V.B.6 High Performance Polymer Electrolyte Membrane Fuel Cell Electrode Structures

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Subcontractors:
- Ion Power Inc., New Castle, DE
- University of Arkansas at Little Rock (UALR) Little Rock, AR

Project Start Date: October 1, 2016
Project End Date: December 31, 2019

Overall Objectives

- Develop improved understanding of the various transport losses in polymer electrolyte fuel cell (PEFC) cathode catalyst layers with state-of-the-art ultra-low platinum group metal (PGM) catalyst loadings.
- Obtain this fundamental understanding by developing and validating a detailed microstructural cathode-catalyst layer model.
- Utilize this validated cathode-catalyst layer model to develop and demonstrate membrane-electrode assemblies (MEAs) that can potentially meet all of DOE's 2020 Technical Targets for MEAs.

Fiscal Year (FY) 2017 Objectives

- Finalize multi-party non-disclosure agreement with all partners, including FC-PAD Consortia members.
- Demonstrate MEA with state-of-the-art performance with ultra-low PGM loadings.
- Complete framework of microstructural cathode-catalyst layer model.

Technical Barriers

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

(A) Durability (Improved understanding of initial transport losses is required to mitigate degradation)

(B) Cost (MEAs with ultra-low PGM loadings have relatively large transport losses)

(C) Performance (Reduced transport losses are required to meet high power density targets)

Technical Targets

- This project is ultimately focused on developing high performance MEAs with ultra-low PGM catalyst loadings. However, to date, the team has focused on MEAs with Pt-only catalysts (i.e., not Pt-alloy catalysts that have higher activities) since these MEAs are less complex.

TABLE 1. Progress towards Meeting MEA Technical Targets for Transportation

Characteristic	Units	DOE 2020 Targets	Project Status (differential operating conditions)
PGM total loading	mg-PGM/cm$^2_{geo}$	≤0.125	0.2 total (0.1 each electrode)
MEA performance	mA/cm$^2_{geo}$ @ 0.8 V	≥300	222 (Pt-only catalyst)
MEA performance	mW/cm$^2_{geo}$ @ rated power (~0.65 V)	≥1,000	722 (Pt-only catalyst)

FY 2017 Accomplishments

- Developed and demonstrated MEAs with improved performance, even with reduced catalyst loadings (i.e., MEAs with 0.2 mg-Pt/cm² exhibited superior performance to initial MEAs with 0.3 mg-Pt/cm²).
- Demonstrated that MEAs with low loadings of Pt-only catalysts exhibit similar transport losses as MEAs with Pt-alloy catalysts, as long as total catalyst surface area is comparable.
- Developed PEFC-electrode model that includes basic framework for microstructural features in state-of-the-art MEAs.
- Have begun fabricating novel thin-film catalysts with varying catalyst densities.

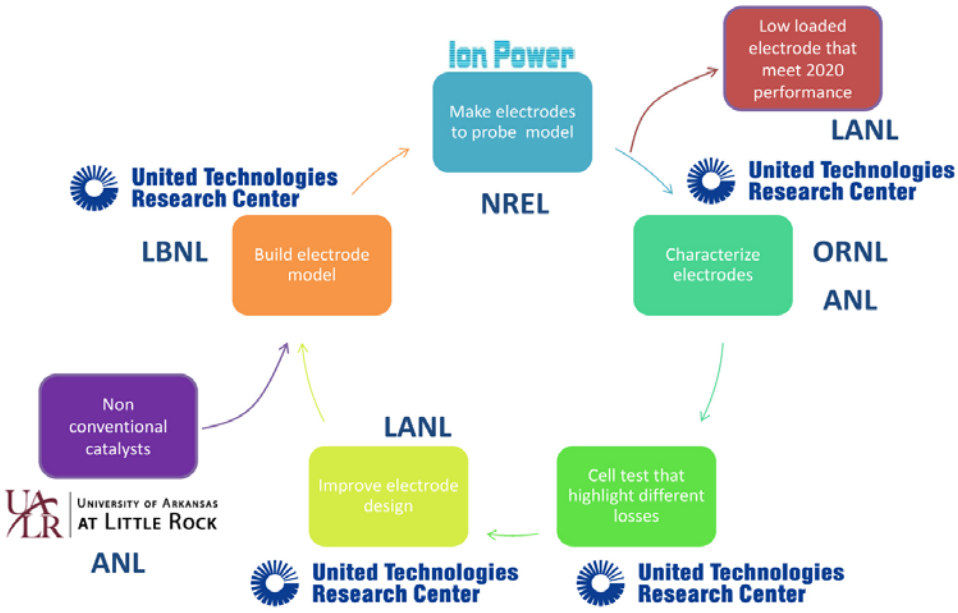
INTRODUCTION

MEAs with ultra-low loadings of highly active Pt-alloy catalysts have already been demonstrated to exceed DOE's 2020 high-efficiency target of >0.3 A/cm^2 at 0.8 V [1]; however, the rated-power target of 1 W/cm^2 cannot be met with these MEAs due to transport losses unique to MEAs with ultra-low catalyst loadings. Therefore, what is primarily needed to fully realize DOE's 2020 targets is mitigation of these transport losses, which is the focus of this project. The initial focus of this project is to improve the fundamental understanding of transport losses in PEFC cathode catalyst layers since the sources of these losses are not sufficiently understood. Subsequently, this improved understanding will be used to design advanced MEAs that have significantly reduced transport losses. This should ultimately enable the simultaneous requirements of high mass activity, low PGM loading, and high power density to be achieved.

