

## V.B.3 FC-PAD: Electrode Layers and Optimization

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Project Start Date: October 1, 2015

Project End Date: September 30, 2021

### Overall Objectives

- Demonstrate improved performance and durability of fuel cells.
- Develop and implement characterization techniques for gas diffusion layers (GDLs), membranes, and ionomers.
- Characterize and understand interfaces and interfacial properties on fuel cell performance and durability.
- Elucidate and mitigate ionomer film resistances in the catalyst layer through model studies to better evaluate performance and durability of fuel cells.
- Explore and optimize transport phenomena related to liquid water.

### Fiscal Year (FY) 2017 Objectives

- Develop and examine new catalyst layer structures.
- Investigate origin of local resistance at low Pt loadings.
- Initiate catalyst layer ink studies.
- Conduct multimodal determination of catalyst layer microstructure.
- Explore multiphase flow and interactions within the GDLs using advanced diagnostics and imaging.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability
- (B) Cost
- (C) Performance

### FY 2017 Accomplishments

- Initiated studies on catalyst layer inks, including investigation of aggregation and stability as a function of solvent dielectric constant.
- Examined water transport throughout the membrane electrode assembly (MEA), including X-ray imaging of phase-change-induced flow in the GDLs.
- Investigated novel microporous layers with hydrophilic additives that demonstrate improved water management and performance.
- Examined local resistance measurements with hydrogen and oxygen limiting current, including delineation of interfacial resistance and carbon structure.
- Developed several novel catalyst layer architectures, including stratified and array ones as well as specific Pt deposition concepts.
- Utilized model and advanced diagnostics to determine catalyst layer microstructure.
- Conducted experiments and developed model of droplet formation and shedding from GDL to flow channel.
- Modeled and validated delta-V and polarization curve analysis utilizing oxygen gain.



## INTRODUCTION

The FC-PAD consortium was formed to advance performance and durability of polymer electrolyte membrane fuel cells to meet DOE targets and further enable the commercialization of fuel cells. The major challenge to be addressed by this consortium is to develop the knowledge base and optimize structures for more durable, high-performing polymer electrolyte membrane fuel cell component technologies, while simultaneously reducing cost. Specifically, we will develop validated models and advanced in situ and ex situ characterization techniques to further improve the performance and durability of fuel cells. We will also evaluate polymer electrolyte membrane fuel cell component issues from low to operating temperatures of interest, including the impact of liquid water. We will characterize and understand components from the membrane to the porous media and their interfaces, with a focus on the ionomer within the catalyst layers.

## APPROACH

The FC-PAD consortium incorporates national laboratory investigators with proven experience (developed in prior projects) related to durability, transport, and performance, and combines them into one highly coordinated effort. The effort is sub-divided into six thrust areas, including three materials-related thrusts and three cross-cutting thrusts. This report summarizes some of the work performed in the three cross-cutting thrust areas: (1) Modeling and Validation; (2) Operando Evaluation: Benchmarking, Accelerated Stress Tests, and Contaminants; and (6) Component Characterization and Diagnostics. The thrust areas of the consortium are highly integrated, and the work performed related to the various specific components is presented in the reports of the three materials thrust areas. The project will also benchmark the performance and durability of state-of-the-art MEAs provided by original equipment manufacturers and materials suppliers. Finally, the project will apply in situ and ex situ characterization techniques to reveal the performance losses and degradation mechanisms operational in fuel cells and propose strategies to improve performance and durability.

