Roll-to-Roll Advanced Materials Manufacturing Lab Collaboration

Collaboration Lead: Claus Daniel (ORNL)
Email: danielc@ornl.gov; Phone: 865-946-1544

Argonne National Laboratory Lead: Gregory Krumdick

Lawrence Berkeley National Laboratory Lead: Vince Battaglia

National Renewable Energy Laboratory Lead: Michael Ulsh

Sandia National Laboratory Lead: Randy Schunk

Oak Ridge National Laboratory Lead: David Wood

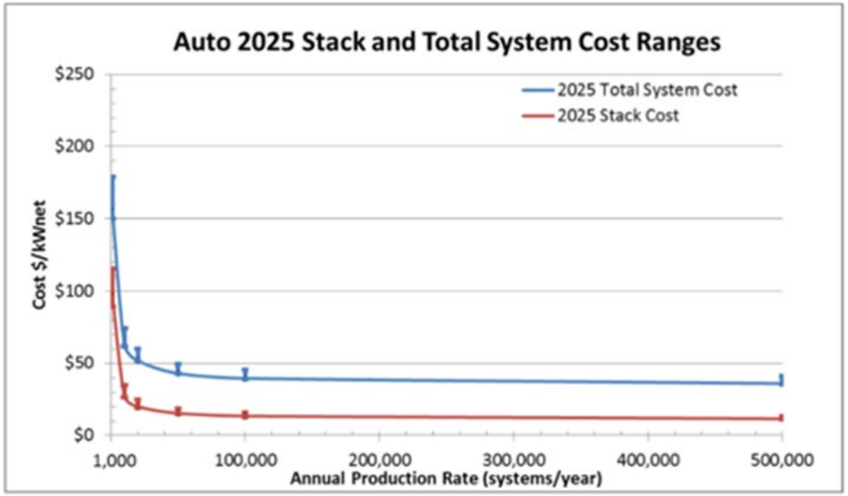
Presenter: David Wood
2020 Hydrogen and Fuel Cells Program
Annual Merit Review
May 21, 2020
Project ID: TA007

Collaboration Update From Last Year

- FCTO and AMO are cost sharing a CRADA at 50/50 ($150K from AMO and $150K from FCTO) with Nel Hydrogen totaling $600K with $300K in-kind from Nel Hydrogen.
- The AMO Collaboration is being supported by FCTO with $850K cost share in addition to AMO's $3M FY20 investment.
  - Scope of work based on input from FC/LTE industry (Nel Hydrogen, Giner Inc., GM, and Plug Power Inc.) and specific to FC/LTE materials
- This presentation will review progress on AMO funded tasks related to fuel cell and electrolysis MEA development.

Relevance

- R2R is the only manufacturing process platform that will meet cost and volume targets for MEAs.
- R2R enables conversion of multiple dissimilar materials into a multi-layer cell.
- All DOE-sponsored cost analyses for high-volume production of MEAs/cells assume R2R processing.
- Cost reduction is needed from ~$125/kW at current production levels (several thousand vehicles per year) to $30/kW ultimate target (at several hundred thousand vehicles per year).



Source: Mass Production Cost Estimation of Direct H2 PEM Fuel Cell Systems for Transportation Applications: 2017 Update, Strategic Analysis Inc.

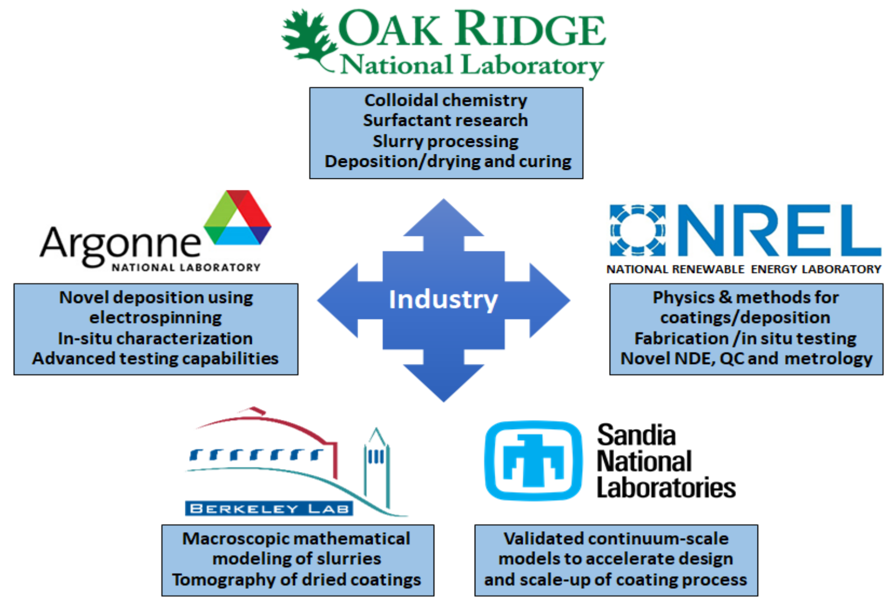
MYRDD Plan - Manufacturing R&D

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.

Approach: Advanced National Multi-Laboratory Roll-to-Roll R&D Collaboration

Challenges and Barriers

- Continuous processing
- Registration and alignment challenges
- Scalability
- Materials compatibility
- Defects in flexible electronics
- Stoichiometry control and bath depletion in electroplating systems
- Availability of materials data
- Real-time process models



Targets

- Develop technologies to reduce the cost per manufactured throughput of continuous R2R manufacturing processes.
- Develop in-line instrumentation tools that will evaluate the quality of single and multi-layer materials during processing.

