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 Laboratories: Randy Schunk
Oak Ridge National Laboratory Lead: David Wood

Presenters: Claus Daniel and Scott Mauger
2019 Hydrogen and Fuel Cells Program
Annual Merit Review
May 1, 2019

TA007

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline and Budget

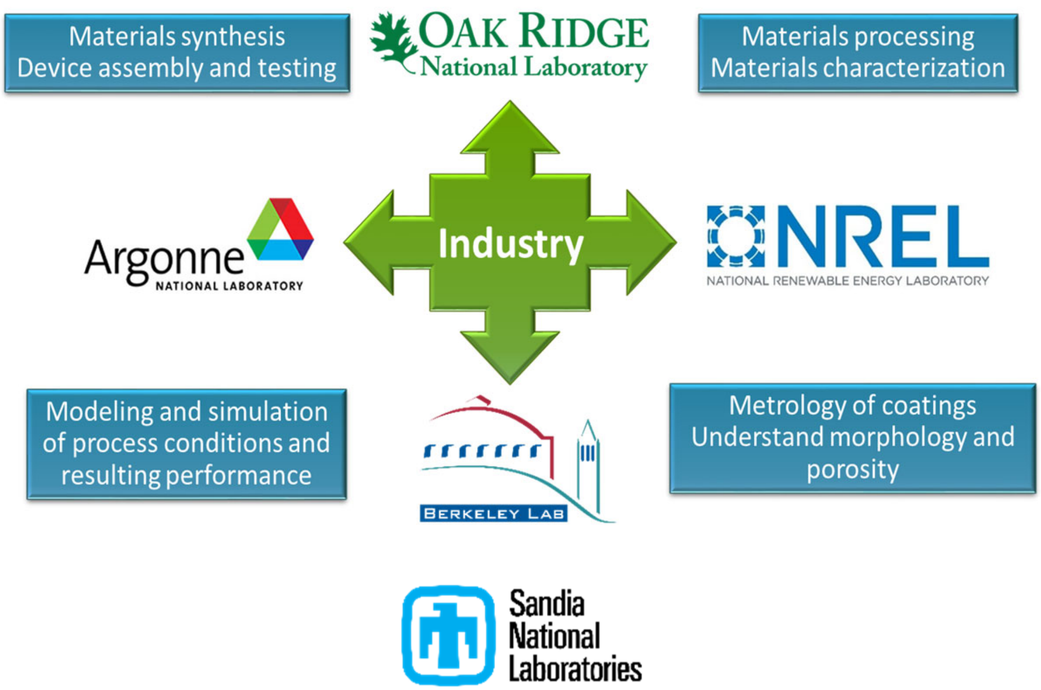
- Project Start Date: 10/01/2018
- Project End Date: 9/30/2021
- FY19 AMO Funding: $4M
- FY19 FCTO: $0 of FCTO
- FY19 planned: $150K of FCTO for new CRADA with Proton OnSite
- $850K of FCTO contribution in negotiation

Technology Barriers

- Develop roll to roll manufacturing techniques to reduce the cost of automotive fuel cell stacks at high volume (500,000 units/year) from the 2008 value of $38/kW to $20/kW by 2025
- Lack of high-volume MEA processes

- Project partners:
  - ORNL, NREL, ANL, LBNL, SNL
  - Proton OnSite
  - Eastman Business Park

Early-stage 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

Targets

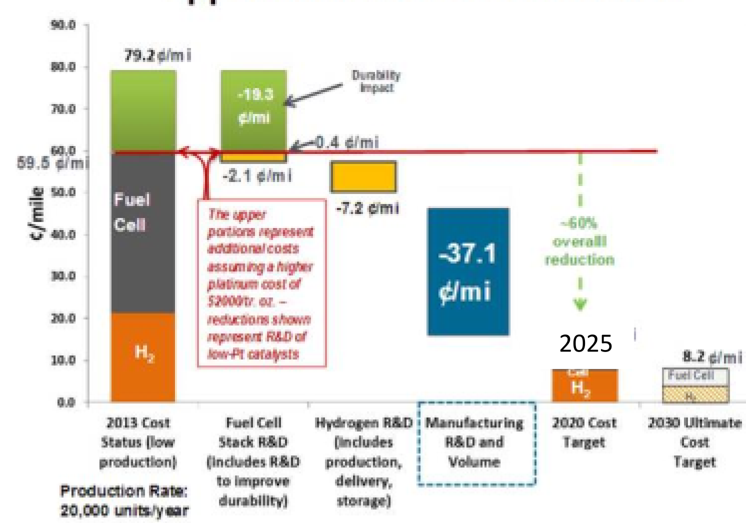
- Cost reduction: from 60 cents/mile in 2013 to 13 cents/mile in 2025 enabling fuel cell cost of $20/kW by 2025 by
  - Developing roll to roll manufacturing techniques to reduce the cost of automotive fuel cell stacks at high volume (500,000 units/year)
  - Develop in-line instrumentation tools to reduce scrap

Collaboration update from last year

- Through AMO competitive solicitation, a new team with the addition of Sandia National Laboratories' Randy Schunk with strong competence and experience in modeling and simulation of coating and drying processes has been added.
- FCTO has decided to 50/50 cost share a CRADA with Proton On-Site/nel and the collaboration totaling $600K with $300K from Proton On-Site/nel, $150K from AMO, and $150K from FCTO.
  - DOE approval pending
- The collaboration is in negotiation for the scope of work supported by FCTO for a $850K cost share in addition to AMO's $4M investment.
- Following presentation will review progress on AMO-funded tasks related to fuel cell 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 need: 60 cents/mile in 2013 to 13 cents/mile in 2025



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.