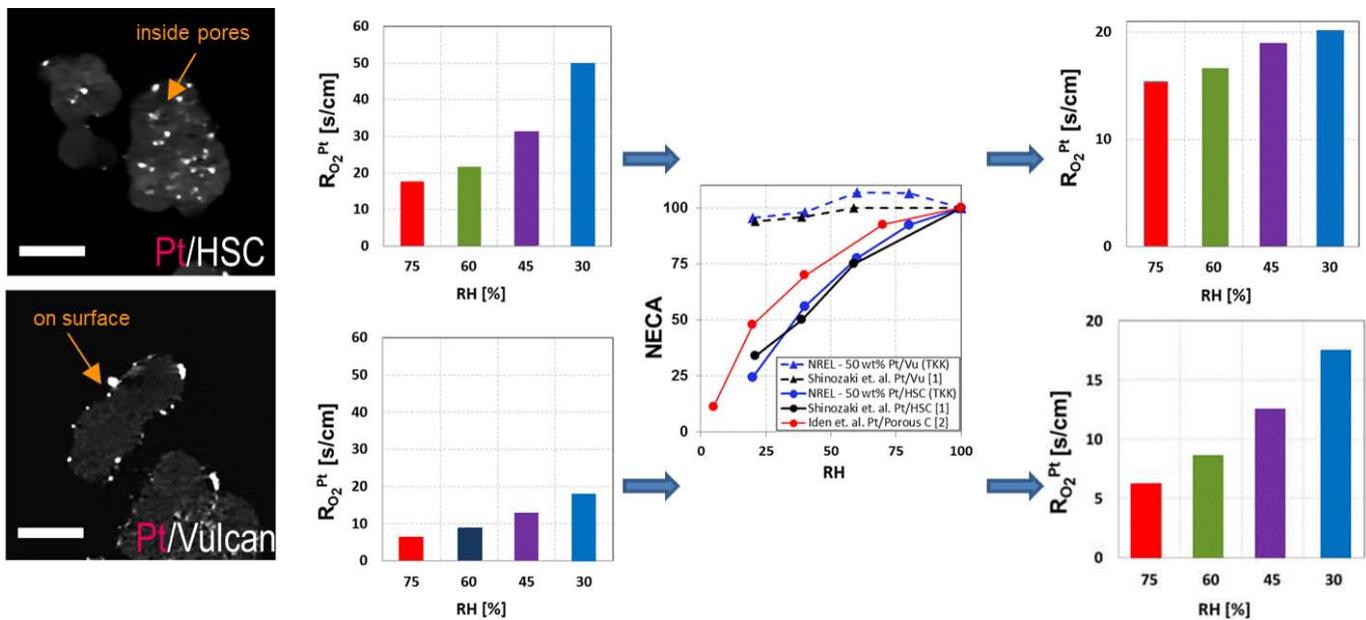
This report focuses on the analysis of electrode layers and their subsequent optimization. Included in this area are integration efforts for both existing and novel catalyst layer structures that improve performance. In addition, work related towards understanding water and thermal management in various components and demonstrating improved performance is also mentioned, including both modeling and experimental diagnostics. Finally, examining the origin of the observed local resistances for low platinum group metal catalyst layers is discussed.

## RESULTS

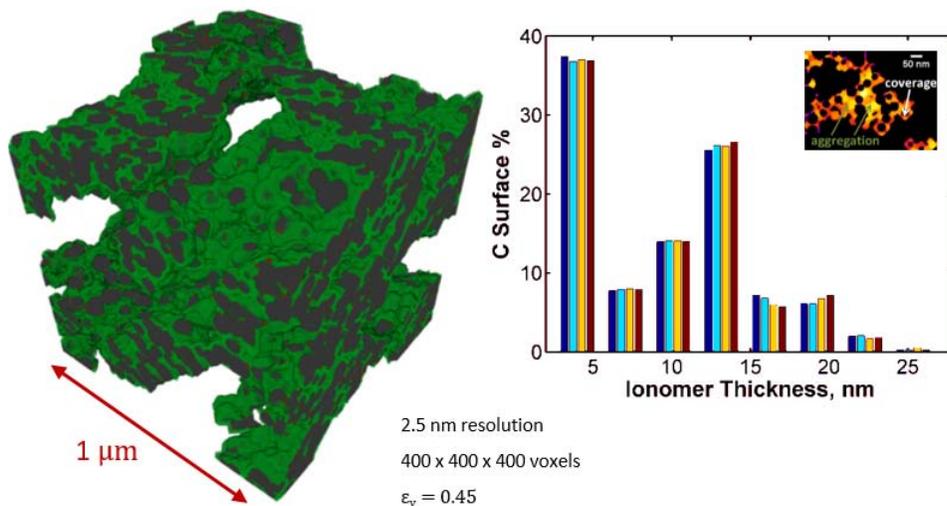
It is well accepted that low-Pt-loaded electrodes suffer from a local resistance that is due in part to mass transport [1,2]. It is believed that such resistance could be due to the ionomer films covering the reaction site, and we have been investigating this using limiting-current techniques. A key issue is that using established methods [3] requires knowledge of the electrochemically active surface area (ECSA). However, this area is not measured under limiting-current conditions. Furthermore, as shown in Figure 1, for high-surface-area carbons (HSC), this is a strong function of relative humidity (RH) due to the fact that over 70% of the platinum particles are within the primary pores of the carbon agglomerates. This is not the case for low-surface-area supports such as Vulcan, where the majority of platinum particles are on the surface. Thus, it makes sense for studies that examine local resistances to use effective ECSAs as well as Vulcan-type supports to probe resistances due to transport through the ionomer thin-films. In addition, the effective ECSA is expected to be even smaller at limiting current since only the surface platinum is active due to limiting-current conditions wherein kinetic overpotentials are not limiting. This is seen when one compares the ECSA slope method utilizing multiple MEAs with that of a single MEA measurement using stacked GDLs. Using Vulcan supports, the resistance in the latter is about 70% of the former, suggesting that not all platinum is active under limiting current and care must be taken when analyzing the data. Finally, comparison between oxygen and hydrogen methods suggests that the bulk of the transport resistance is due to traditional diffusional-type mass transport losses.