Technical Approach

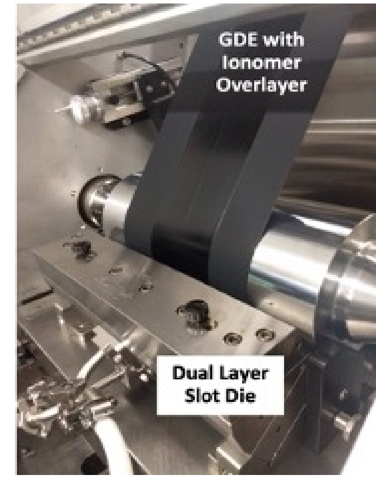
- Broad range of research task areas focused on roll-to-roll manufacturing
  - Coating, drying and consolidation modeling (LBNL, SNL)
  - Particle-scale ink modeling (LBNL)
  - Coating flow modeling (SNL)
  - Colloids and rheology studies (NREL, ORNL, SNL)
    - Ink characterization: USAXS, SANS (ANL, ORNL)
  - Coating Methodologies
    - Multilayer die coating studies (NREL, ORNL, SNL)
    - Electrospinning (ANL, ORNL, ANL)
  - Electrode characterization: XCT, electron microscopy, XRF (ANL, ORNL, NREL)
  - MEA fabrication and testing (NREL)
  - QC development (NREL)

- Task areas will include continued research on fuel cell and low-temperature electrolysis materials

Multilayer Coatings

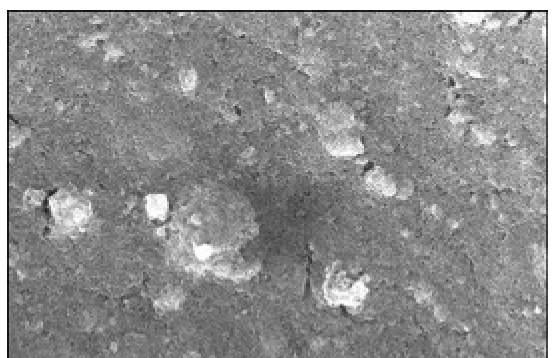
Accomplishments: High Concentration Inks and Multilayer Slot Coating (ORNL)

- Developed formulations and mixing conditions of high solids catalyst inks for multilayer slot-die coating:
  - 12 wt% solids ink formulated, mixed, and coated
  - Optimized coating conditions to achieve cathode target loading of 0.1 mg_{Pt}/cm^2
- Determined that rotor-stator mixer yielded dispersions with smaller agglomerates than blade mixer
- Conducted dual-layer slot coating of catalyst ink and ionomer dispersion



4 ft/min. 5.7 mL/min.

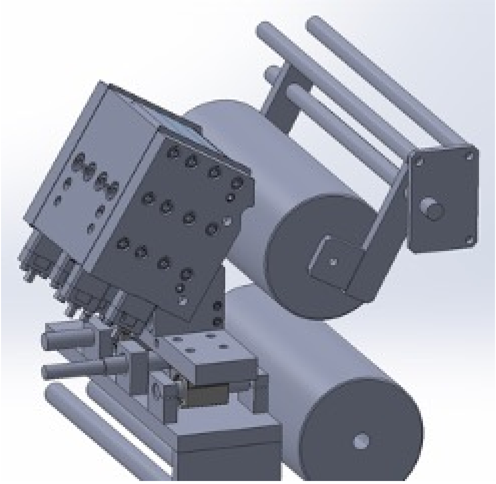
Blade Mixer

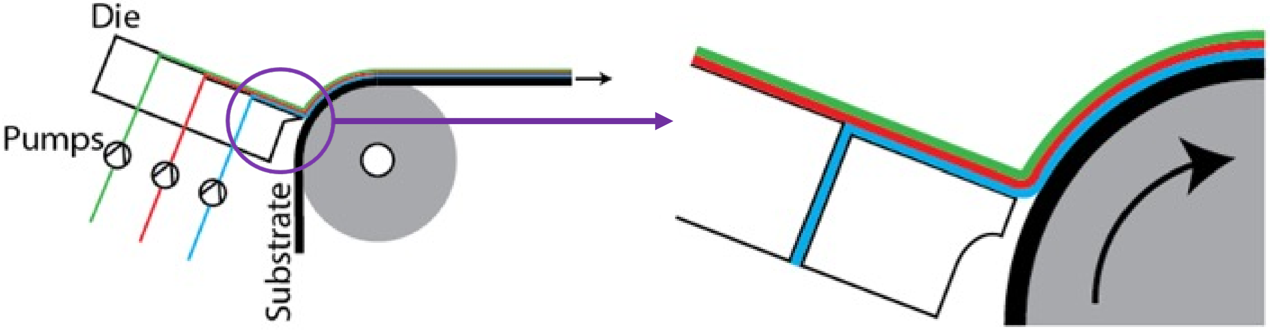


Rotor-Stator Mixer

Progress: Initiated Acquisition and Set-up of Multilayer Slide Die (NREL)

- Three-layer slide die acquired by NREL for coating studies (received late due to delays with manufacturer)
- R2R coating station being modified for mounting of die
- Test flow setup designed for slide flow tests
- Die will be used to coat multilayer structures for fuel cells and LTE
- Experimental data will be used to support SNL continuum models





Argonne National Laboratory · Berkeley Lab · NREL National Renewable Energy Laboratory · Oak Ridge National Laboratory · Sandia National Laboratories

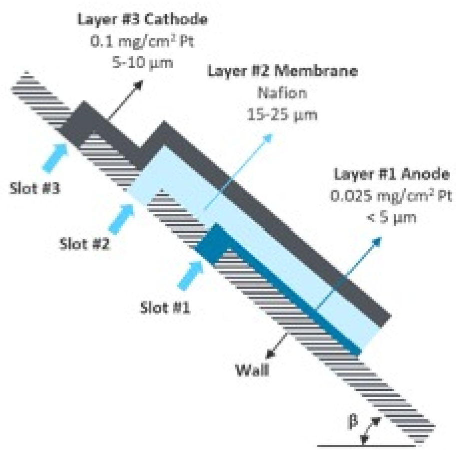
Accomplishments: Design of Experiments (DoE) to Parameterize Ink Formulation (NREL)

- Multilayer coating requires layer properties to be tuned for stable flows.
- Catalyst ink properties are sensitive to changes in formulation.
- Utilized Box-Behnken design for DoE.
- Parameterization allows for rational formulation of inks.

