

V.B.3 FC-PAD: Electrode Layer Integration

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Project Start Date: October 1, 2015
 Project End Date: September 30, 2020

Overall Objectives

- Demonstrate improvements in component stability and durability.
- Demonstrate improvements in cell performance due to optimized transport.
- Develop new capabilities (such as advanced diagnostic tools or models) to aid developers, advance knowledge of component properties, and develop advanced structures, strategies, and methods to achieve these objectives.
- The consortium will provide technical capabilities to future projects focusing on performance and durability of polymer electrolyte membrane fuel cells as a resource to DOE and industrial developers.

Fiscal Year (FY) 2016 Objectives

- Identify sources for state-of-the-art (SOTA) electrocatalysts that meet or exceed the DOE mass activity targets of 440 mA/mgPt.

- Integrate SOTA electrocatalysts that meet or exceed the DOE mass activity targets of 440 mA/mgPt and optimize the catalyst layer to attain the DOE peak power density requirements of 1 W/cm² and 0.125 gPt/kW while simultaneously meeting durability targets.
- Identify the source(s) of the unanticipated substantial performance losses observed at loading below 0.1 mgPt/cm² using existing and novel diagnostic techniques.

Technical Barriers

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

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

Technical Targets

See Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and Membrane Electrode Assemblies (MEAs) for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (50 cm ² cell, differential conditions)
Mass activity	A/mg _{Pt} @ 0.9 mV _{IR-free}	≥0.44	≥0.44
PGM total loading	mg-PGM/cm ² _{geo}	≤0.125	0.1, cathode
MEA performance	mW/cm ² _{geo} @ 600 mV	≥1,000	700–800

PGM – precious group metals; IR - Internal resistance

FY 2016 Accomplishments

- Three SOTA catalyst layers were identified.
- Catalyst layers evaluated have all met the DOE mass activity target of 440 mA/mgPt.
- Progress has been made on understanding transport through the layer using diagnostic tools and modeling using limiting current diagnostics and kinetic studies.



INTRODUCTION

The primary objective of the FC-PAD consortium is to implement improvements to polymer electrolyte membrane fuel cells and their components with respect to cost, durability, and performance. Although catalysts that have met the DOE targets of oxygen reduction reaction (ORR) activity have been demonstrated in half-cells, implementing them in cathode catalyst layers at low loadings while maintaining low mass transport at high current densities has been elusive due to the presence of an additional transport resistance at the catalyst-ionomer interface.

The consortium will develop new capabilities (such as advanced diagnostic tools or models) to aid developers, advance knowledge of component properties, and develop advanced structures, strategies, and methods to achieve these objectives that may be summarized as:

- Improvements in component stability and durability
- Improvements in cell performance due to optimized transport
- Development of new diagnostics, characterization tools, and models

The expected outcome will be polymer electrolyte membrane fuel cell MEAs and components that demonstrate world-class performance and durability, meeting and exceeding the 2020 targets listed in the consortium-related target tables in the addendum. The major durability targets to be met include 5,000 h of operation under simulated vehicle power cycling and shut-down/start-up cycling with <10% loss in rated power. In terms of performance, the key targets are meeting efficiency, power, startup time and energy, and related metrics within the cost and durability constraints. In specific developing MEAs with SOTA catalysts that demonstrate performance $>1 \text{ W/cm}^2$ with Pt loading $<0.125 \text{ mg/cm}^2$.

APPROACH

Our approach involves identifying SOTA catalysts, optimizing them in catalyst layers, developing diagnostics to help resolve the high current density, low loading problem and mitigating the problem through the use of novel electrode design, novel components, novel diagnostics techniques all complemented with modeling. The research concentrates on improving the performance of low Pt loaded electrode layers at high current densities and limiting the degradation losses at the electrode layer level, including electrocatalyst and support composition and morphology changes and electrode-structure changes. Mass-transport issues are a performance limitation at high current densities and during operation under non-optimal conditions, such as with high water content (e.g., encountered at low temperature), with

