
Material-Process-Performance Relationships in Polymer Electrolyte Membrane Catalyst Inks and Coated Layers

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direction determined annually by DOE

Overall Objectives

- Develop 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 2020.
- Study material-process-performance relationships for membrane electrode assembly (MEA) materials in scalable processes, providing guidance for new process development to lab and academic partners, including via Energy Materials Network consortia.
- Increase understanding of interparticle interactions between ionomers, catalysts, supports, and solvents to better understand their influence on ink structure and stability and relationship to material performance.
- Develop scalable processes to demonstrate manufacturing pathways for new materials or device constructions.

Fiscal Year (FY) 2019 Objectives

- Perform ink development studies of unsupported low-temperature electrolysis (LTE) catalysts to understand the influence of

solvent and catalyst materials on ionomer-catalyst interactions.

- Characterize the influence of coating flow types on catalyst layer morphology.
- Determine the influence of solvent formulation on ionomer adsorption on catalyst/support.
- Evaluate ink formulations, drying conditions, and substrates to reduce crack formation in fuel cell and electrolysis catalyst layers coated using scalable methods.

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 Plan¹:

- (A) Lack of high volume MEA processes.

Contribution to Achievement of DOE Milestones

This project will contribute to 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 1.2: Develop processes for direct coating of electrodes on membranes or gas diffusion media. (4Q, 2017)
- Milestone 1.3: Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)
- Milestone 1.6: Develop fabrication and assembly processes for polymer electrolyte membrane fuel cell (PEMFC) MEA components leading to an automotive fuel cell stack that costs \$20/kW. (4Q, 2020).

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

FY 2019 Accomplishments

- Characterized the influence of coating flow conditions on catalyst layer morphology and electrochemical properties.
- Determined the influence of catalyst ink solvent formulation on roll-to-roll (R2R) coated PEMFC catalyst layer microstructure and electrochemical properties.
- Performed rheology, zeta potential, and stability studies of unsupported (LTE and platinum-group metal [PGM]-free) and supported catalysts.
- Collaborated with coworkers and the Fuel Cell Performance and Durability Consortium (FC-PAD) to understand the influence of catalyst ink solvents on ionomer adsorption on catalyst particles and resulting catalyst layer microstructure and electrochemical properties.
- Characterized interactions in IrO₂-Nafion ink and determined electrosteric stabilization of IrO₂ by Nafion.
- Determined the influence of materials, process conditions, and ink formulations on catalyst layer cracks.

INTRODUCTION

To produce fuel cell and electrolysis MEA components at the scales necessary to achieve DOE cost targets, continuous coating methods will be required. To enable the use of these methods, especially with regard to early-stage activities at universities, small companies, and lab-based consortia for new material development (e.g., via the ElectroCat and HydroGEN Energy Materials Network consortia), there is a need for elucidation of material-process-performance relationships in continuous coating processes that would be used to produce fuel cell and electrolyzer components. Critical to these relationships for the heterogeneous dispersions used to coat active layers is a foundational understanding of the interparticle interactions and their relationship to the structure and behavior of ink constituents in different formulations and preparations and under different shear regimes. Particle-polymer-solvent interactions in these inks must be better understood. Relative to coating methods, NREL has used internal investments to source, install, and commission a multi-technology coating station. We have shown the capability to coat active layers of interest for PEMFCs using methods understood in the coating industry. Importantly, different coating techniques of interest have different intrinsic physics, which may affect morphology, uniformity, and performance—these behaviors must be explored.

We have addressed these topics through studies of interparticle interactions in catalyst inks to understand how catalyst or polymer properties influence their interactions and how this leads to a better understanding of the parameters that control catalyst layer microstructure and electrochemical properties. Similarly, we have also worked to explore the effects that different continuous coating methods have on catalyst layer microstructure and electrochemical properties. Through these efforts we are developing a better picture of how catalyst layer materials and ink formulations impact the outcome of different coating methodologies.