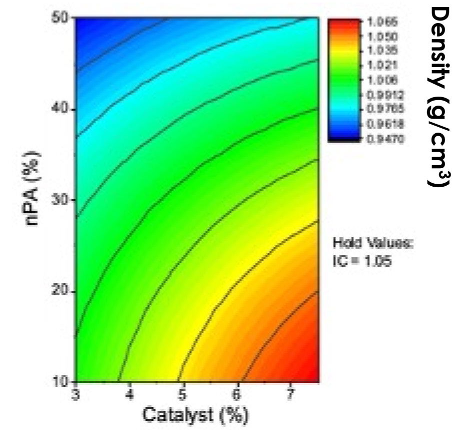
Ink Properties
- Density
- Viscosity
- Surface Tension

Formulation Variables
- Solid %
- I/C
- Water/1-propanol

CCM Coating



DoE Surface Plot



Parameters	Guidelines
Surface tension	$\sigma_3 < \sigma_2 < \sigma_1, \frac{\sigma_n}{\sigma_k} \approx 1$
Density	$\rho_1 < \rho_2 > \rho_3$
Viscosity	$\mu_1 < \mu_2 > \mu_3, \frac{\mu_n}{\mu_k} \approx 1$
Thickness	$t_1 < t_3 < t_2$

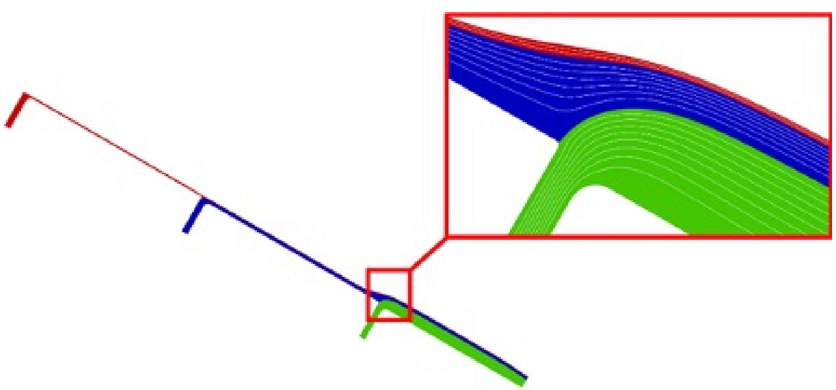
Regression model (*A*: catalyst, *B*: nPA, *C*: I/C ratio)
Density (g/cm³) = $0.02132A - 0.03748B + 0.000685417C - 0.0031A^2 - 0.01B^2 + 0.0003333C^2 - 0.00644AB + 0.00398AC - 0.0085BC + 1.01279$

[1]Buerkin, Cornelia K., et al. *Journal of Coatings Technology and Research* 14.5 (2017)
[2]Weinstein et al. *Physics of Fluids A: Fluid Dynamics* 3.11 (1991)

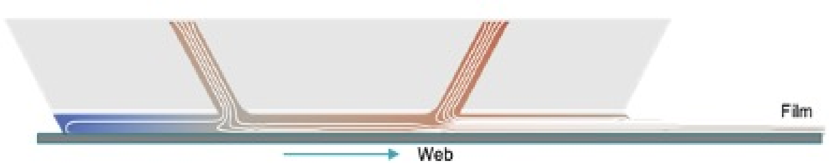
Accomplishments: Multilayer Coating Flow Models (SNL)

- Models will provide valuable design tool for ink-tuning/selection, process parameter space understanding, and process operating window prediction.
- Completed initial single- and two-layer slot-die model and workflow and single- and two-layer slide-die process models. Validated single-layer cases against ORNL trials on FC inks.
- Efforts will continue to guide ink-design work of NREL slide-coating exemplar with single layer model (rheologies, process parameters). Demonstrate/validate two-layer slot-die deposition model with ORNL coating trials.
- Developing graphical user interface (GUI) tools for the community.

3-layer slide flow model (NREL Slide Die)



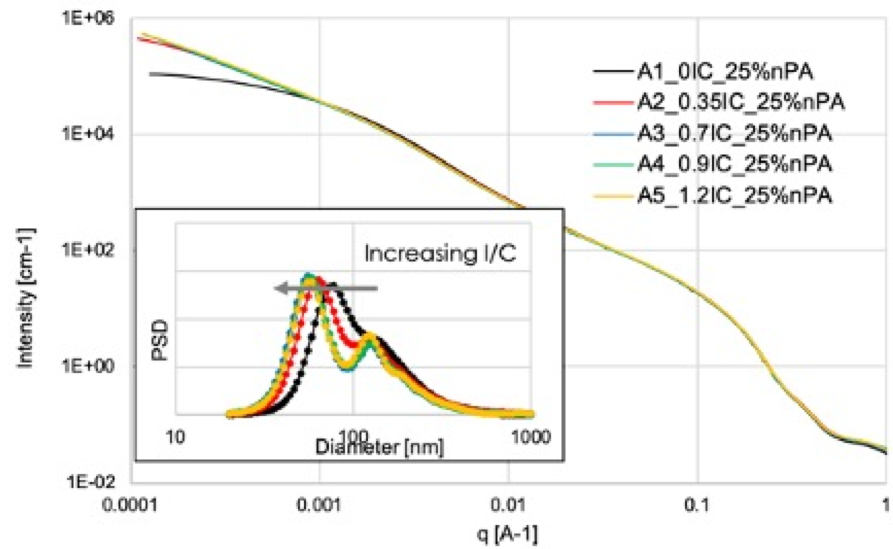
Two-layer slot deposition model (ORNL Slot Die)



Accomplishments: X-ray Scattering Studies of Catalyst to Determine Agglomeration Behavior (ANL)

