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# Roll-to-Roll Advanced Materials Manufacturing Lab Consortium

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#### Partners:

- Argonne National Laboratory, Lemont, IL
- Lawrence Berkeley National Laboratory, Berkeley, CA
- National Renewable Energy Laboratory, Golden, CO
- Eastman Business Park, Rochester, NY
- Proton OnSite, Wallingford, CT

Project Start Date: October 1, 2016  
Project End Date: September 30, 2019

## Overall Objectives

Oak Ridge National Laboratory (ORNL), Argonne National Laboratory (ANL), Lawrence Berkeley National Laboratory (LBNL), and the National Renewable Energy Laboratory (NREL) in collaboration with Eastman Kodak Business Park (Kodak) formed a Roll-to-Roll Advanced Materials Manufacturing (R2R-AMM) multi-lab collaboration to:

- Broadly disseminate materials, process science, and advanced technologies to industry in R2R manufacturing.
- Enable advanced R2R manufacturing R&D to demonstrate a materials genomic approach to optimization of process parameters for finding new transformational improvements in manufacturing technologies enabling clean energy applications.

## Fiscal Year (FY) 2018 Objectives

For its fuel cell core lab project, the multi-lab collaboration will:

- Develop ink formulations and understand interparticle interactions and the impact of dispersion methods using rheology, zeta potential, and ultra-small-angle X-ray scattering (USAXS) measurements.
- Initiate a rheological model for inks containing carbon-supported platinum catalysts, ionomer, and solvents.
- At various scales and using different processes, coat phase-segregated and multi-layer ionomer-rich-surface (IRS) gas-diffusion electrodes (GDEs).
- Perform advanced ex situ characterization, including X-ray computed tomography (XCT), of coated GDEs to understand the impact of formulation and process parameters on electrode morphology.
- Perform in situ testing to understand the impact of formulation and process parameters on membrane electrode assembly (MEA) performance.
- Initiate a new cooperative research and development agreement (CRADA) project in the hydrogen and fuel cells space.

## Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

- (A) Lack of High Volume MEA Processes.

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<sup>1</sup> <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

## Contribution to Achievement of DOE Manufacturing Milestones

This project contributes to the achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- Milestone 1.6: Develop fabrication and assembly processes for polymer electrolyte membrane (PEM) fuel cell MEA components leading to an automotive fuel cell stack that costs \$20/kW. (4Q, 2020)

## FY 2018 Accomplishments

The multi-lab collaboration accomplished the following in FY 2018:

- Performed USAXS measurements of inks in situ during mixing, with different supported catalysts, ionomer ratios, solvent mixtures, and dispersing methods to elucidate the impact of these variables on the time required to fully disperse the supported catalysts and the level of agglomeration in the ink.
- Performed Kelvin probe measurements of the R2R gravure-coated IRS GDEs to understand the impact of formulation and drying parameters on enabling segregation of the ionomer during the drying process.
- Performed in situ testing (polarization, mass activity, transport resistance) of the same GDEs to understand the correlation between achieving an ionomer-rich surface and achieving target MEA performance.
- Developed an open-source software tool to perform equivalent-circuit modeling for the analysis of fuel cell electrochemical impedance spectroscopy (EIS) measurements.
- Performed XCT of IRS GDEs to understand the impact of ink and process parameters on ionomer, pore size, and solid-particle size distributions in the electrode.
- Initiated the development of a fuel cell catalyst ink rheology model to elucidate particle-ionomer-solvent interactions.

- Studied high-solids ink formulation, mixing, and the resulting particle size to support initial slot-die coating studies.
- Awarded a new CRADA project with Proton OnSite to collaborate on high-volume methods for PEM electrolysis MEA fabrication.