APPROACH

NREL and its partners are addressing the DOE manufacturing milestones listed above by performing R&D to elucidate how material and fabrication parameters impact MEA performance. We utilize industry relationships to understand MEA material, structure, and processing directions and challenges. We utilize a variety of experimental methods including rheometry, dynamic light scattering (DLS), zeta potential measurement, and X-ray scattering to characterize ionomer-particle interactions in catalyst inks. These learnings are leveraged to understand the influences of materials and catalyst ink formulations and MEA performance. NREL's R2R coating facilities are used to study the influence of fabrication methodology on catalyst layer structure and electrochemical properties. Catalyst layers are studied using electron microscopy and electrochemical properties are analyzed using several in situ electrochemical characterization techniques.

RESULTS

We continued our efforts to study the interactions between IrO₂ catalysts and ionomers in LTE catalyst inks. This fiscal year, work focused on two variables: IrO₂ concentration and ionomer content (relative to IrO₂). These inks were studied primarily using rheometry, zeta potential, and DLS. Supporting experiments were also performed using ultra-small-angle and small-angle X-ray scattering (USAXS/SAXS) in collaboration with Argonne National Laboratory. Figure 1 shows zeta potential measurements, USAXS/SAXS, and dynamic

oscillatory shear rheology of IrO₂ catalyst inks. The zeta potential measurements in Figure 1a show a decreasing trend in zeta potential with increasing ionomer content. This trend is indicative of ionomer adsorbing to the surface of the IrO₂ catalyst particles. Since Nafion is an anionic polymer, the negatively charged sulfonic acid groups will contribute more negative surface charge to the catalyst particles.

Figure 1b shows the results of USAXS/SAXS measurements of IrO₂ catalyst inks with and without ionomer. These measurements show that the addition of ionomer stabilizes the IrO₂ particles against agglomeration in two ways. First, it can be clearly seen that the addition of ionomer decreases the radius of gyration (which is fit from the data) from 465 nm to 54 nm. And second, the slope in the low-*q* region ($q < 0.001 \text{ \AA}^{-1}$) provides a qualitative measure of large-scale agglomeration within the ink. It can be seen that the ionomer significantly decreases the slope in this region, again showing that the ionomer is stabilizing these inks against large scale agglomeration. The ionomer provides stabilization through two mechanisms: (1) electrostatic repulsion (as shown by the zeta potential measurements) and (2) steric stabilization.

Rheological studies allow us to study catalyst-ionomer interactions as a function of concentration and ionomer content. Figure 1c shows dynamic oscillatory shear rheology of IrO₂ catalyst inks with and without ionomer. Through these measurements, the elastic (G') and viscous (G'') modulus are determined providing information about the interactions and gelation in the ink. Without ionomer, the G' and G'' are independent of frequency indicating the IrO₂ catalyst particles have agglomerated and formed a gel. At 9 wt % ionomer, the moduli scaling of the frequency-sweep response changes to $G' \sim \omega^1$ and $G'' \sim \omega^2$ where $G'' > G'$. Such scaling behavior is a characteristic response of liquid-like materials and indicates the particles are not agglomerated, consistent with USAXS/SAXS. With further increases in ionomer loadings beyond 9 wt % up to 23 wt %, the moduli magnitudes begin to increase, and the behavior predominantly remains viscous-like with $G'' > G'$ throughout the frequency range. However, the moduli scaling behavior changes, where they now scale similarly with frequency as $G' \sim G'' \sim \omega^n$, where $n \sim 0.7$ and 0.8 for 16 wt % and 23 wt % ionomer, respectively. Such scaling behavior has been observed in flocculated colloidal dispersions where attractive interparticle interactions are at play, which suggests the existence of a fractal-like flocculated structure of the particles. The conclusion from this work is that at low ionomer loadings the IrO₂ catalyst is stabilized by ionomer but at higher ionomer contents, the ink starts to agglomerate again.