Relevance:

Roll to roll manufacturing has the potential to reduce cost by 63% compared to state of the art decal transfer

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$)	$52.59	$9.14	$4.92	$4.00	$2.93	**$1.30**
Kapton web material ($/$m^2$)	$4.14	$1.38	$1.30	$1.25	$1.13	$1.08
Hot Press Process ($/$m^2$)	$5.04	$2.65	$2.33	$2.26	$1.13	$1.09
Total Additional Cost for Decal Transfer ($/$m^2$)	$9.19	$4.03	$3.63	$3.51	$2.26	**$2.17**
Total Cost of Catalyst Application with Decal Transfer ($/$m^2$)	$61.77	$13.17	$8.55	$7.51	$5.19	$3.47
Percentage of Additional Decal Transfer Cost	15%	31%	42%	47%	44%	**63%**

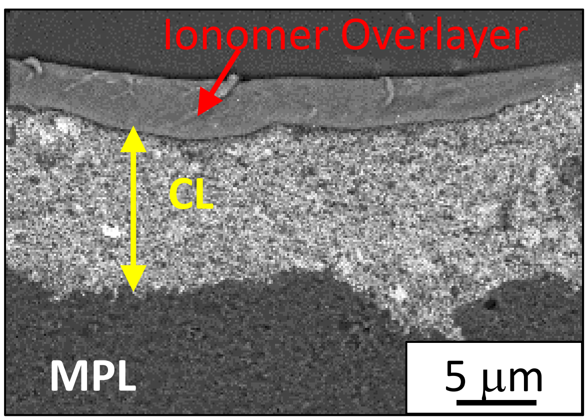
Data provided by Strategic Analysis, Inc.

Approach: Fuel Cell Core Lab Project

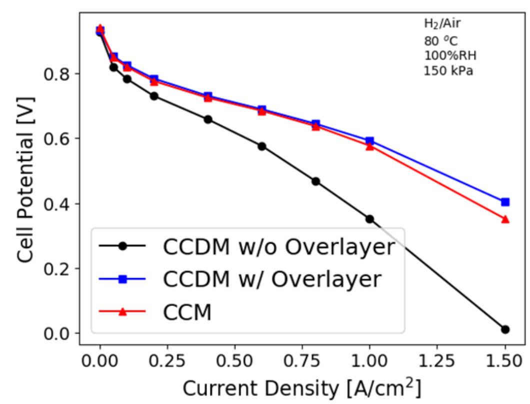
- **The goal of this project is to explore, understand and optimize material and process parameters for single-process (no extra ionomer over-layer) R2R manufacturing of Gas diffusion electrodes (GDEs) with comparable performance to Catalyst-Coated Membranes (CCMs)**
- Current standard manufacturing practice for most PEM MEAs is by fabricating CCMs
  - The electrodes are coated onto separate transfer liners and then hot-pressed onto the membrane, or
  - The electrodes are directly coated onto the membrane
- Limits 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

Approach: Fuel Cell Core Lab Project (cont.)

- GDEs 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



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)

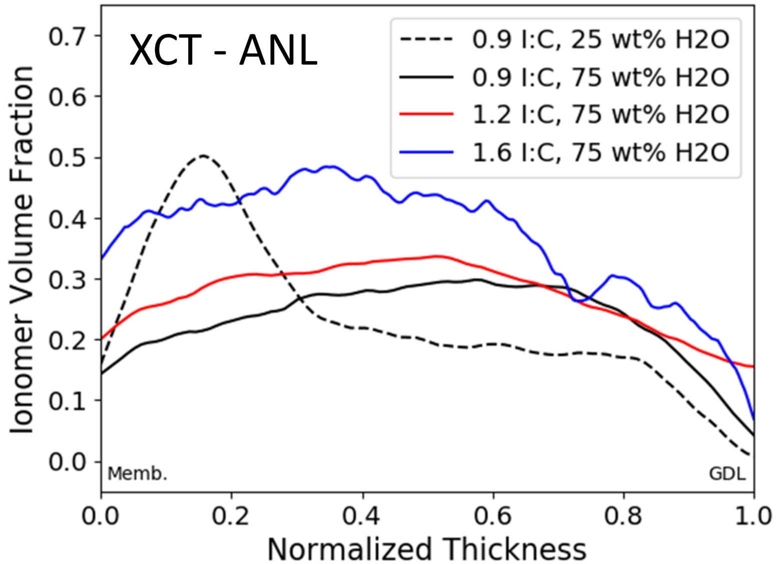


Collaborations: Lab Roles

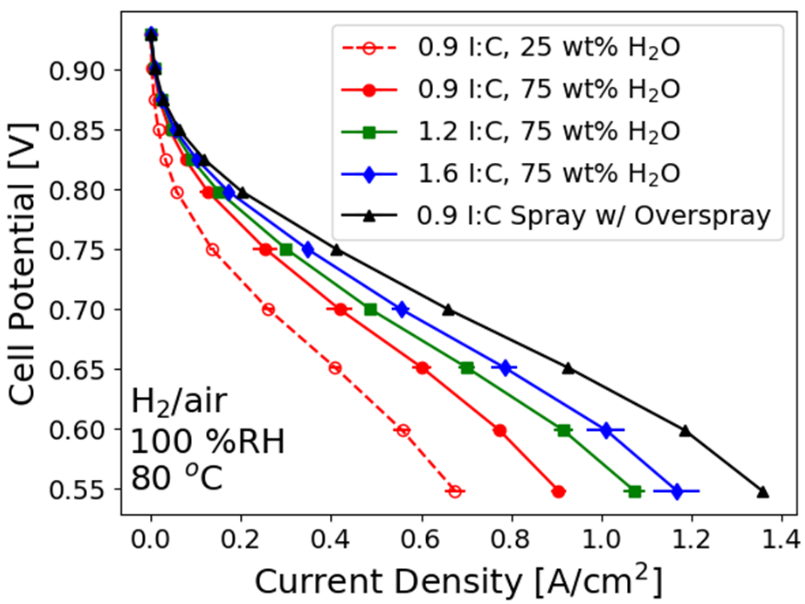
- Gas diffusion electrode studies
  - Gravure, slot die, and dual-slot coating (NREL, ORNL)
  - Coating consolidation modeling (LBNL)
  - X-ray computer tomography (XCT), Electron Microscopy, Kelvin Probe and XRF characterization (ANL, ORNL, NREL)
- Ink studies
  - Formulation, mixing and rheology (NREL,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