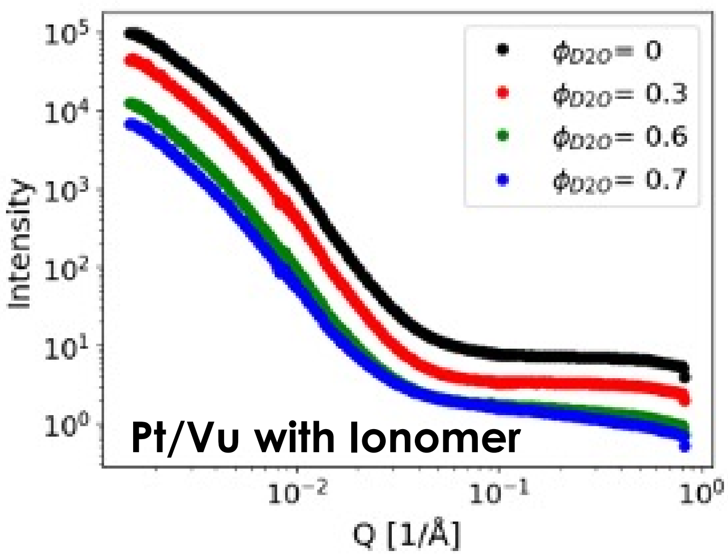
- Measured catalyst inks to study effect of ionomer-to-carbon ratio and water/1-propanol ratio on agglomeration.
- Ultra-small-angle x-ray scattering (USAXS) extends measurable length scales beyond typical SAXS.

- Results demonstrate increasing ionomer content reduces particle size.
- Also determined that water/1-propanol ratio influences particle size.
- Results can be utilized to understand catalyst-ionomer interactions and be related to ink properties such as viscosity (NREL).



Progress: Performed SANS Experiments of Catalyst Inks (ORNL, NREL)

- Utilized ORNL High-Flux Isotope Reactor (HIFR) neutron source to conduct experiments on fuel cell catalyst inks
- Used contrast variation-small angle neutron scattering (CV-SANS) to study ionomer structure and Pt/C ionomer interactions
- Two carbon black supports (with and without Pt) and water/1-propanol ratios were studied to understand how Pt location, carbon chemistry, and dispersion media influences ionomer adsorption and conformation
- Data reduction and model fitting in progress



Supports – High Surface Area Carbon, Vulcan XC72

Ionomer – Nafion 1000 EW
Water/1-propanol: 75/25 and 50/50

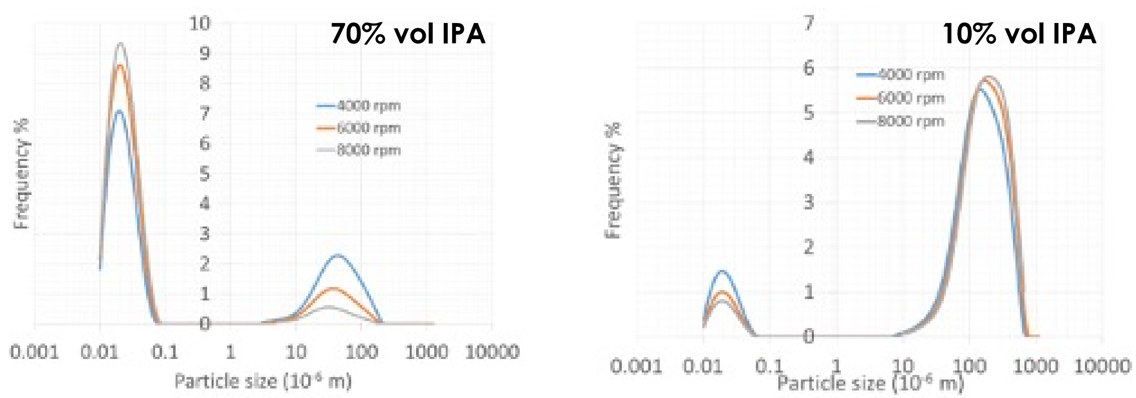
Contrast Variation – 5 levels

Progress: Developed Particle-Scale Instruments and Models (LBNL)

- Goal is to develop methodology for using results to build component aggregation models.
- Use computer control to create readily-reproducible experimental conditions, monitor with multiple complementary analytical tools.
- Upcoming: computer-controlled temperature bath, in-line microscopy, flow-through FTIR, separate coating drying dynamics observation table.
- Preliminary experiments with carbon black in water/alcohol suggest strong influence of solvent composition.

Computer-Controlled Mixer

Particle Size Distribution Experiments

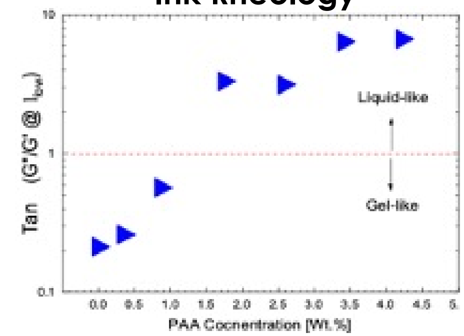


Electrospinning

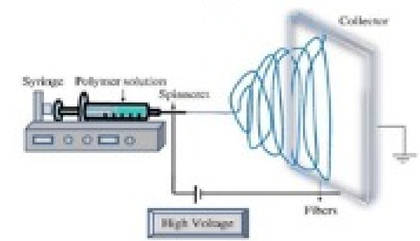
Accomplishments: Ink Interactions, Rheology and Fiber Morphology Relationships for Electrospun Nanofiber Electrodes (NREL)

- Demonstrated PAA concentration significantly affects catalyst agglomerated structure
  - Identified optimal PAA concentration for maximum stability of catalysts ink structure
- Correlated ink structure and rheology to fiber morphology
  - Stable catalysts result in better fibers
  - Optimal PAA concentration resulted in uniform fiber formation