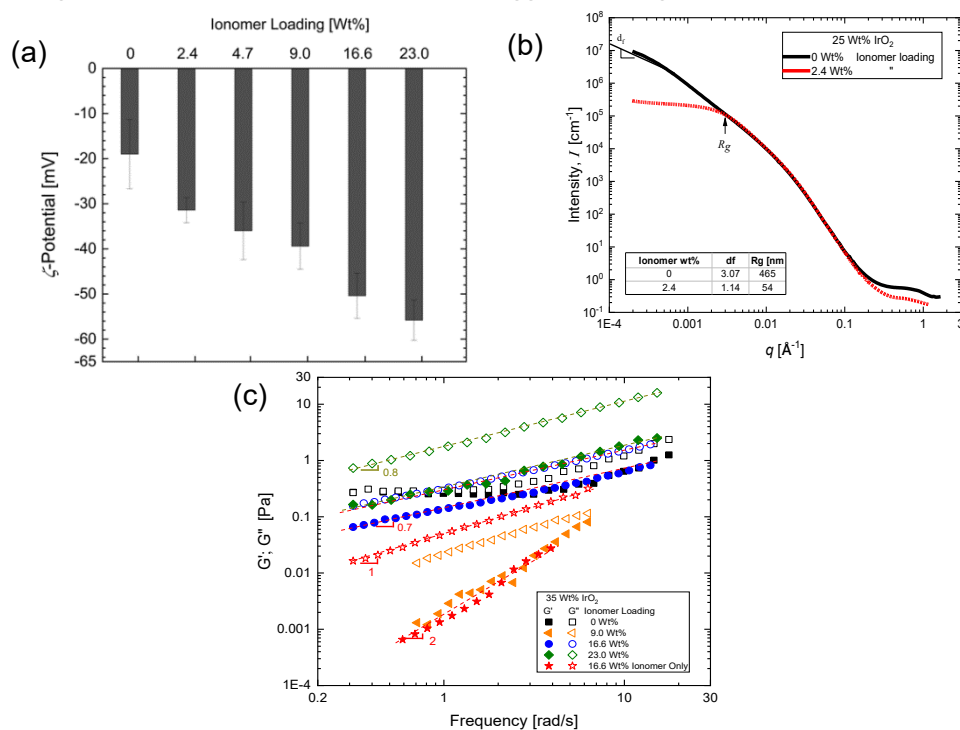


Figure 1. (a) Zeta potential measurements of IrO₂ catalyst ink at various ionomer loadings. (b) USAXS/SAXS of IrO₂ ink with and without ionomer. (c) Frequency sweep measurement at multiple ionomer loadings.

We also continued our work studying the influence of coating methodology on fuel cell catalyst layers. Catalyst layers were coated using R2R slot-die and gravure directly onto gas diffusion media to create gas diffusion electrodes. These were assembled into MEAs for subsequent electrochemical testing. It was found that slot-die coating resulted in better fuel cell performance than gravure coating as shown in Figure 2. This was also found to be independent of the solvent mixture in the catalyst ink. Electrochemical impedance spectroscopy showed that the performance differences were due to a higher protonic resistance in the gravure coated catalyst layers. Using transmission electron microscopy, we were able to see that the gravure-coated catalyst layers had a lower ionomer content than slot-die-coated catalyst layers, which was responsible for the higher protonic resistance. We believe this difference is due to the slot-die-coated catalyst inks being subjected to high shear rate flow conditions for much longer than the gravure-coated inks, which leads to breakup of agglomerated catalyst particles and a more homogeneous distribution of ionomer.

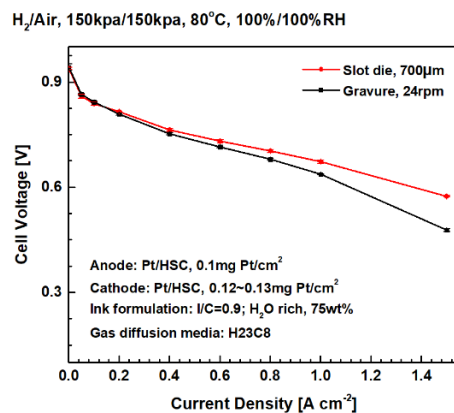


Figure 2. Air polarization curves of MEAs with R2R cathodes coated with slot die (red) or gravure (black).