## INTRODUCTION

GDEs are recently garnering high interest in the industry as an alternate or possibly combined fabrication pathway for MEAs, as opposed to the more standard catalyst-coated membrane (CCM) approach. GDEs provide a different set of fabrication and performance variables that may provide improved performance and lifetime in some cases. However, fabrication of MEAs based on GDEs can require different material structures than CCMs, and, for scaling of GDE-based MEAs, this means potentially different process techniques and conditions. For example, an additional layer of ionomer, which would require another processing step, is often required between the GDE catalyst layer and membrane to achieve comparable performance to CCMs. The goal of this project is to explore, understand, and optimize material and process parameters for scalable processes to support increased throughput, increased quality, and reduced cost for high-volume production of MEAs by developing single-process methodologies to coat IRS GDEs via R2R processes with comparable performance to baseline CCMs.

## APPROACH

The approach is to understand the fundamental (nano- and micro-scale) interactions in the heterogeneous electrode ink that lead to macro-scale properties determined by rheology, which ultimately impact coating and drying parameters as well as device performance (NREL and ORNL). NREL and ORNL will leverage coating technologies across several scales to fabricate IRS GDEs. Advanced characterization tools at ANL and ORNL (USAXS and XCT at ANL's Advanced Photon Source [APS] and electron microscopy at ORNL) will be leveraged to understand the dispersion of particles and polymer in the ink and to image the morphology through the thickness of the electrode layer as a function of material, ink, and process parameters. Modeling capabilities at LBNL will be leveraged to help understand the complex interparticle interactions in the electrode that impact rheology, coatibility, and the electrode layer morphology. NREL will utilize standard in situ testing to quantify impact of ink and process parameters on performance.

## RESULTS

We performed USAXS measurements of inks with different catalyst supports, ionomer-to-carbon ratios (I:C), and solvent mixtures at the APS at ANL. The measurements were made in an in situ apparatus, designed such that samples of the ink could be directly measured during the dispersing process as a function of time. Figure 1 (a) shows the raw USAXS intensity data as a function of the scattering vector ( $Q$ ), where increasing  $Q$  is associated with decreasing particle size. In this example, data for four different durations of bath sonication are shown. Figure 1 (b) then shows the USAXS intensity as a function of time for the  $Q$  values associated with nominally  $3\ \mu\text{m}$  ( $Q = 0.0002$ ) and nominally  $300\ \text{nm}$  ( $Q = 0.002$ ) structures. We observe that, for the first 10 minutes of sonication, larger agglomerates are broken up, leading to an increase in smaller, aggregate particles. After 10 minutes of sonication, no further breakup of particles is observed. MEAs were made with inks of the same formulations, and in situ polarization and mass activity results indicated that a 10-second tip sonication prior to bath sonication resulted in improved performance over that of bath sonication alone, and that, subsequent to a 10-second tip sonication, 20 minutes of bath sonication led to higher performance and mass activity than for 5- and 1-minute bath sonication durations.

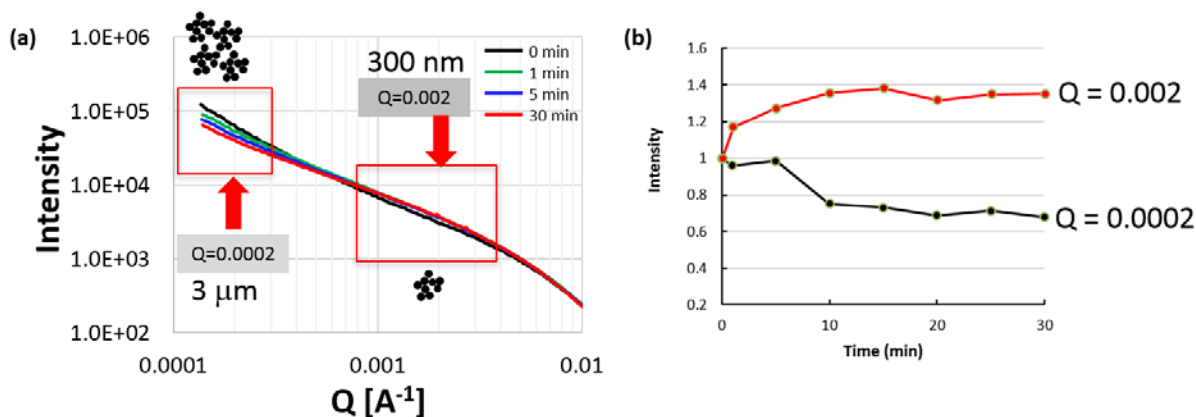


Figure 1. (a) Raw USAXS intensity data for an example ink sonicated for four different durations, and (b) USAXS intensity data associated with agglomerate ( $Q = 0.0002$ ) and primary aggregate ( $Q = 0.002$ ) particles in the ink as a function of mixing time