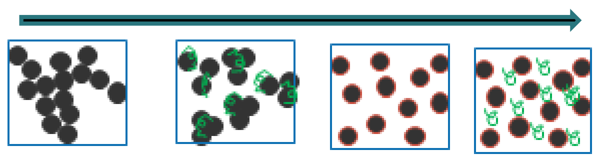
Ink Rheology



Electrospinning Process



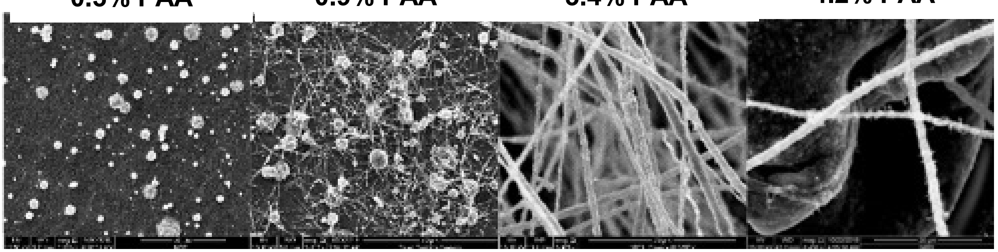
Source: https://bioinicia.com/electrospinning-equipment-fiber-fabrication/electrospinning-process-bioinicia/

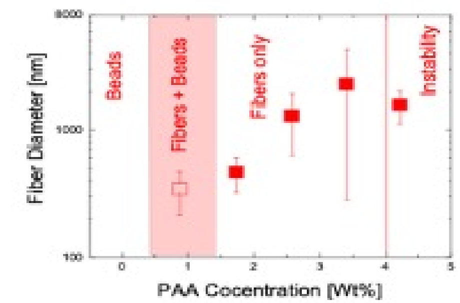


Agglomerated **Partially stabilized** **Well-dispersed**

Fiber Morphology

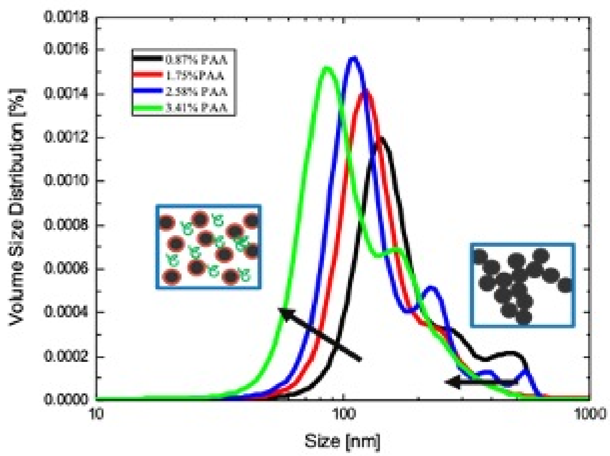
Beads	Beads + Fibers	Uniform Fibers	Defective Fibers
0.3% PAA	0.9% PAA	3.4% PAA	4.2% PAA

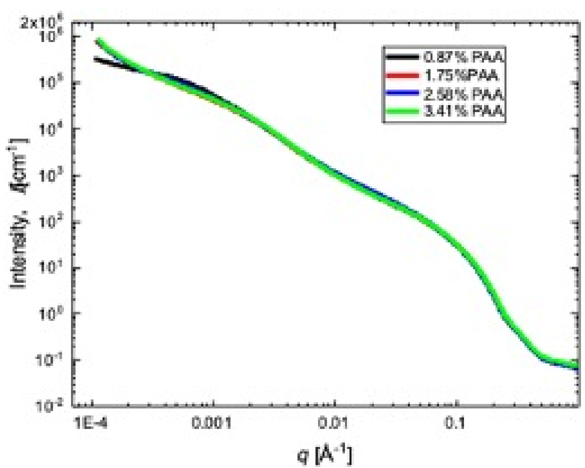




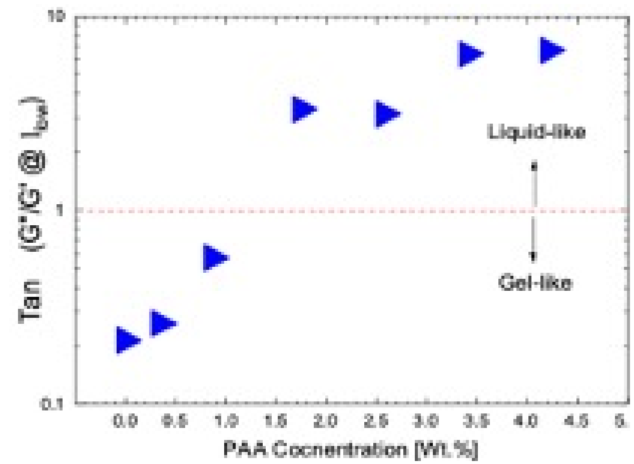
Accomplishments and Progress: Characterized Structure of Electrospinning Inks by USAXS (ANL)

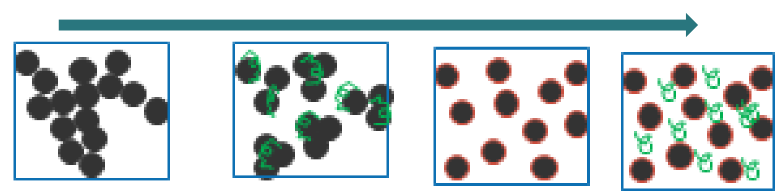
- USAXS results support rheological observations on carrier concentration effect on catalyst agglomerated structure (NREL).
- Increasing PAA concentration reduces the catalyst agglomerated structure.