In collaboration with the FC-PAD consortium members at NREL, we studied the influence of catalyst ink solvents on ionomer interactions with the catalyst and support and their effects on electrochemical performance. Using DLS and zeta potential, we were able to understand how different ratios of water and 1-propanol changed how Nafion adsorbed onto a platinum on Vulcan carbon catalyst (Pt/Vu). We found that at all water:1-propanol ratios studied, the addition of ionomer to a Pt/Vu ink resulted in the zeta potential becoming more negative (Figure 3), like was observed with IrO₂, indicating ionomer adsorption. We furthered this study by adding salt to the inks to diminish the effects of electrostatic repulsion and limit stabilization to steric repulsion. With the addition of NaCl, there was significant increase in particle size (measured by DLS) at 24 and 83 wt % water, whereas there was only a small increase in particle size at 62 wt % water. This behavior may indicate either a stronger association with Pt/Vu or a more expanded polymer structure at 62 wt % water than in the other solvent ratios. Through electrochemical testing of MEAs, our collaborators were able to show that inks formulated with a 62 wt % water solvent ratio resulted in the highest MEA performance, linking catalyst ink formulation to catalyst layer electrochemical properties. In the case of R2R coated catalyst layers, it was also observed that catalyst inks with similar water contents resulted in higher performance than catalyst inks that were 1-propanol rich.

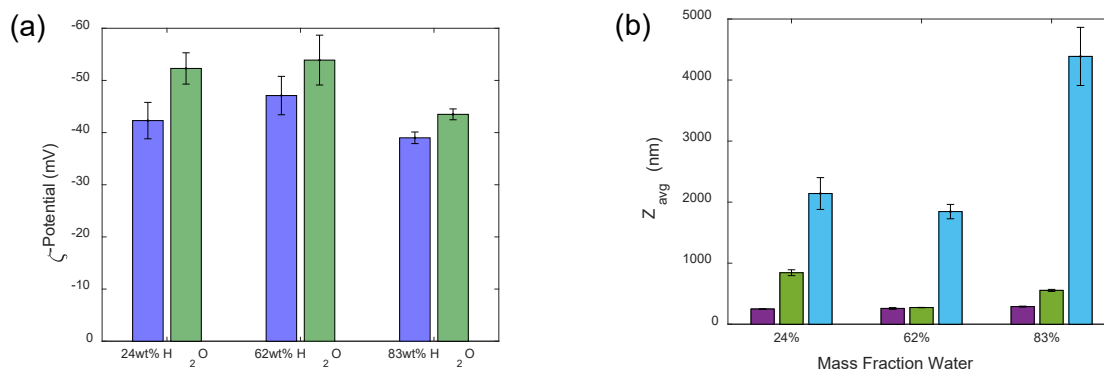


Figure 3. (a) Zeta potential measurements of Pt/Vu catalyst inks with (green) and without (blue) ionomer. (b) Z-average particle size for Pt/Vu catalyst inks with ionomer as a function of NaCl concentration.

We have also started work to understand the factors that control cracking in catalyst layers and strategies to reduce cracking. We have found that the structure of the substrate influences cracking. As shown in Figure 4, it is seen that a gas-diffusion layer with a cracked microporous layer (MPL) leads to a cracked catalyst layer, whereas a crack-free MPL leads to a crack-free catalyst layer. We have also initiated exploration of the role that catalyst ink formulation plays in this behavior, for both PGM and PGM-free catalysts. To date, we have seen that increasing the alcohol content of the catalyst ink decreases cracking and have also seen that a higher ionomer concentration reduces cracking.

