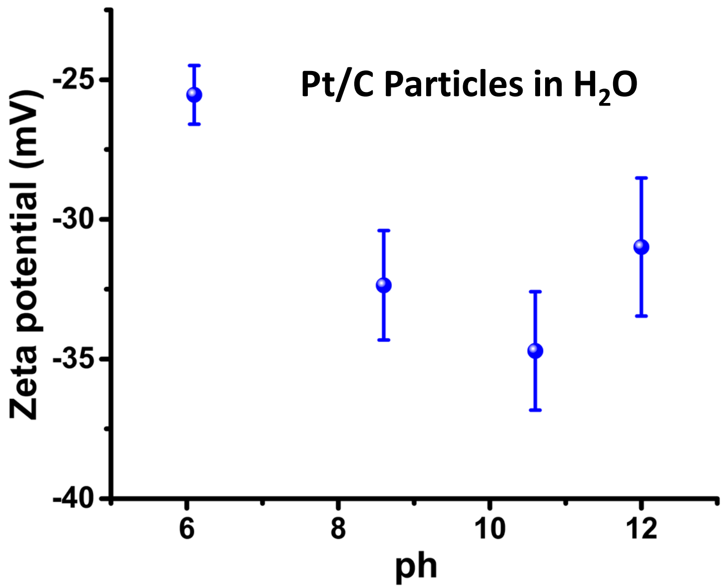
<u>Impact of Viscosity Ratios and Layer Thickness on Stability</u>



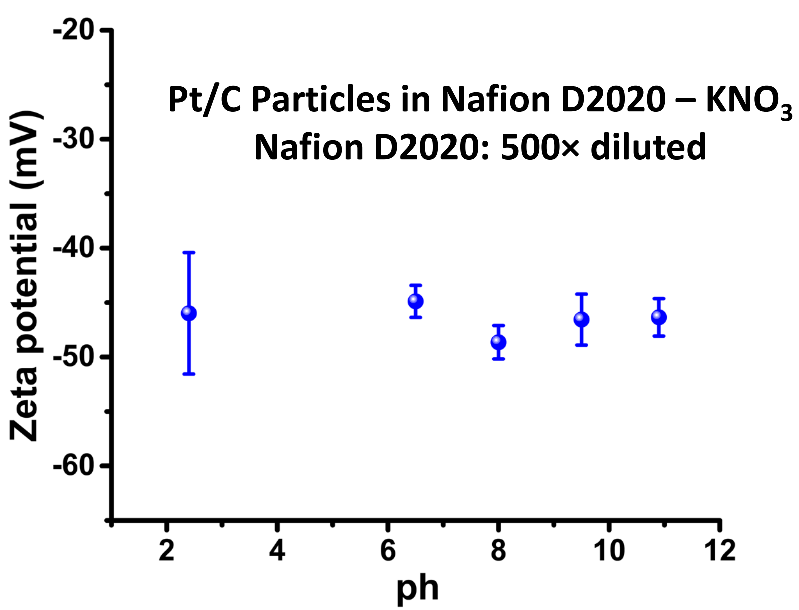
Weinstein and Kurz, *Phys. Fluids A* **3** *(11), 1991*

Accomplishments and Progress
Ink Characterization (Zeta Potential)

- Nafion and 1-propanol Are Effective at Stabilizing the Surface Charge of Pt/C Particle Dispersions



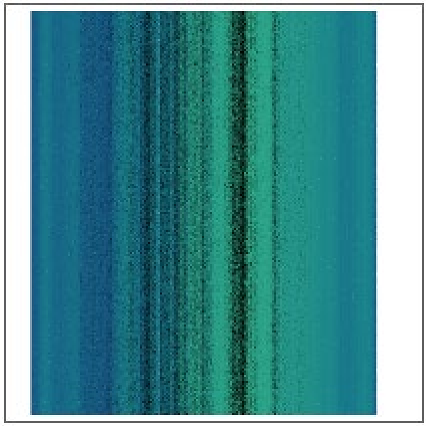
wt. fraction (D2020)	
Nafion	0.2
1-propanol	0.46
Water	0.34



Accomplishments and Progress
In-line Metrology for Membranes

- Continued to study multi-spectral techniques for in-line real-time imaging of thickness of commercially available, proprietary, and experimental polymer films for various applications, including barrier films and energy conversion
  - Performed UV-Vis and near-IR fast spectroscopy (single-point) to establish feasibility of the method on a range of membrane materials and structures
  - One output is that membranes thicker than ~50 µm (required for many applications) will require a higher wavelength range than our current imager
  - Performed thickness imaging in-line on a 100+ meter roll with several membrane materials

NREL metrology web-line with multi-spectral imager, multiple light source, and membrane web path (below) in a reflectance configuration for thickness imaging



In-line thickness map of a commercial barrier film