low surface area catalysts at low loadings, and with alloy catalysts, particularly at low relative humidity. In this project, the impact of different catalyst-layer compositions (including low equivalent-weight ionomer) will be explored to ascertain how transport phenomena change. Applying existing diagnostics using limiting current and developing new techniques, the transport limitations will be quantified and the resistance better defined. The formation of electrode layers is still a black art. In this work, various techniques including rheology, dynamic light scattering, etc., will be applied to ink formulations to determine the critical properties to ensure optimal layer structure and performance and durability. Changes including altering the ionomer-solvent-catalyst ink composition, solvent removal methods, and/or ionomer properties, such as equivalent weight, will be explored in coordination with related activities. In addition, to increase high-current-density performance, new electrode-layer structures will be explored including those involving two separate phases of ionomer in the catalyst layer (i.e., a very thin first layer coating the catalyst surfaces to provide local conductivity with a minimal transport barrier and a second phase of a solid network to provide bulk ionic conductivity and structural integrity) as well as extended PGM skins, both of which can be utilized with electrospun ionomer.

RESULTS

Sources and Benchmarking of Catalysts and MEAs

Sources of state-of-the-art (SOTA) and baseline catalysts were identified and obtained from (i) commercial vendors or suppliers of catalysts who can supply hundreds of grams of catalyst, and (ii) novel catalysts that have been developed under DOE programs by various national laboratories that may be available in gram quantities. Ideally, FC-PAD would prefer catalysts that can be analyzed thoroughly before and after performance and durability studies without any restrictions.

IRD, New Mexico, is one of the vendors that provided catalyst and catalyst layers for evaluation by the FC-PAD. Los Alamos National Laboratory obtained catalyst coated membranes (CCMs) from IRD and distributed it to the FC-PAD labs. Catalyst from Umicore, Germany, catalysts have been studied in rotating disk electrode at NREL and their PtCo/C has shown enhanced activity over Pt/C. Umicore has provided Pt/C and PtCo/C catalysts for the FC-PAD through NREL to the various labs for MEA preparation and performance evaluation. General Motors (GM) provided proprietary SOTA MEAs for evaluation. Prior to MEA fabrication and evaluation, screening of some of the catalysts and comparisons were made using Rotating disk electrode techniques [1-6].

Activity and Performance of Baseline and SOTA MEAs in Fuel Cells

The objective was to fabricate and optimize cathode catalysts layers have loadings approaching $\sim 0.1 \text{ mg/cm}^2$ that have high performance and durability for conventional supported catalysts and to develop and apply novel diagnostics to understand issues at high current densities. As new fabrication technology and materials and diagnostics are developed, they will all be applied to obtain MEAs that perform to DOE targets but catalyst layers in this work were fabricated using spray-coating techniques.

The ORR activity of baseline Pt/C has not been updated and reported recently in the literature using a clearly defined test protocol [7]. Prior to evaluating the SOTA MEAs, the baseline MEAs were evaluated and the results summarized in Figure 1. Baseline as well as SOTA catalysts and catalyst layers were imaged using transmission electron microscopy at Oak Ridge National Laboratory as shown in Figure 2. The ORR activity of PtCo/C SOTA MEAs were evaluated using the same hardware and test protocols as the baseline MEAs. The Tafel plots for the three SOTA MEAs as well as a table reporting the ORR activity and surface area are presented in Figure 3. All the SOTA MEAs met the DOE targets of ORR activity at beginning of life. These results corroborate studies in rotating disk electrode that demonstrated these PtCo/C catalysts as having higher activity compared to baseline

Pt/C. The performance of these MEAs under wet hydrogen-air conditions are compared in Figure 4. At this time in the first iteration of fabricating these catalyst layers, the MEAs