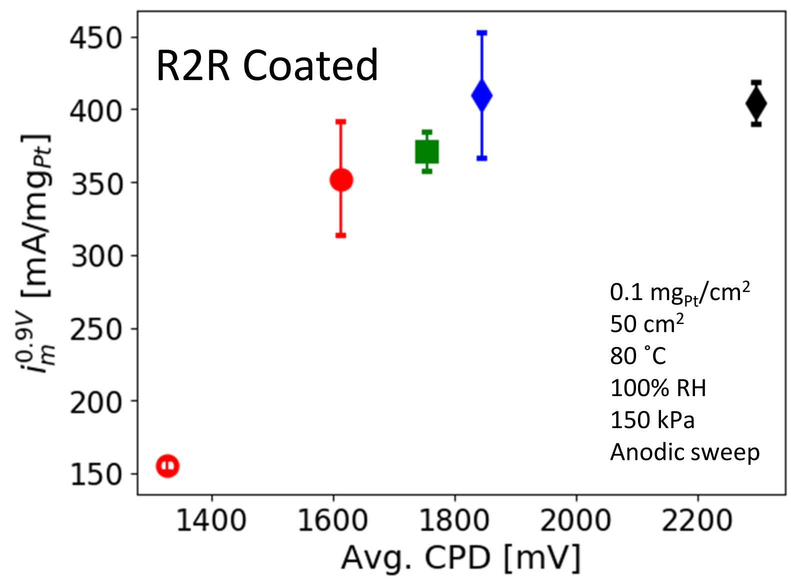
Accomplishments and Progress:

R2R Electrodes Achieved Equivalent Mass Activity to Spray-Coated Electrodes
2018 Status



- Used XCT and Kelvin probe to determine ionomer distribution
- Compared to spray-coated GDEs with ionomer overlayer, R2R coated electrodes without ionomer overlayer had
  - Same ORR mass activity
  - 85% of high-current density performance in air

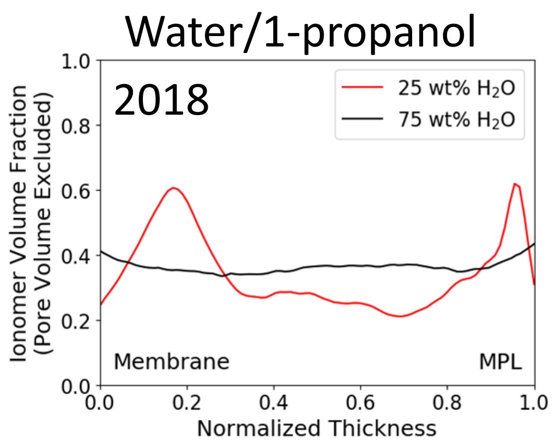


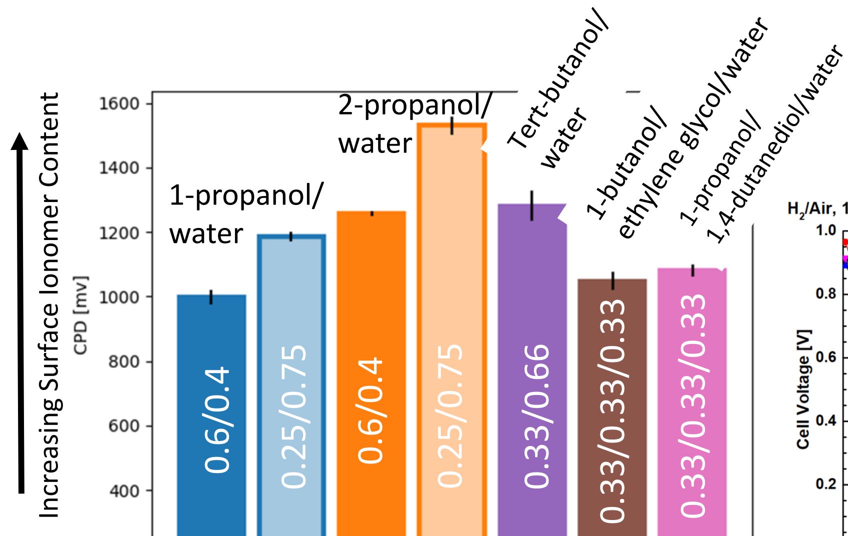


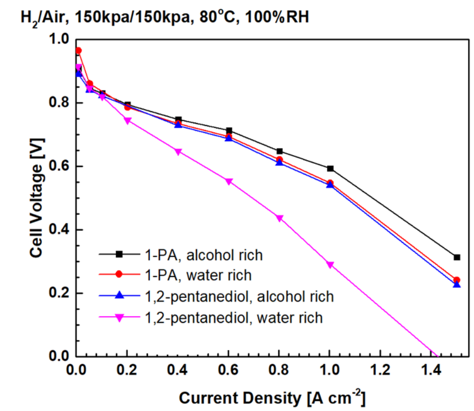
Accomplishments and Progress

Explored Different Solvents to Control Ionomer Distribution

Question: Can higher boiling point solvents be used to increase the surface ionomer content?