Ink Rheology





Agglomerated

Partially stabilized

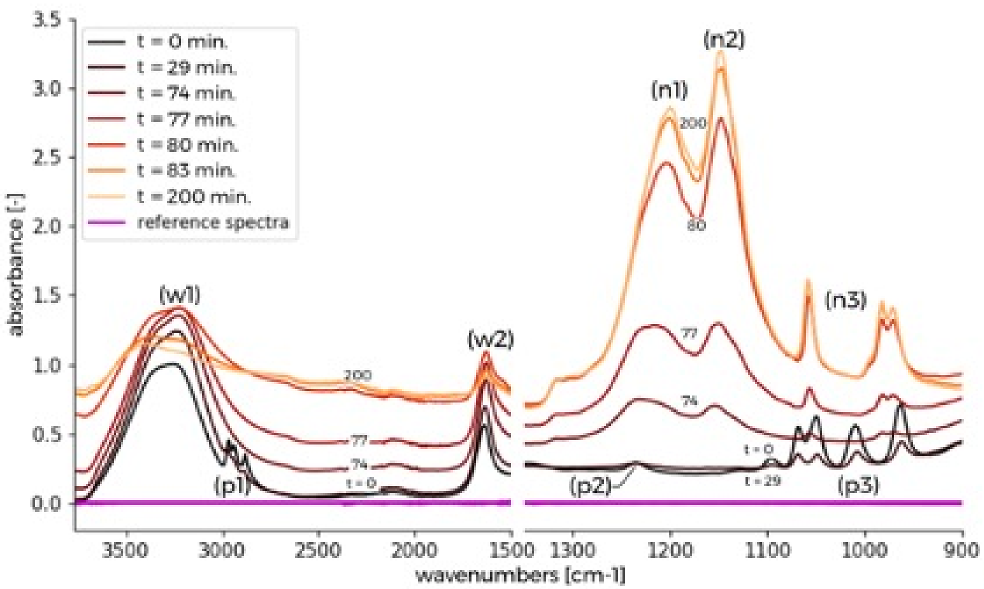
Well-dispersed

Metrology for Multi-Layer and Electrospinning Structures

Argonne NATIONAL LABORATORY | BERKELEY LAB | NREL NATIONAL RENEWABLE ENERGY LABORATORY | OAK RIDGE National Laboratory | Sandia National Laboratories

Progress: Conducted Spectroscopy Studies for In-Process Ink and Drying Measurements (NREL)

- Explored multiple spectroscopy methods for ionomer content in inks, membranes and coated electrodes.
- As an example output using ATR-FTIR, we identified a methodology for tracking the evolution of coated polymer and solvent species during the drying process.
  - Potential use for in-process ink measurement as well as real-time drying studies

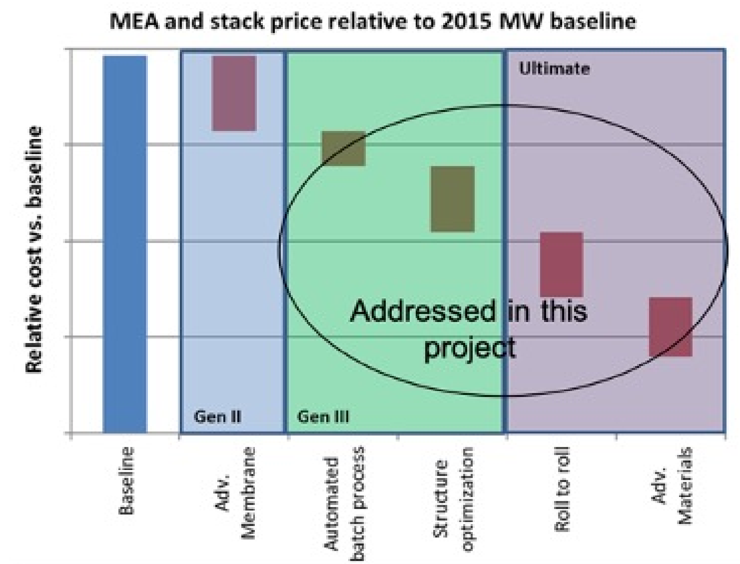


ATR-FTIR absorbance spectra showing evolution of water (w), solvent (p), and polymer (n) response during drying process

Tech Transfer Activities – Nel Hydrogen CRADA

“Roll to Roll Manufacturing of Electrolysis Electrodes for Low Cost Hydrogen Production”

- Project funding:
  - $300K in-kind cost share from Nel Hydrogen
  - $300K funding from DOE (50:50 FCTO, AMO)
- Nel Hydrogen collaborators: Chris Capuano, Kathy Ayers
- Lab collaborators: NREL, ORNL, ANL
- Task areas:
  - Fundamental studies of ink formulation, rheology, and stability (NREL, ORNL)
  - Demonstration of R2R direct coating of electrode onto membrane (NREL, ORNL)
  - Advanced characterization of coated electrodes (ANL, ORNL)
  - In situ testing to verify performance targets (Nel Hydrogen)
  - Development of in-line electrode inspection (NREL)
- Project Kickoff Meeting – March 11, 2020

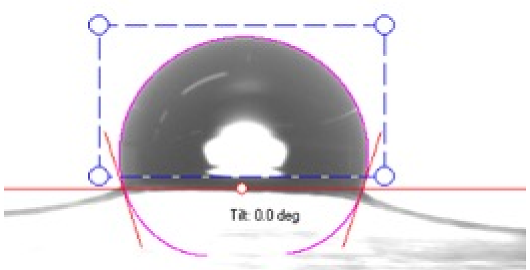


Nel Hydrogen

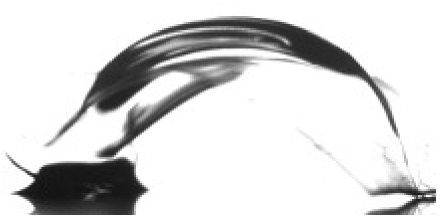
Tech Transfer Activities – Nel Hydrogen CRADA Progress: Conducted Studies of Ink-Membrane Interactions (ORNL, NREL, ANL)

- Experiments performed to understand solvent-membrane interactions (ORNL, NREL):
  - Static contact angle
  - Solvent uptake