In analyzing local resistances and understanding transport through the catalyst layer, there is a need to be able to probe the catalyst layer structure. We have shown that advanced transmission electron microscopy can determine some ionomer distributions in the catalyst layer, including preferential agglomeration towards Pt compared to carbon, yet the finest structure on the 10 nm or so scale remains elusive. To overcome this bottleneck, we have utilized a combined approach of stochastic modeling and realizations with advanced X-ray and electron microscopy studies. As shown in Figure 2, we utilize measured distributions for solids and catalyst with a random carbon nucleation and growth to reconstruct the catalyst layer. By subtracting the carbon distribution from the measured solid distribution, we can determine the ionomer film thickness and its subsequent coverage. As shown, various realizations demonstrate that the majority of the carbon surface is covered by ionomer films less than 10 nm in thickness.

While knowing the catalyst layer structure is one thing, there is a need to optimize it, especially for performance. To do so, we investigated several approaches, including catalyst layer architectures based on more rational design and fabrication of ionomer and even platinum nanoparticles.



**FIGURE 1.** Transmission electron microscope micrographs showing platinum on higher-surface-area carbon and low-surface-area carbon that results in different effective ECSA values (net electrochemical activity [NECA]). Local resistances when corrected for NECA result in less humidity dependence and similar values for the two different supports.

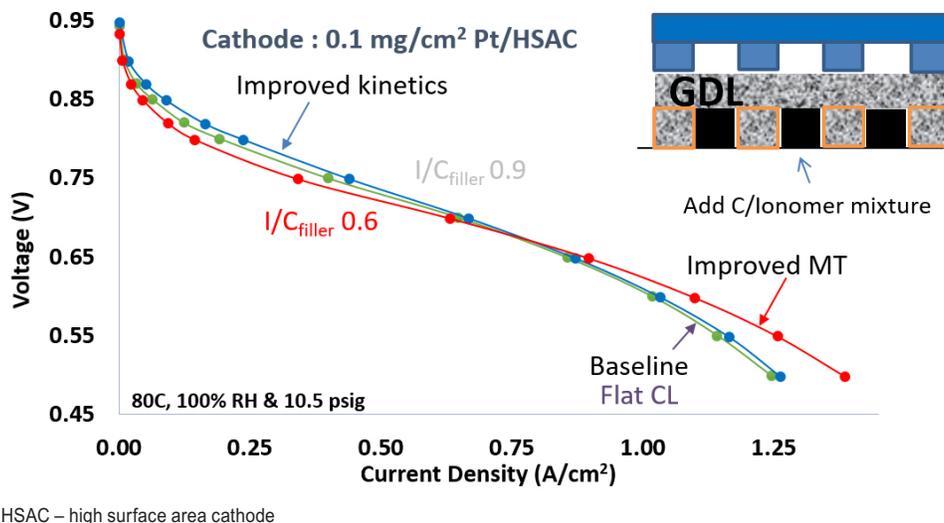


**FIGURE 2.** Catalyst layer reconstruction from nano X-ray tomography and stochastic nucleation modeling resulting in shown ionomer film distribution.

One such approach is shown in Figure 3, where modeling and subsequent experiments were conducted and demonstrated that placing the platinum-containing catalyst layers in a stratified manner can increase overall performance, especially in the mass transfer (MT) regime, without requiring an increase in loading. Placing the active catalyst layer (CL) under the channels more so than the lands provided for more efficient water management and higher performance compared to baseline samples. It was also observed that there is a need to still have blank carbon in

the nonactive catalyst layer regions to ensure adequate water removal pathways as well as to mitigate possible durability concerns.

For exploring multiphase water interactions, both modeling and experimental studies were conducted. It was shown how analysis of oxygen gain and polarization curves can be used as a diagnostic to determine the key limiting phenomena. In addition, the often suspected phase-change-induced flow, where water moves down a temperature gradient, was quantified using X-ray microtomography. Also,



HSAC – high surface area cathode

FIGURE 3. Polarization curves with stratified catalyst layers. Inset shows the stratification structure.

the impact of water dynamics and droplet shedding from the GDL to the flow channel was visualized and modeled. Finally, to improve water management and in agreement with mathematical predictions [4], microporous layers with hydrophilic additives were explored. As shown in Figure 4, such structures provide for better performance due to their ability to remove liquid water from the catalyst layer, which agreed with X-ray tomographic observations of liquid water in the microporous layers. In particular, the addition of carbon nanotubes demonstrated the best performance. This performance gain was not only quantified in terms of lower water content, especially in the cathode, but also a decreased adhesion force at the GDL boundary with the flowfield that enables more efficient water movement. This more efficient

water management not only resulted in better performance, but also increased durability during wet drive cycle testing.