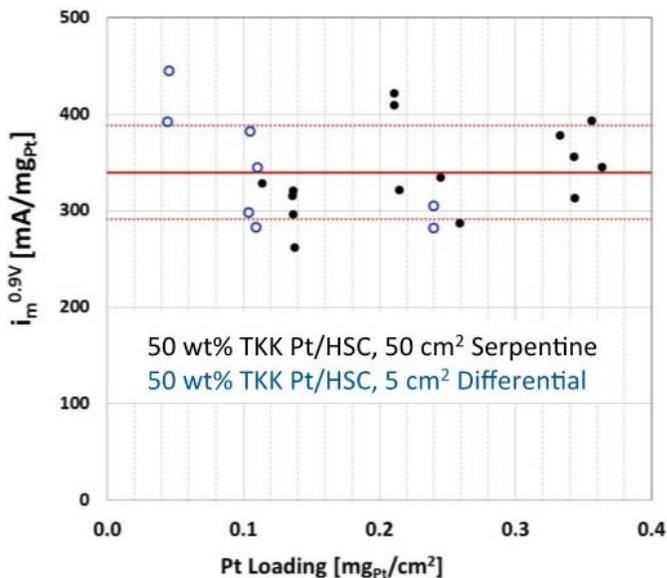


FIGURE 1. Mass activity vs. catalyst loading for 50 wt% baseline Pt/HSC MEAs fabricated at NREL using TKK TEC10E50E Pt/C at various loadings and operating conditions as well as hardware conducted using FC-PAD protocols

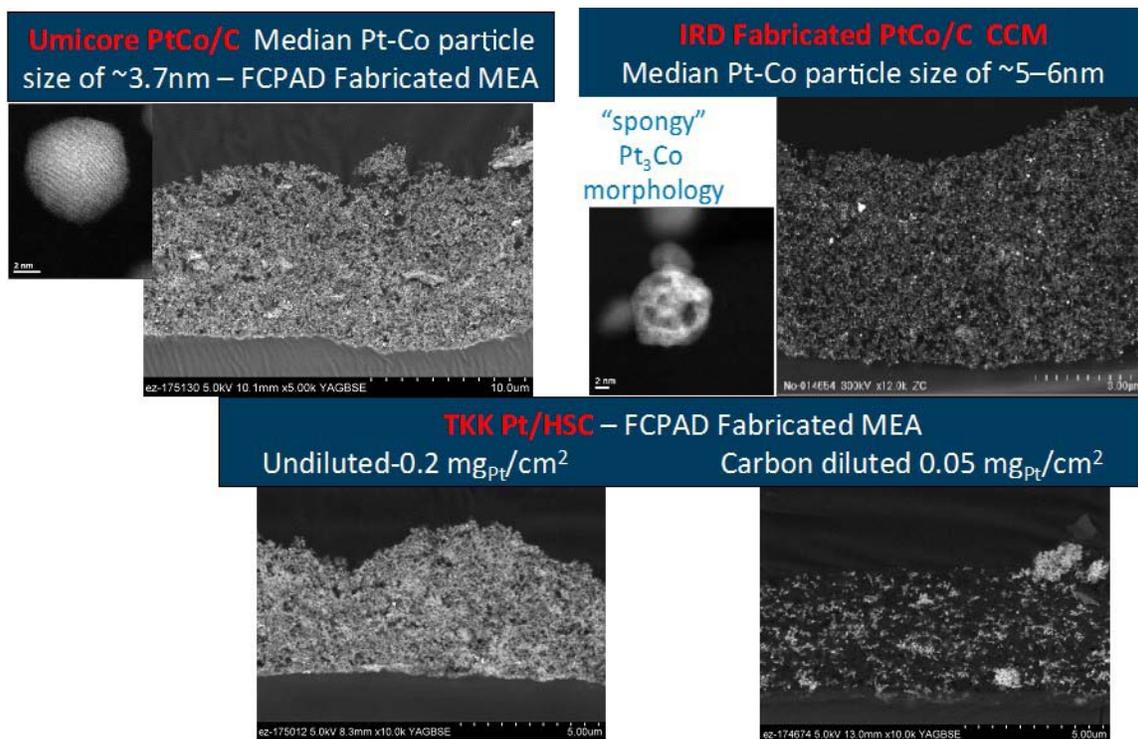
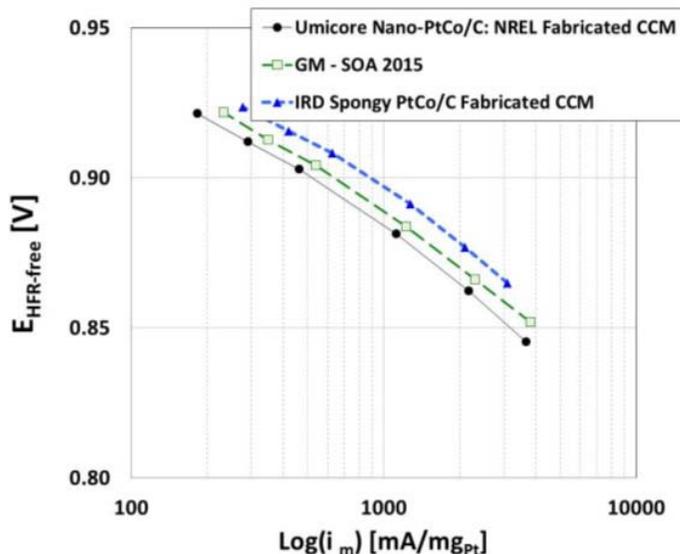