We also performed unique NREL-developed oxygen-transport limiting current analysis and EIS to understand the oxygen transport (non-Fickian) resistance and bulk catalyst layer resistances in these MEAs. We observed that the optimal case (10-s tip + 20-min bath) had a lower resistance than a comparator (1-min bath) case, which experienced ineffective dispersion and thus had larger catalyst agglomerates. Similarly, the EIS measurements indicated that the 10-s tip + 20-min bath and 20-min bath cases had the least catalyst layer proton resistance. The 20-min tip sonication case had higher resistance due to excessive sonication that detached Pt from the carbon support, whereas the 1-min bath case had the highest resistance due to insufficient dispersion. To assist with data analysis for these in situ studies, we developed a methodology and associated open-source code to perform equivalent-circuit modeling of fuel cell MEA EIS data. This code helps us to understand the resistances in the various MEA layers as a function of the various ink and process parameters, including protonic resistance of the cathode. The open-source code has been provided to the community via NREL's website.

We performed Kelvin probe measurements of R2R gravure-coated GDEs, which provide a rapid indication of the amount of ionomer on the surface of the electrode. Figure 2 (a) shows these results, which indicate that higher I:C and higher fraction of water in the water/1-propanol solvent mixture lead to higher surface content of ionomer. We then performed in situ testing of MEAs made from these GDEs. Figure 2 (b) and (c) show that the oxygen-reduction-reaction mass activity and  $H_2$ /air polarization performance, respectively, both improve for conditions that optimize ionomer content on the GDE surface.

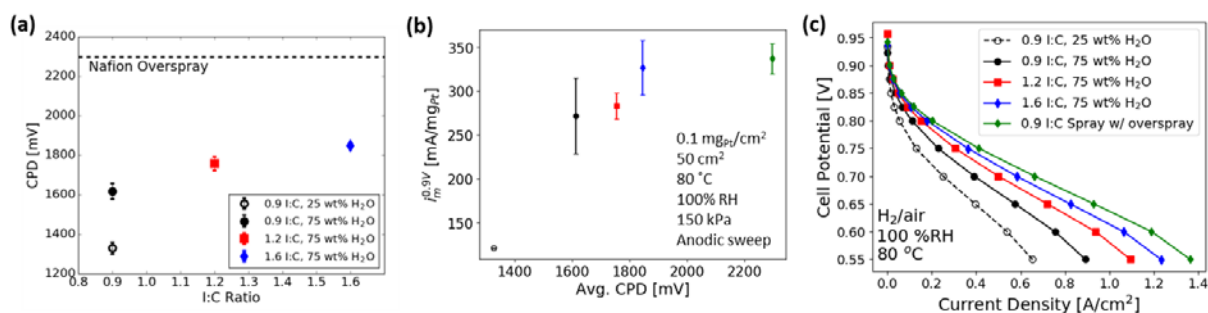


Figure 2. (a) Kelvin probe contact potential difference as a function of I:C for inks with different I:C and solvent ratio, (b) mass activity as a function of contact potential difference for MEAs made from the same four inks as well as for the comparator GDE with a separate ionomer overcoat (same legend as [c]), and (c)  $H_2$ /air polarization for the same MEAs

XCT of these GDEs was also performed at the APS to understand how ink and process parameters impact the morphology of the electrode. Figure 3 (a) shows a 3-D reconstruction of the microstructure of one of the electrodes. Figure 3 (b) shows profiles of ionomer distribution through the normalized thickness of the electrode as a function of water/1-propanol mixture and I:C. The electrodes cast from the water-rich solvent (solid data lines) have a more uniform distribution because the ionomer associated with the catalyst particle is not mobile during the drying of the electrode. We also see that higher I:C leads to an increase in the ionomer surface content. In the electrode cast from the 1-propanol-rich dispersion, the ionomer is not associated with the catalyst, so it is more mobile and can redistribute itself within the electrode as it dries.