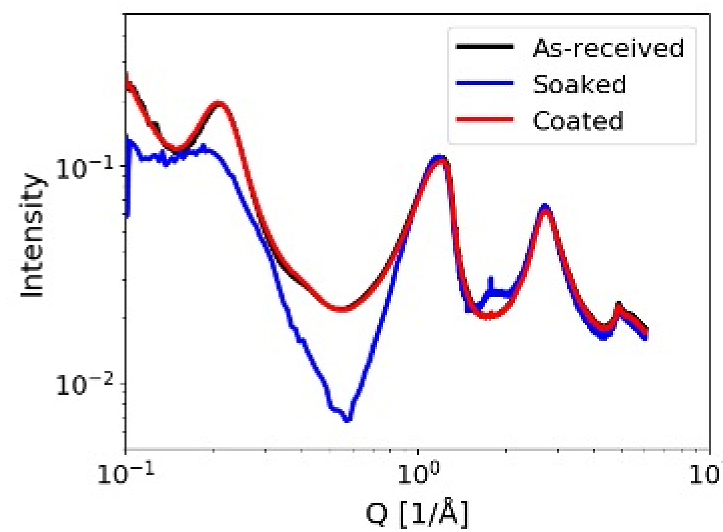
- Wide-angle x-ray scattering showed that coating should not alter the structure of membrane (ANL).



Water



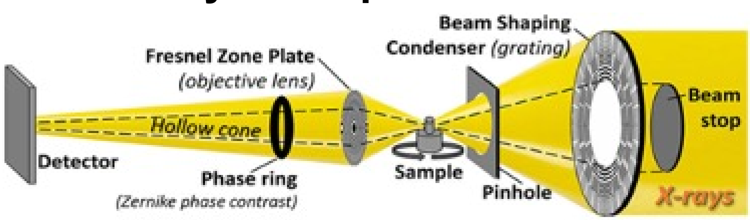
1-propanol



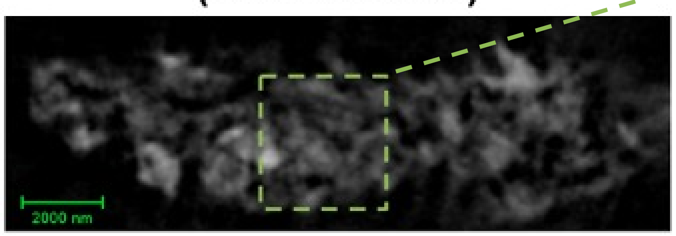
Tech Transfer Activities – Nel Hydrogen CRADA Progress: Performed Beamline Studies of Catalyst Inks and Layers (ANL)

- NREL prepared IrO_2 catalyst inks and catalyst layers that were provided to ANL.
- ANL measured ink with USAXS and catalyst layers with USAXS and nano X-ray tomography (nano-XCT).

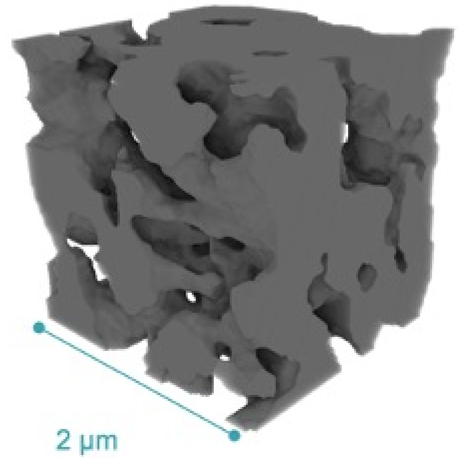
Hard X-ray Nano-probe at 32-ID APS



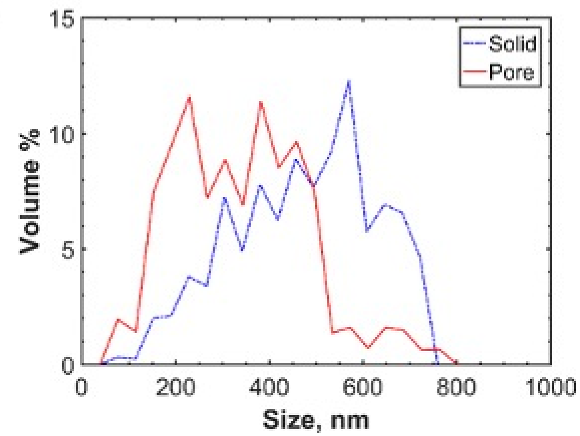
Phase contrast image cross section (50/50 H2O-nPA)



Segmented 3D Sub-volume



Pore Size Distribution



Tech Transfer - FCTO-Funded R2R Activity

- $850K total funding to the five labs to assist industry with MEA scale-up
- Initial workplan developed by labs to maximize leveraging of AMO-funded R2R process work
- Workplan revised per the inputs from four industry participants (GM, Plug Power Inc., Nel Hydrogen, Giner Inc.)
  - Ensured effort will address specific relevant scale-up needs for PEM FC & EC MEAs
  - Prioritized work and developed key deliverables for first year of effort
  - Will provide ongoing guidance and feedback as work progresses
- Revised workplan approved by industry participants and FCTO
- Major task areas:
  - Model development (particle-level ink model, coating flow model, consolidation model)
  - Ink and colloid studies and characterization
  - Coating studies and electrode characterization
  - Real-time quality method development (coatings and inks)
  - In situ testing to validate the impact of ink and process parameter studies
- Lab roles: same as for overall AMO effort
- Status: funding distributed to labs, kick-off meeting held, experimental work initiated

Argonne National Laboratory | Berkeley Lab | NREL National Renewable Energy Laboratory | Oak Ridge National Laboratory | Sandia National Laboratories

Response to Reviewer Comments

"manufacturing…should normally be left up to industry"

The combination of unique equipment and techniques of this collaboration does not exist in industry, which enables us to develop a more fundamental understanding of topics than industry. The modeling and simulation tools and the subject matter expert base is nonexistent in industry.