FIGURE 2. Transmission electron microscopy images of electrocatalysts and electrode layers based on SOTA catalysts and baseline Pt/C catalysts



ORR Activity @ 0.90 V

	MA	SA	ECA
Umicore	514 ±40	1406 ±135	37 ±2
GM	620 ±60	1440 ±130	43 ±1
IRD	820 ±20	2000 ±6	41 ±1

MA = mA/mg_{Pt} ; SA = μA/cm²_{Pt} ECA = m²/g_{Pt}

SOA – State of the art; ECA – Electrochemical surface area; SA – specific amperage

FIGURE 3. ORR activity of three SOTA catalysts and tabulated activity values. Operating conditions for evaluation are: H₂, O₂ 150 kPa, 80°C, 100% RH, S = 2/9.

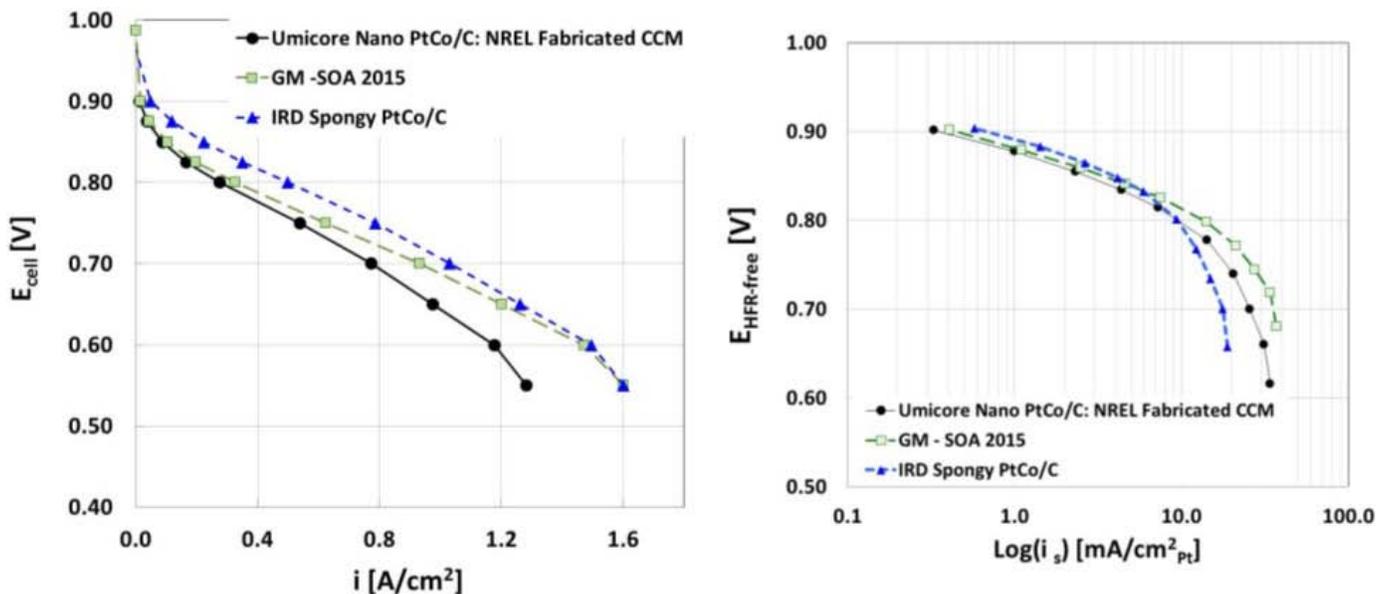


FIGURE 4. H₂-air performance of SOTA catalysts conducted under wet conditions, 80°C, 150 kPa, and 100% RH.

do not meet the high current density or peak power density DOE target. Optimization of these layers is likely to improve the high current density performance approaching limiting currents. Results and insights from parallel work being conducted to diagnose and mitigate the losses at high current density at low catalyst loadings will be applied to the catalyst layers to improve their performance in the future.

Mass Transport Diagnostics Development

In order to understand and resolve the complex issue of lower than expected performance at high current densities for low loaded cathode catalyst layers that have been observed by a majority of groups [8-15], development and refinement of diagnostic techniques is necessary to identify the source(s) of additional losses and find mitigation pathways. FC-PAD will study both existing diagnostics and establish and verify their

value at several labs as well as develop new techniques that may provide insight into the problem.

Several diagnostics have been recently established that involve limiting current studies as well as kinetic studies. Diluted oxygen as well as pure oxygen was employed to obtain limiting currents. The following limiting diagnostics were evaluated:

- Dilute oxygen in nitrogen limiting current data was acquired on Pt/Vu as a function of Pt loading, relative humidity (RH), and oxygen partial pressure.
- Pure oxygen limiting current measurements under vacuum conditions were performed on Pt/Vu as a function of Pt loading, RH, and oxygen partial pressure.
- CO limiting current data was acquired on Pt/Vu electrodes to assess the relevance of such measurements in the future towards the elucidation of local Pt transport resistance.