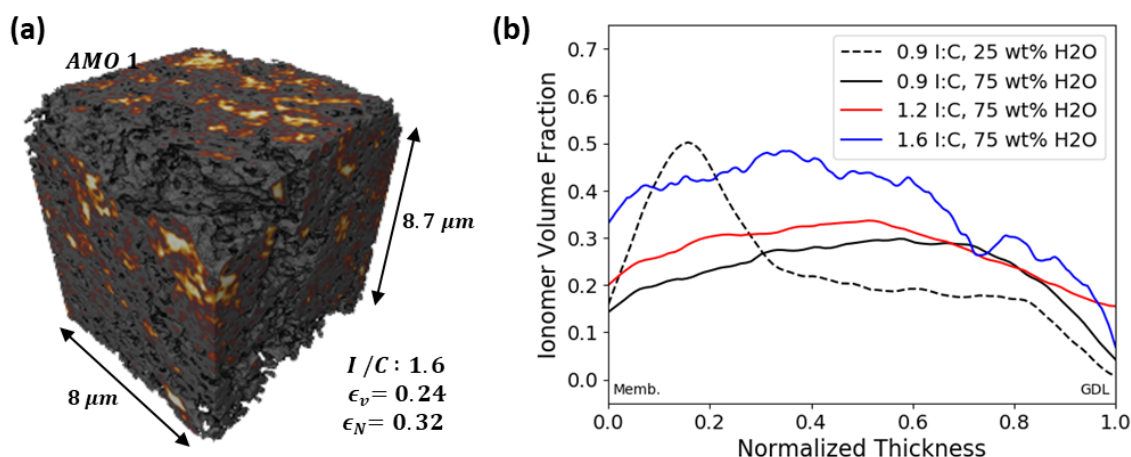


Figure 3. (a) 3-D visualization of the example electrode, and (b) through-the-thickness ionomer profiles from XCT

In preparation for slot-die coating of catalyst inks, we performed rheology and particle-size studies of high-solids-loading carbon-only inks to understand processing limitations with these materials. Figure 4 (a) shows rheology data for three of the carbon-only inks, with solids loadings between 10% and 13%. The rheological behavior of all three inks is shear thinning, and the viscosity is seen to increase with solids loading. Figure 4 (b) shows an image of the slot-die-coated carbon ink on the coating line at ORNL.

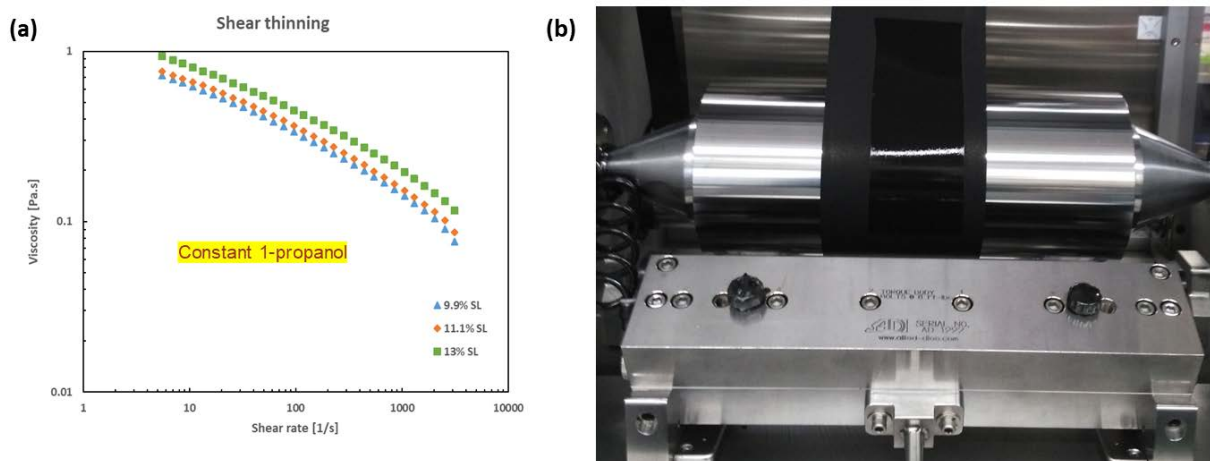


Figure 4. (a) High-solids-loading ink viscosity as  $f(\text{shear rate})$ , and (b) image of slot-die coated carbon-only ink