### CONCLUSIONS AND UPCOMING ACTIVITIES

To optimize performance and durability of fuel cell components including ionomers, interfaces, and diffusion media in this thrust of FC-PAD, we have enacted a synergistic combination of the crosscutting thrusts to explore component properties, behavior, and phenomena. Combined modeling and experiments to understand interfaces demonstrated the importance of water droplets at the GDL/flowfield boundary as well as the possible increase in

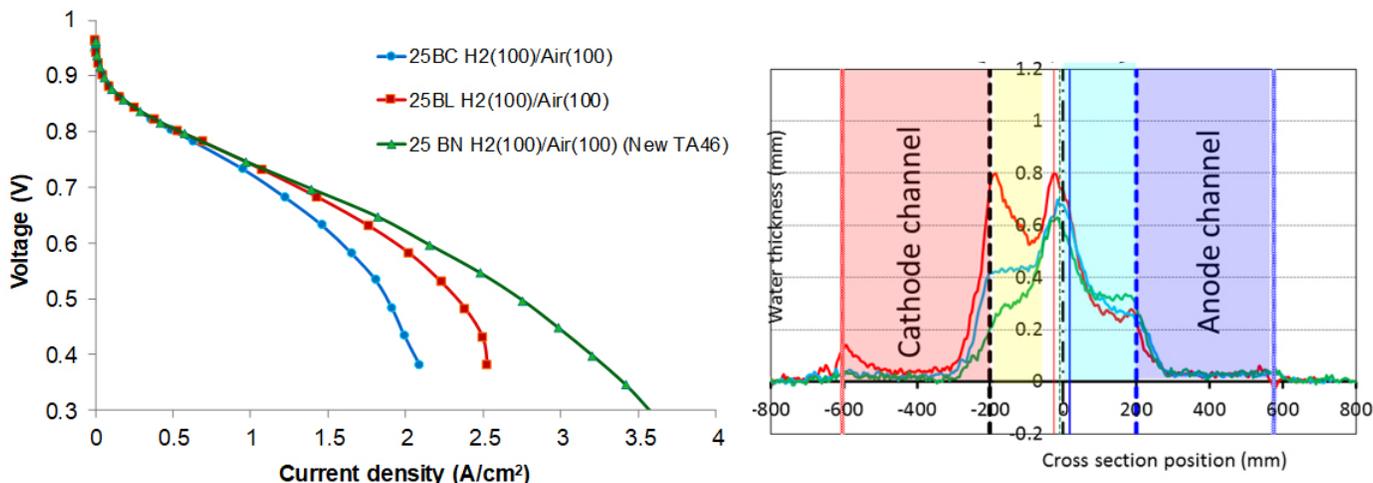


FIGURE 4. Polarization curves at 80°C, 100% relative humidity and neutron imaging demonstrating that microporous layers with hydrophilic additives (either carbon nanotube [BN] or aluminasilicate [BL] fibers) demonstrate better performance and differences in cell water content.

performance through catalyst layer architecture optimization. Limiting-current diagnostics across a systematic study of different catalyst layers demonstrated the importance of accurate effective active area measurements as well as the apparent dominance of diffusion-like transport at the local ionomer scale.

For upcoming activities, we plan to focus on elucidating critical bottlenecks for performance and durability from ink to formation to conditioning to testing. We will continue work on optimizing catalyst layer structure for high performance at low loadings. This includes exploration of different architectures, including stratified, array, electrospun, HSC/Vulcan-layered, and specific Pt deposition. Along with this will be microstructural modeling of both catalyst-layer structure as well as transport through the layer. This modeling will work in tandem with the multiscale modeling of cell and components to understand water and thermal management and their impact on durability and performance. The models will also be validated by comparison with various differential, integral, and segmented cell data. Finally, we will explore the genesis of membranes and thin films and their associated properties. This includes both ex situ studies of thin-film morphology with various cations and under electrochemical potential as well as in situ limiting-current interrogations under a variety of conditions, techniques, ionomers, gases, temperature, and humidity.

## FY 2017 PUBLICATIONS/ PRESENTATIONS/HONORS

1. Please see the FC-PAD: Overview annual report for the complete list of 61 presentations, 20 publications, 2 invention disclosures, and 4 awards.

## REFERENCES

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