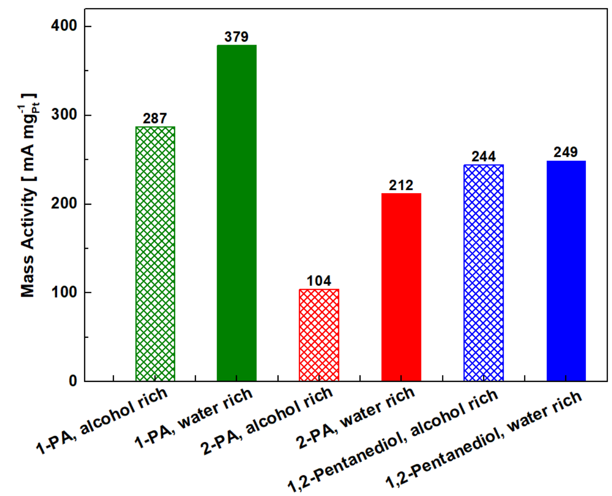






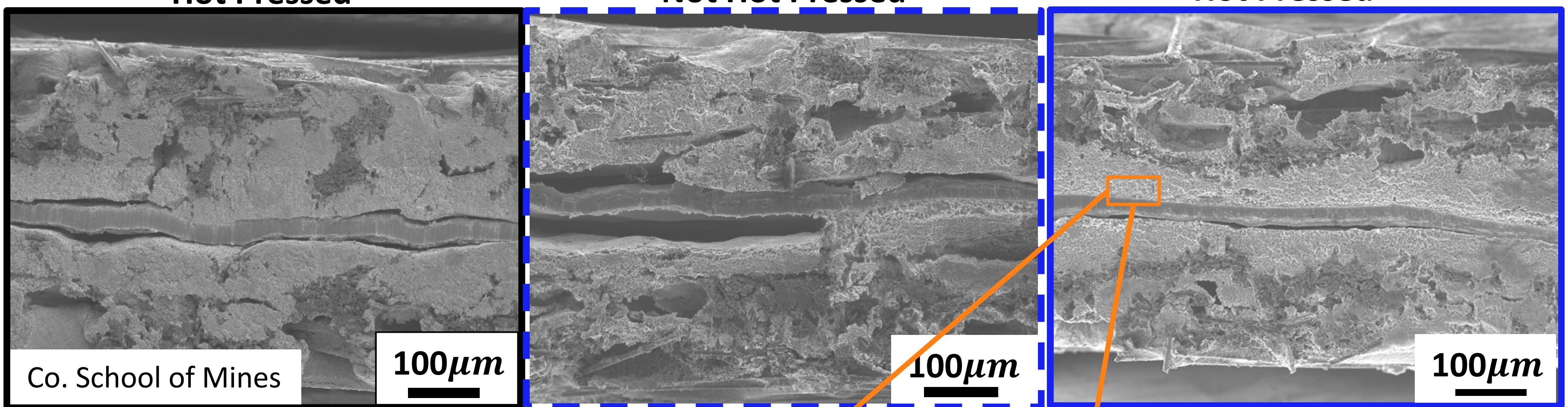
Solvents
1-propanol
2-propanol
1-butanol
Tert-butanol
Ethylene glycol
1,2-butanediol
1,4-butanediol
1,2-pentanediol

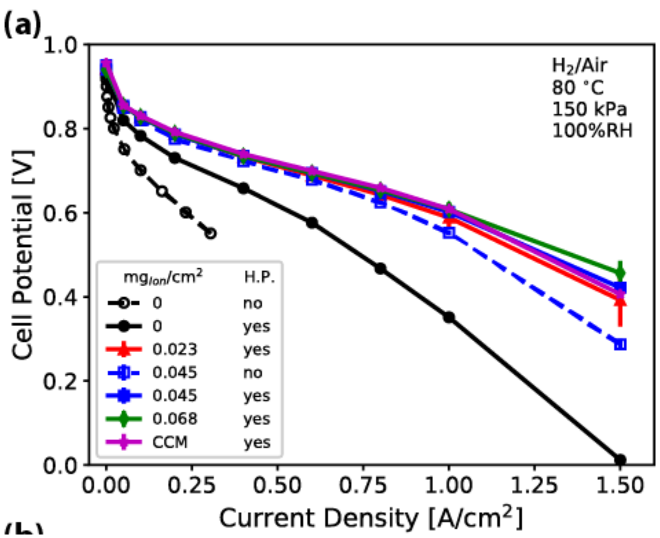
- Modifying solvent composition was able to change ionomer surface content
- This did not translate to improvements in fuel cell performance
  - Likely due to changes in electrode morphology