## CONCLUSIONS AND UPCOMING ACTIVITIES

- As shown in Figure 2, the R2R-coated IRS GDEs to date have demonstrated equivalent mass activity to the baseline CCM, although the high-current-density performance is not yet comparable. These data show strong potential for meeting the goal of replacing a two-layer (electrode + ionomer overcoat), two-process-step GDE fabrication methodology with one having a single layer and comparable performance to the CCM baseline.
- Future work under consideration toward fully meeting the project goals (depending on future funding and prioritization) includes dual-slot simultaneous two-layer coating of the electrode and ionomer layers, single-layer segregated coatings at higher drying temperature and using alternate solvents, further development of the fuel cell ink rheology model, and initiation of consolidation and coating physics models.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. P. Rupnowski, M. Ulsh, B. Sopori, B.G. Green, D.L. Wood III, J. Li, and Y. Sheng, “In-line monitoring of Li-ion battery electrode porosity and areal loading using active thermal scanning – modeling and initial experiment,” *J. Power Sources* 375 (2018):138–148.
2. B.L. Sopori, M.J. Ulsh, P. Rupnowski, G. Bender, M.M. Penev, J. Li, D.L. Wood III, and C. Daniel, “Batch and Continuous Methods for Evaluating the Physical and Thermal Properties of Thin Films,” U.S. Patent Application no. 15/554,551, March 8, 2018.
3. J. Park, N. Kariuki, D.J. Myers, S.A. Mauger, K.C. Neyerlin, and M. Ulsh, “In Situ X-Ray Scattering Characterization of PEMFC Catalyst Ink Microstructure during Ink Processing,” Oral presentation MA2018-01 at the 233<sup>rd</sup> ECS Meeting, Seattle, WA, May 2018.
4. C. Daniel, S. Mauger, G. Krumdick, R. Prasher, M. Ulsh, and D. Wood, “Roll-to-roll Advanced Materials Manufacturing Lab Consortium,” Oral presentation at the Hydrogen and Fuel Cell Program Annual Merit Review and Peer Evaluation Meeting, Washington DC, June 2018.
5. M. Ulsh, S. Mauger, S. Khandavalli, J. Pfeilsticker, M. Wang, K.C. Neyerlin, D. Wood III, J. Li, M. Wood, D. Myers, N. Kariuki, J. Park, C.F. Cetinbas, R. Ahluwalia, G. Krumdick, A. Weber, F. Ma, and R. Prasher, “PEM Fuel Cell Gas-diffusion Electrodes with Ionomer-rich Surface Layer,” Poster presentation at the Advanced Manufacturing Office Peer Review Meeting, Washington DC, July 2018.
6. S.A. Mauger, C.F. Cetinbas, J.H. Park, K.C. Neyerlin, R.K. Ahluwalia, D.J. Myers, S. Khandavalli, L. Hu, S. Litster, and M. Ulsh, “Control of ionomer distribution and porosity in roll-to-roll coated fuel cell catalyst layers,” Poster presentation at the Fuel Cells Gordon Research Conference, Smithfield, RI, July 2018.
7. S.A. Mauger, C.F. Cetinbas, R.K. Ahluwalia, D.J. Myers, J. Park, K.C. Neyerlin, L. Hu, S. Litster, and M. Ulsh, “Control of ionomer distribution and porosity in roll-to-roll coated fuel cell catalyst layers,” Oral presentation at the International Symposium of Coating Science and Technology, Long Beach, CA, September 2018.