Since it is not known if the kinetics of ORR changes at low potentials and low oxide coverage, it is important to determine the kinetics accurately so that any additional losses can be identified and attributed to alternative sources that are relevant to high current density operation. This kinetic information is also crucial for inputting in models. Sub-ambient ORR kinetic measurements were conducted along with Pt oxide dependent kinetics on Pt/Vu electrodes using a vacuum panel system and a highly automated test stand. These measurements were coupled with the Pt oxide measurements to produce a Pt oxide dependent kinetic model. Analysis of the magnitude of local resistance at the catalyst-ionomer interface from limiting currents is elucidated in Figure 5.

Electrode-Layer Designs and Fabrication

The cathode catalyst layer structure is typically based of an ink of Pt/C, ionomer and solvents that are sonicated or mixed together to form a slurry. Advancement of the

catalyst layer is possible through the separation of some of the functions and better pathways for protonic transport. Excessive ionomer mixed with an ink leads to catalyst layers that flood due to plugged pores. By providing a major low resistance highway for protons to move through the catalyst layer by means of fibers or a network and lowering the amount of ionomer that is applied directly to the catalyst surface, it may be possible to obtain a much higher performance electrode. Ionomer adsorption may also be reduced if less ionomer is in direct contact with the Pt. Using electro-spun fiber in the catalyst layer is one of the design pathways. Issues such as fiber integrity are being addressed by choice of solvent, use of TBA⁺ blended with Na⁺ and heat treatment. Temperature and TBA⁺ can be tailored to obtain preferred structures. Spray coating of the ink onto the membrane requires elimination of the hot pressing step and cryo-milling of the fibers. Insights from these studies will be input into obtaining high performance using commercial as well as laboratory synthesized scale state-of-the-art catalysts. Research was conducted at Los Alamos National Laboratory on improving the solubility resistance of electro-spun ionomer fibers to withstand MEA processing conditions by using the TBA⁺ ionomer form. For example, Na⁺ form ionomer fibers heat treated at 200°C are substantially distorted and dissolved or recast by simple additions of methanol. Varying TBA⁺/Na⁺ ratios and heat treatments: by exchanging the Nafion in the electro-spinning solution into the tetrabutyl-ammonium cation (TBA⁺) form, the spun fibers become thermoplastic. Thus heat treatments substantially improve the durability of the spun fibers. However, the extremely thin fibers melt very easily and coalesce even at relatively modest temperatures if the ionomer is in the purely TBA⁺ form. Thus, work progresses in identifying suitable TBA⁺/Na⁺ ratios and treatment temperatures. Even the low TBA⁺ content results in appreciable fusion, but if carefully controlled the process can potentially yield highly advantageous fiber networks.