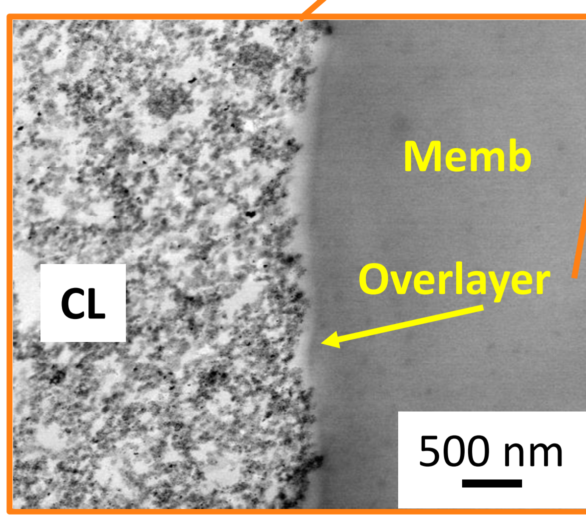


Accomplishments and Progress
Determined Function of Ionomer Overlayer

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

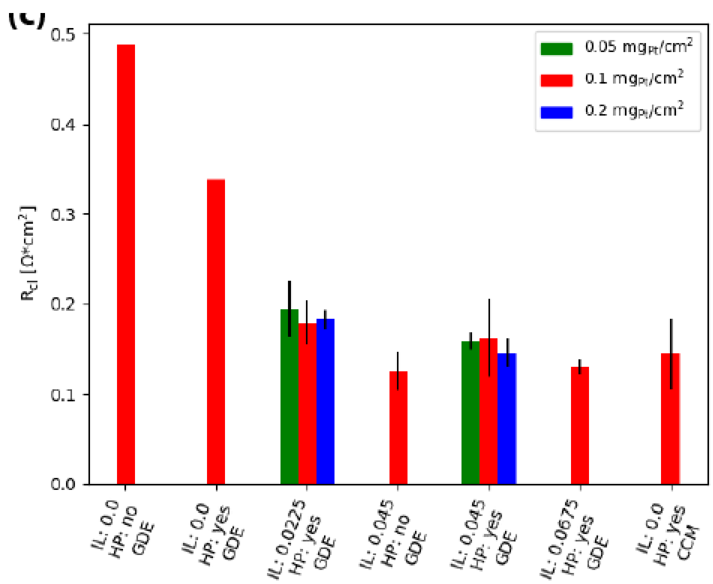
Accomplishments and Progress

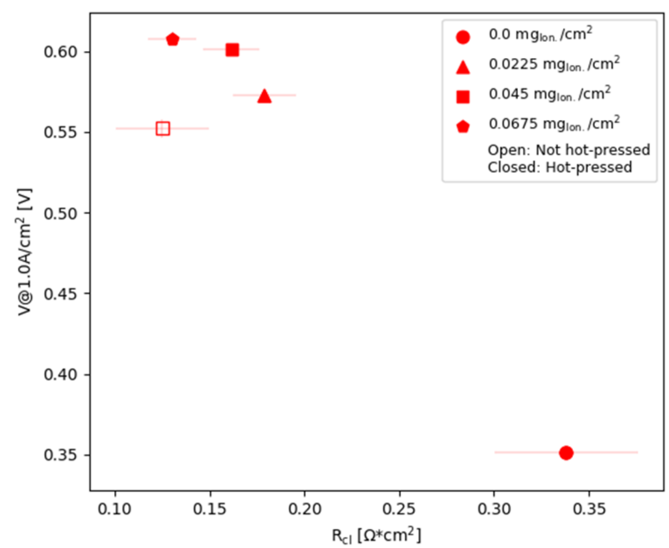
Better CL-membrane interface leads to lower R_{CL}, which reduces ohmic losses and results in better performance

Physics-Based H_2/N_2 Impedance Model

$$Z(\omega)_{model} = j\omega L_{wire} + R_{mem} + \sqrt{\frac{R_{cl}}{Q_{dl}(j\omega)^{\varphi}}}\coth\left(\sqrt{R_{cl}Q_{dl}(j\omega)^{\varphi}}\right)$$

Setzler & Fuller, JES 2015, 162(6), F519-F530

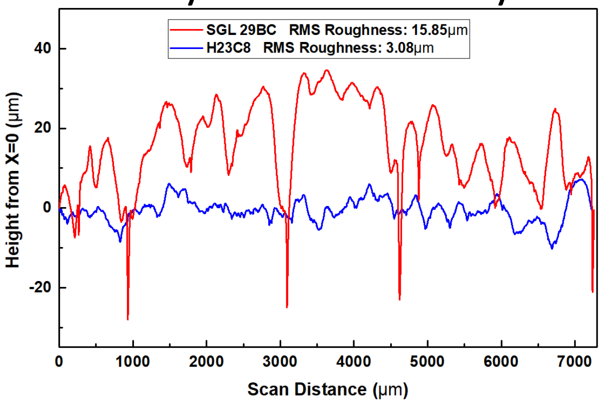




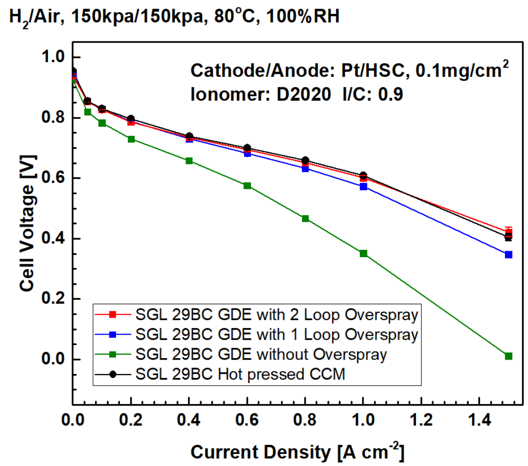
- H_2/N_2 EIS modeling shows that overlayer and hot pressing reduce catalyst layer proton resistance (R_{CL})
- R_{CL} is strongly correlated to fuel cell performance