APPROACH

The project objective will be realized by first developing and validating a detailed microstructural cathode-catalyst layer (CCL) model. CCLs are complex structures and there are many constituents and mechanisms within this critical layer that may make significant contributions to the observed transport losses. Furthermore, the relative importance of processes may vary with operating conditions. One needs to be able to differentiate between the wide variety of possible microstructures and phases within the electrodes with sufficient geometric detail in order to discern the transport-loss mechanisms. UTRC has begun to develop a detailed geometric model of the CCL that can be used to uniquely determine what components and mechanisms are major contributors to transport losses in this critical layer. A wide variety of CCL-characterization methods are being used to validate the model's geometric details and testing of a variety of MEAs under various operating conditions will enable validation of the model's performance-prediction capabilities.

The core project team has the capability to fabricate state-of-the-art MEAs using conventional carbon-support catalysts. In addition, UALR has unique capabilities to fabricate thin-film catalysts architectures, which shall eventually be used to develop CCLs with alternative electrocatalyst structures. Therefore, the team has ability to make both state-of-the-art MEAs and novel catalyst materials, and these capabilities will be used to design innovative catalyst-layer morphologies in order to achieve high performance at both high and low power densities. Discerning the sources and magnitudes of the various losses requires testing a matrix of CCLs that provide sufficient variations in the underlying parameters to highlight the different losses. Furthermore, each CCL variant needs to be subjected to a battery of diagnostic tests that help to quantify the different overpotentials. The iterative process to develop these high-performance MEAs is depicted in Figure 1, which includes utilizing the world-class capabilities of the FC-PAD Consortium.



LBNL – Lawrence Berkeley National Laboratory; NREL – National Renewable Energy Laboratory; LANL – Los Alamos National Laboratory; ORNL – Oak Ridge National Laboratory; ANL – Argonne National Laboratory

FIGURE 1. Simple graphical summary of the team's approach to achieving the project's objectives

RESULTS

UTRC has developed a framework of a microstructural geometric model of the CCL that can be used to determine what components and mechanisms are major contributors to transport losses in this critical layer. The general structure is similar to film-plus-core models of agglomerates like those reviewed by Weber [2]. In the case of conventional Pt alloy on carbon catalysts, emphasis is placed on the contents and structure of the agglomerate. Figure 2 shows calculated values for the number of carbon particles per agglomerate (n_c/n_a) and ionomer film thickness assuming that the ionomer forms a spherical shell around the C particles. The number of C particles per agglomerate and the thickness of the ionomer film increases with agglomerate diameter and both of these effects tend to decrease oxygen transport to catalyst sites. Packing more C particles in an agglomerate increases the flux through the ionomer film, while increasing the film thickness increases transport resistance. Most of the C particles should contact the ionomer shell when the number of carbon particles per agglomerate is small. Pt located on C that is disconnected from the ionomer may be underutilized when the fuel cell is operated. Understanding the distributions of catalyst and ionomer on carbon are essential to the unlocking of the microstructure of the CCL.

Limiting current densities for oxygen transport in the CCL can be derived for different geometries. Examination of limiting cases is instructive as it shows how to construct test electrodes that may help to discriminate the best approximation to the true electrode structure. For example, Figure 3 shows four interesting limiting cases for oxygen diffusion in the CCL that have already been included in the UTRC model. Each of the four limiting cases depicted in Figure 3 have different limiting current densities, which have unique dependencies on key CCL geometric parameters. Therefore, these limiting cases provide a useful starting point for the process of understanding the structure-performance relationships of the CCL. The various unique dependencies on CCL parameters can also be organized and used to guide the preparation of MEAs that highlight the differences between these limiting cases. Additional limiting cases are also possible and will be included in the model.