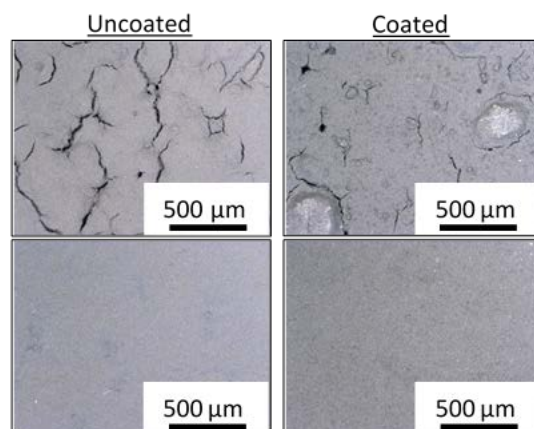


Figure 4. Optical microscopy images of uncoated MPL (left) and catalyst layers coated onto the MPLs using R2R coating (right).

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2019, we continued our work related to materials-process-performance relationships in PEMFC and LTE. This work resulted in the following conclusions.

- Ionomer stabilizes IrO₂ particles in catalyst ink, though large amounts of ionomer can lead to agglomeration of the particles.
- Slot-die coating leads to higher-performance PEMFC catalyst layers than gravure coating does.
- Catalyst ink solvent ratio influences the ionomer adsorption onto the catalyst particles and provides stabilization of the particles against agglomeration.
- Cracked substrates and water-rich catalyst inks lead to more cracking in catalyst layers cast using scalable methods.

In FY 2020, we will continue with work in the following areas:

- Preparation of advanced alloy catalyst layers using scalable methods for performance and durability testing.
- Characterization of the influence of ionomer chemistry on catalyst-ionomer interactions in catalyst ink dispersions.
- Characterization of the influence of catalyst ink solids concentration on catalyst layer microstructure and performance for electrodes coated using scalable coating methods using at least two different catalyst types (e.g. Pt/C, LTE, PGM-free) and three concentrations.
- Exploration of additives (e.g., binder materials) and/or catalyst ink modifications (e.g., sample preparation methodology) to mitigate catalyst layer cracks.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. S. Khandavalli, J.H. Park, N.N. Kariuki, D.J. Myers, J.J. Stickel, K. Hurst, K.C. Neyerlin, M. Ulsh, and S.A. Mauger, “Rheological Investigation on the Microstructure of Fuel Cell Catalyst Inks,” *ACS Applied Materials Interfaces* 10, no. 50 (2018): 43610–43622.
2. S. Khandavalli, J.H. Park, N.N. Kariuki, S.F. Zaccarine, S. Pylypenko, D.J. Myers, M. Ulsh, and S.A. Mauger, “Investigation of the Microstructure and Rheology of Iridium Oxide Catalyst Inks for Low-Temperature Polymer Electrolyte Membrane Water Electrolyzers,” *ACS Applied Materials Interfaces*, submitted (2019).
3. T. Van Cleve, S. Khandavalli, A. Chowdhury, S. Medina, S. Pylypenko, M. Wang, K.L. More, A. Weber, S. Mauger, M. Ulsh, and K.C. Neyerlin, “Dictating Pt-based Electrocatalyst Performance in PEFCs; from Formulation to Application,” *ACS Applied Materials Interfaces*, submitted (2019).
4. S. Khandavalli, J.H. Park, N.N. Kariuki, D.J. Myers, J.J. Stickel, K. Hurst, K.C. Neyerlin, M. Ulsh, and S.A. Mauger, “Rheological investigation of fuel cell catalyst inks,” Presentation at the Society of Rheology meeting, Houston, TX, October 2018.
5. M. Ulsh, S. Mauger, S. Khandavalli, J. Pfeilsticker, M. Wang, and K.C. Neyerlin, “Understanding how Ink Formulation, Processing, and Coating Affect the Morphology, Coatability and Performance of Polymer Electrolyte Membrane Fuel Cell Electrodes,” Invited oral presentation at the 7th De Nora R&D Symposium, Cleveland, OH, October 2018.
6. M. Ulsh and S. Mauger, “Material-Process-Performance Relationships in PEM Catalyst Inks and Coated Layers,” Oral presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, April 30, 2019.