Accomplishments and Progress
Roughness reduces performance

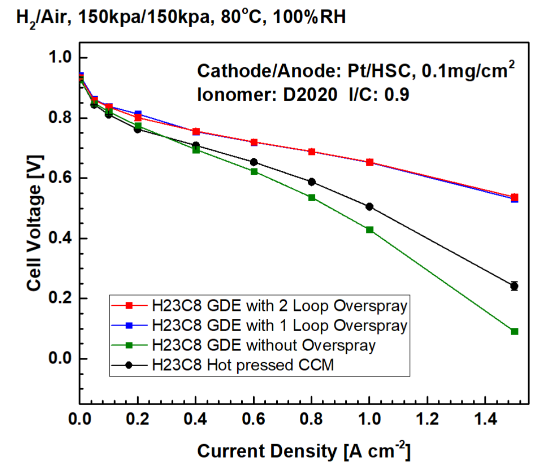
Stylus Profilometry



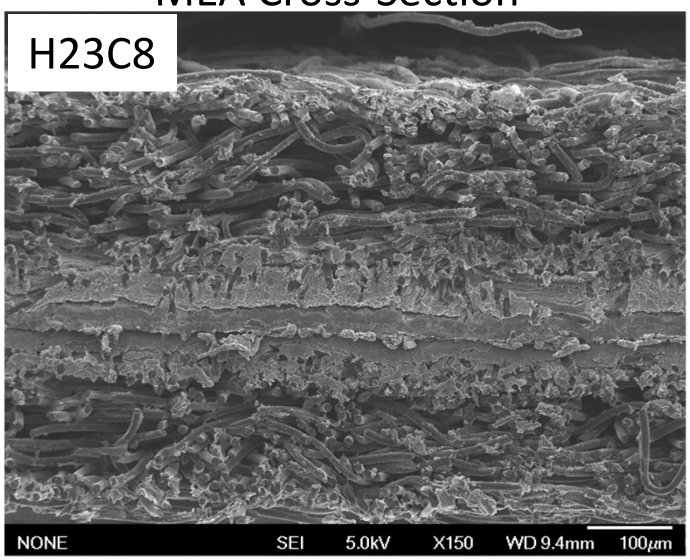
SGL 29BC - Rough



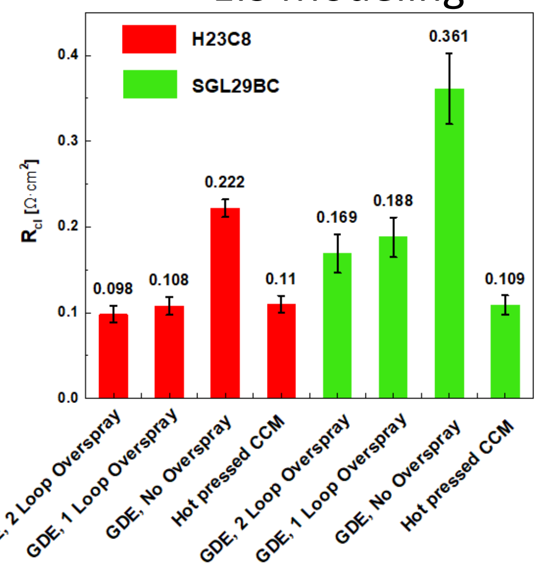
H23C8 - Smooth



MEA Cross-Section



EIS Modeling

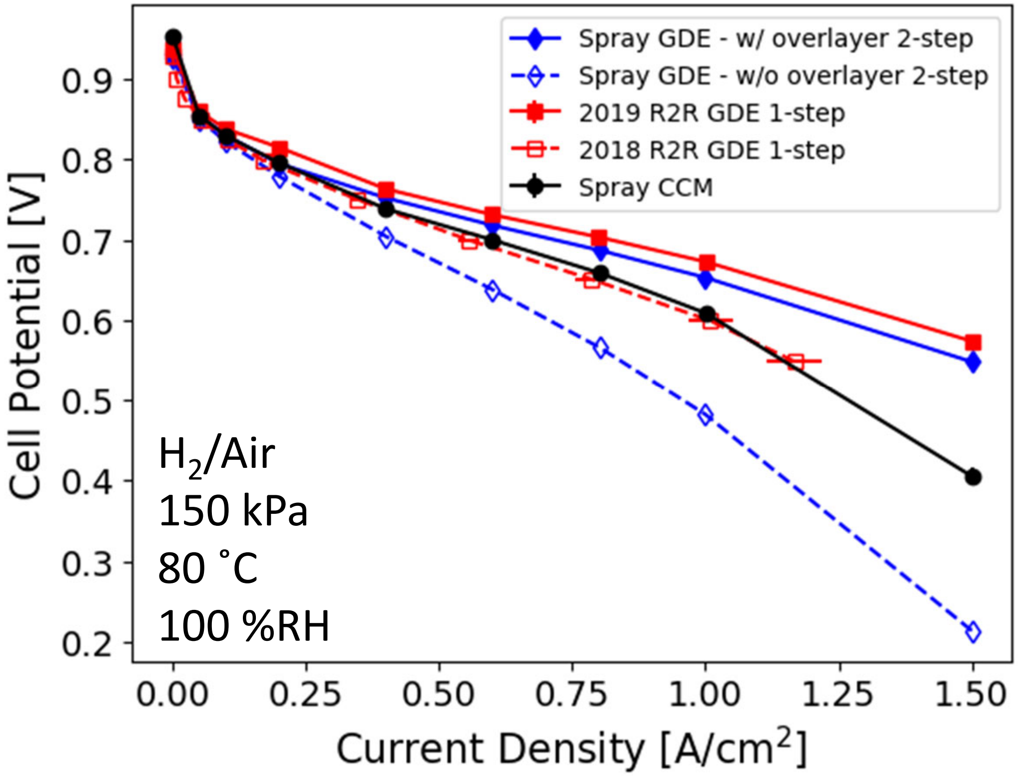


Smoother MPL leads to:

- **Less ionomer needed in overlayer**
- **Lower R_{CL}**
- **Expected to be better for R2R GDEs**

Accomplishments and Progress
Single-Process R2R GDE Surpasses Project Goal

*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 GDEs with comparable performance to CCMs***