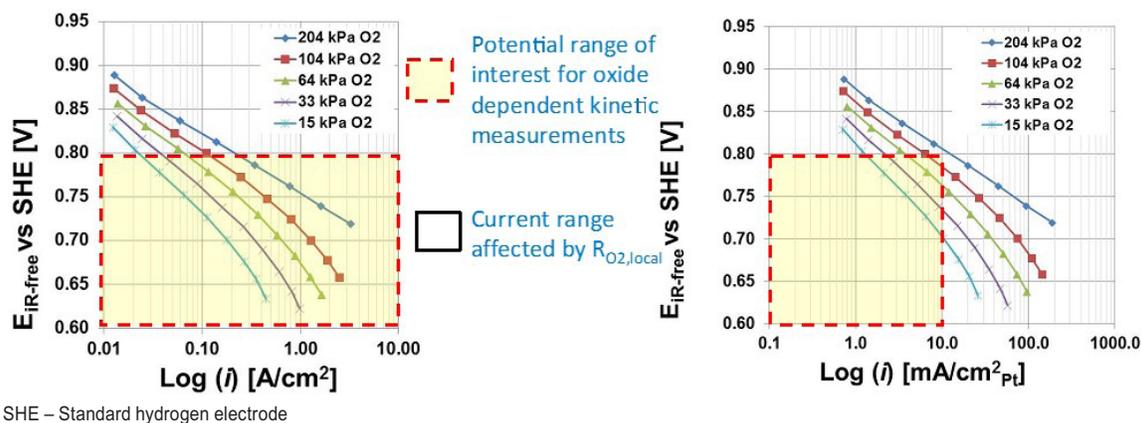


FIGURE 5. Oxide dependent Pt kinetics for Pt/Vu 0.05 mg_{Pt}/cm² conducted under H₂/O₂ 80°C, 100% RH and 150 kPa

Optimization of the electrode components like ionomer morphology and content are being pursued to improve fuel cell performance at high current densities. Modeling results have indicated that controlled thickness and density variations in the catalyst layer can lead to improved water management and better fuel cell performance. To make controlled Pt layer stratifications, multiple approaches are being explored; the primary progress towards catalyst layer stratification was by developed designed catalyst layer structures via a spray coating technique. This technique is used to fabricate electrodes with stratified catalyst layers with alternating thick and thin layers providing a pathway for the liquid water to efficiently exit the catalyst layer efficiently, thus preventing flooding at high current densities.

CONCLUSIONS AND FUTURE DIRECTIONS

All three SOTA catalyst layers evaluated so far have met the DOE MA target of 440 mA/mg_{Pt} but do not meet the peak power requirements. Preliminary work has been conducted on developing modified electrode layer designs intended to reduce mass transport in the catalyst layer. Progress has been made on understanding transport through the layer using diagnostic tools and modeling.

Future work involves the following: (a) determine whether kinetics actually comes into play at high current densities; (b) identify and implement alternative ionomers in catalyst layers to examine effects on performance; (c) model performance diagnostics data at high current densities; and (d) identify alternative designs for cathode catalyst layer that enhance both performance and durability at high current densities.

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