"investment was made with minimal industrial involvement"

"project needs to add an automotive original equipment manufacturer (OEM) to help guide priorities"

We have worked to engage industry more this year with the FCTO-funds that are being leveraged to specifically address research topics defined by Tier 1 suppliers' inputs.

"Understanding the structure, property, and performance issues as a function of the drying rate and solvents used would be a better use of effort"

The project has topic areas focused on drying (new for FY20) and ink formulation, which include experimental and theoretical work.

Collaborations

Laboratory	Contributors	Tasks
ORNL	Claus Daniel, David Wood, Erin Creel, Georgios Polyzos, Jaswinder Sharma, Kelsey Grady	Colloids, rheology studies, multilayer slot coating studies, electrode characterization, ink characterization
NREL	Mike Ulsh, Scott Mauger, Janghoon Park, Min Wang, Jason Pfielsticker, Sunil Khandavalli, Nisha Sharma-Nene, Sadia Kabir	Colloids, rheology studies, multilayer slide coating studies, MEA fabrication and testing, electrode characterization, QC development, electrospinning
ANL	Greg Krumdick, Debbie Myers, Jae Hyung Park, Firat Cetinbas, Yuepeng Zhang, Erik Dahl	Ink characterization, electrode characterization, electrospinning
LBNL	Vince Battaglia, Kenny Higa	Particle-scale ink and consolidation modeling
SNL	Randy Schunk, Kristianto Tjiptowidjojo	Flow and consolidation modeling

Future Work

- Continue efforts on FCTO-funded FC/LTE-specific work
- Continue development of coating flow models for FC/LTE specific inks
- Use flow modeling to guide multilayer coating studies
- Continue multilayer coating studies of FC/LTE materials
- Continue development of particle-scale instrumentation and QC tools
- Continue studies on R2R electrospinning of catalyst inks
- Continue work on Nel Hydrogen CRADA
  - Ink formulation
  - R2R catalyst layer coating
  - X-ray scattering studies
  - QC

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

Summary

Relevance:

- R2R is the only manufacturing process platform that will meet cost and volume targets for PEM MEAs
- Cost reduction need: $125/kW (2008) to $30/kW (2025)

Approach:

- Leveraging unique capabilities, facilities, expertise across the five labs
- Focusing on multilayer coating processes and electrospinning
- Addressing topics of interest to FC/LTE through FCTO-funded SOW and Nel Hydrogen CRADA

Collaborations:

- ORNL, ANL, LBNL, NREL, SNL, Nel Hydrogen, Giner Inc., GM, Plug Power Inc.

Accomplishments:

- Developing coating flow and film consolidation models
- Using multilayer coating methods for FC/LTE manufacturing studies
- Appling advanced scattering techniques to understand interparticle interactions in catalyst inks
- Initiated work on Nel Hydrogen CRADA

Technical Backup Slides

Tech Transfer Activities – Key Industry Input

- **Model development**: (1) models based on basic material properties that enable the prediction of constituent (catalyst, ionomer, solvent) interactions and resulting macro-scale properties (rheology), (2) models that enable predictive capabilities for *coating flow and consolidation physics*

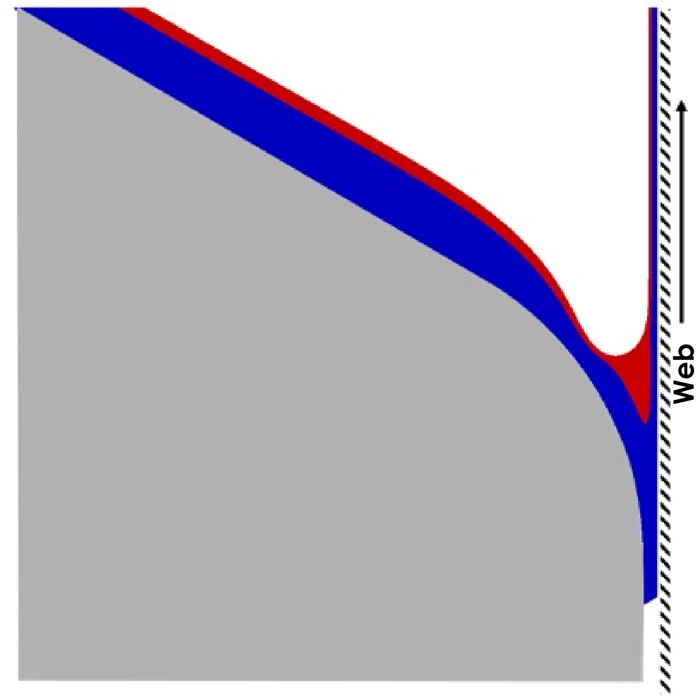
- **Ink studies**: (1) characterization of ink rheology to validate model development and assess coating suitability, (2) evaluation and comparison of ink dispersion methods and scalability of those methods, (3) characterization of ink-substrate interactions to optimize coating, e.g. membrane swelling associated with direct coating

- **Coating studies**: 1) parametric studies to understand the fundamental physics and defects (e.g. crack formation) of scalable coating processes as a function of ink composition/properties, desired film thickness, and structure, and 2) behavior of adjacent layers by hot pressing, lamination or multilayer coating, relevant to the different methods of MEA build (i.e. CCM-based, GDE-based, decal-based, etc.)

- **Quality inspection development**: (1) quality assurance for as-dispersed inks prior to and/or during coating, (2) in-line quality inspection for substrates, coatings, and multilayer MEA structures.

Accomplishments and Progress: Developed Slide Coating Bead Modeling (SNL, NREL)

- Completed a steady-state two-layer model:
  - Layer 1: Nafion 20% solution
  - Layer 2: 3% Pt-Vulcan in 10% n-propanol solution
  - Die geometry of Allied Die AD-3527



- Continued to develop steady-state solutions at other operating conditions. Rheological properties remain a challenge due to:
  - Nonlinearity due to shear-thinning of the catalyst ink
  - Excessive mesh deformation, especially at the flow turnaround region
- Continued developing a graphical user interface (GUI) to facilitate the effort.