<u>R2R Coated GDEs</u>

Slot die

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
- Reduced I:C (1.6 → 0.9)

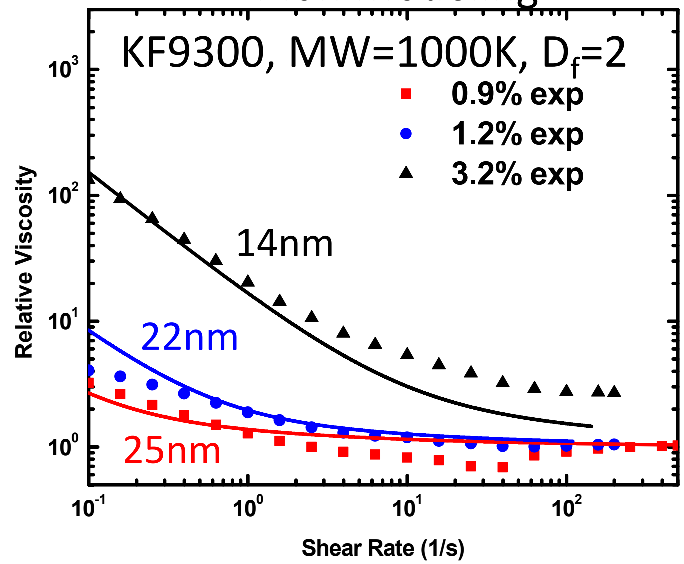
<u>Keys to High Performance R2R GDEs</u>

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

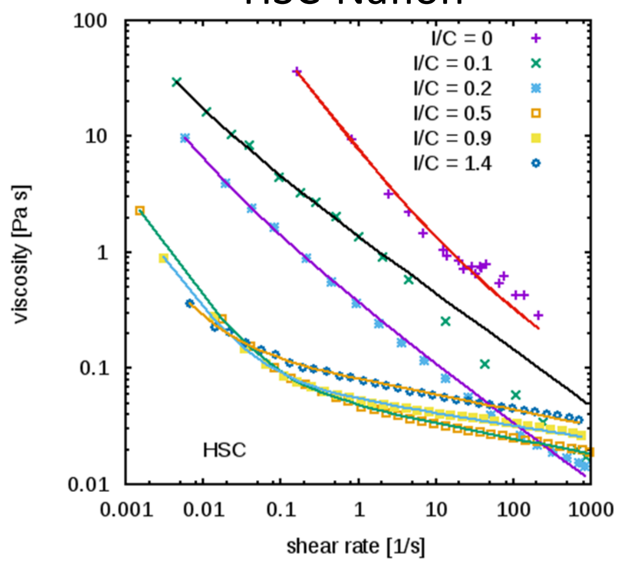
Accomplishments and Progress
Translated Battery Anode Slurry Model to Fuel Cell Catalyst Ink

- Rheological model developed as part of Li-ion Battery Structured Electrode core lab project
- Model describes colloidal interactions between carbon black particles and binder polymer
- Fitting parameters
  - polymer coating length
  - fractal dimension of aggregates
- Framework used to develop model for fuel cell catalyst ink
- Work continuing in FY19 to relate mathematical forms to physics

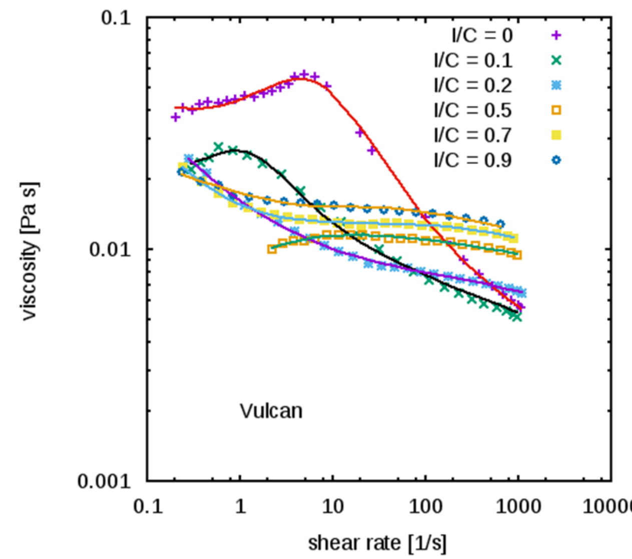
Li-ion Modeling



HSC-Nafion



Vulcan-Nafion



Model Framework

$$\eta_{total} = \eta_{hydr} + \eta_{struct}$$

Potanin, et al, J. Chem. Phys. 102(14) 1995
Krieger IM, Dougherty TJ. Trans Soc Rheol 1959;3:137
Kim et al, Polymer, 2015, 7(7), 1346-1378

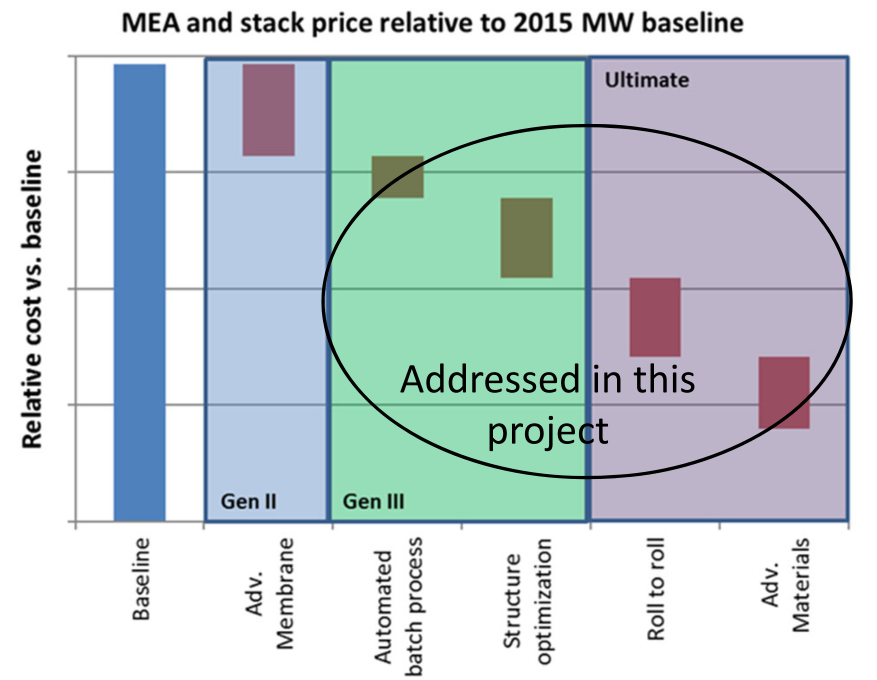
HSC: $\eta = \frac{A}{\ } + \frac{B}{C}$

Vulcan: $\eta = \frac{A}{\frac{D}{\gamma^{E}} +} + \frac{B}{C}$

Tech Transfer Activities

CRADA Project with Proton OnSite: “Roll to Roll Manufacturing of Electrolysis Electrodes for Low Cost Hydrogen Production”

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



Proton OnSite

Future Work

FY19 AMO FOA Award – R2R Advanced Materials Manufacturing Multi-Lab Collaboration

- Five Lab Collaboration
  - National Renewable Energy Laboratory
  - Oak Ridge National Laboratory
  - Argonne National Laboratory
  - Lawrence Berkeley National Laboratory
  - Sandia National Laboratories (NM) – new member
- Broad range of research task areas focused on roll-to-roll manufacturing
  - Multilayer coating
  - Ink formulation and rheology
  - Drying/Curing
  - Flow modeling
- Task areas will included continued research on fuel cell and low-temperature electrolysis materials

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: 60 cents/mile in 2013 to 13 cents/mile in 2025

Approach:

- Leverage unique capabilities, facilities, expertise across the four labs
- Focus on MEA structure of industrial interest (GDEs)
- Achieve reduction in process steps and energy consumption

Collaborations:

- ORNL, ANL, LBNL, NREL, Eastman Business Park, industry

Accomplishments:

- Determined function of ionomer overlayer in spray-coated GDEs
- Characterized influence of MPL roughness on GDE performance and properties
- Developed materials and process for single-process R2R GDEs with performance better than spray-coated CCMs or GDEs – **ACHIEVED PROJECT GOAL**

Response to Reviewer Comments

- It is true that R2R manufacturing has considerable applications in fuel cell manufacturing, but even so, as in all manufacturing, one first has to know the raw materials and structures to be made with the manufacturing procedure. It is true that a manufacturer will have select materials for their process. We have selected representative materials to generate knowledge that can be leveraged by a manufacturer and applied to their own materials or aid them in selecting materials.
- These investigations should be extended to explore the influence of the ionomer overlayer, as well. We agree, some details of this work were presented in the backup slides of the 2018 presentation and further study of this was presented in this presentation.
- The PI mentioned advantages of casting ink directly on the gas diffusion layer (GDL). However, the advantage of casting ink on liner is faster line speeds; GDL line speeds will be limited. According to Strategic Analysis, Inc.'s analysis of R2R electrode production in a decal based process the liner and hot press account for 63% of the production costs (500,000 sys/yr). Faster line speeds would not be able to overcome the higher materials and process costs of using a liner.
- The project is based on improving (including lowering the cost of) technology that is already in use…there is a manufacturing technology in place, and this activity seems to ignore that fact. Siemens is installing PEMFCs in the submarines they are selling in global markets. If existing players are experiencing problems with MEA manufacturing, that fact was not presented. This project may well be adding value, but there was nothing described that might suggest that was or was not happening. DOE has defined direct casting of electrodes to membranes or GDL as a MYRD&D Milestone. Based on FCPAD's analysis of the Mirai MEA, both electrodes are prepared with a transfer process. We know from personal discussions that other FC manufacturers are also using a decal/liner transfer process. At low volumes using a decal liner does not add too much to the total cost, but it is significant at large volumes. These volumes have likely not been reached yet. We don't believe the ability to manufacture high-performance direct cast GDE-based (or CCM) MEAs is widespread in industry.
- It is uncertain whether studies of fuel cell performance belong within the scope of this project. We believe there must be some studies of fuel cell performance to quantify the impact of new formulations and procedures and understand if they are leading towards the project goal.
- This team should include the impact of different manufacturing methods on the cost of the final product, including material yield impacts. These have been added.

Acknowledgement

Thanks to all collaborating researchers at ORNL, NREL, ANL, and LBNL

Funding from DOE-EERE-AMO and FCTO

Technical Backup Slides

Reviewer Only Slides

Publications and Presentations

Presentations

- Scott A. Mauger, C. Firat Cetinbas, Rajesh K. Ahluwalia, Deborah J. Myers, Jae Hyung Park, K.C. Neyerlin, Leiming Hu, Shawn Litster, and Michael Ulsh, "Control of ionomer distribution and porosity in roll-to-roll coated fuel cell catalyst layers", *Fuel Cell Gordon Research Conference, 2018*
- Scott A. Mauger, C. Firat Cetinbas, Rajesh K. Ahluwalia, Deborah J. Myers, Jae Hyung Park, K.C. Neyerlin, Leiming Hu, Shawn Litster, and Michael Ulsh, "Control of ionomer distribution and porosity in roll-to-roll coated fuel cell catalyst layers", *19th International Coating Science and Technology Symposium*, 2018