UALR has been working on density-modulated platinum thin film (Pt-TF) catalysts produced by high-pressure sputtering deposition. Change of working gas pressure of the sputtering system from low to high values during film growth can result in denser film bottoms and more porous tops. It is hypothesized that low-density film tops can provide effective transportation of oxygen and water, which could enhance catalyst utilization and result in reduced Pt-loading and enhanced activity. Porous, yet interconnected, networks of Pt atoms in the low-density Pt-TF surface can also potentially mitigate agglomeration and dissolution problems. In addition, high-density film bottom is expected to provide a strong adhesion to the substrate, potentially leading to enhanced physical and electrochemical stability of the Pt-TF. Stronger bonds, along with self-protection against the acidic environment due to the dense-packing of Pt atoms at the interface with the substrate, can hinder leaching of Pt and avoid the detachment of large regions of Pt-TF from the substrate as a whole. Additionally, high-density layer can reduce contact resistance and enhance the electronic conductivity. UALR has fabricated Pt-TFs with different

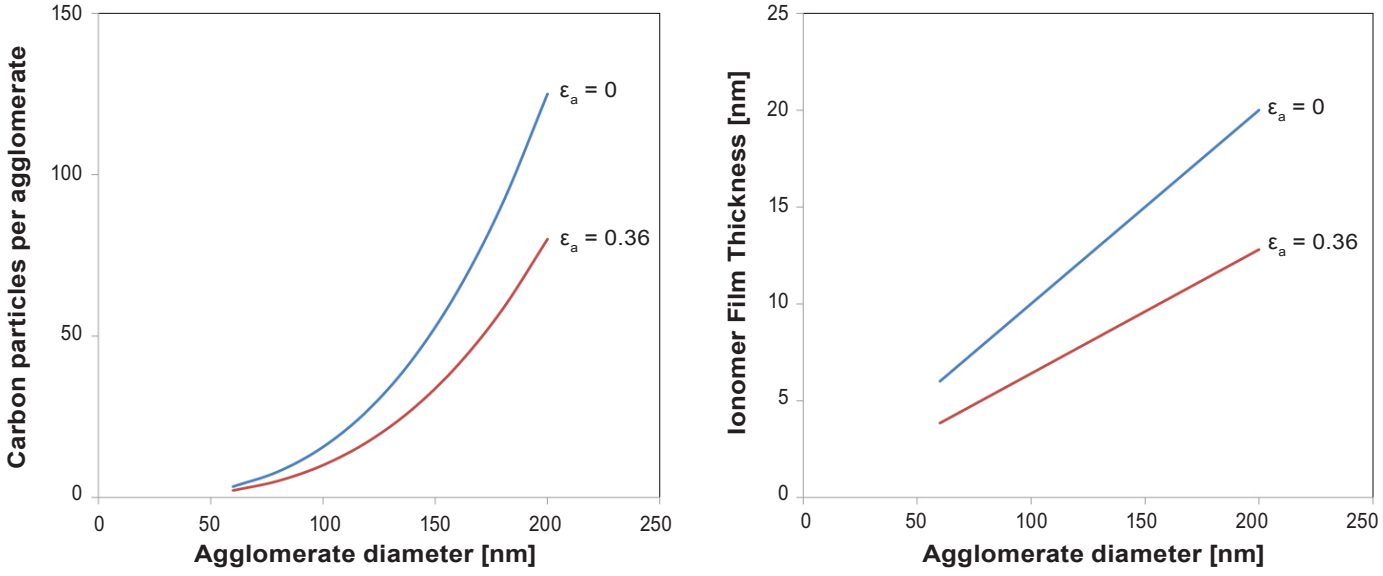


FIGURE 2. Carbon particles per agglomerate and ionomer-film thickness as a function of agglomerate diameter. The C particles are assumed to be 40 nm in diameter and the ionomer-to-C ratio is assumed to be 0.6. Two values of the intra-agglomerate porosity are assumed: $\varepsilon_a = 0$ and $\varepsilon_a = 0.36$, which is the porosity of a bed of randomly close packed spheres.

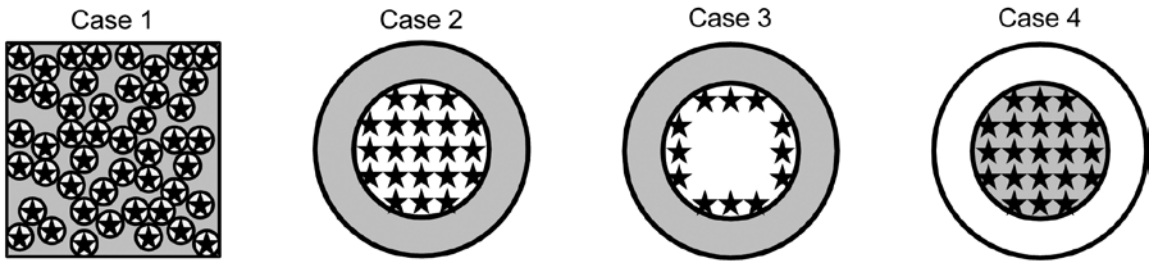


FIGURE 3. Schematic illustration of four limiting cases for O_2 transport in the CCL. Grey represents regions of hindered transport in all cases, while white denotes regions where transport is facile. O_2 reduction occurs at the black stars. Case 1 treats diffusion through the thickness of the electrode. Case 2 treats diffusion through an ionomer film surrounding spherical agglomerates where all interior catalyst sites are fully utilized. Case 3 is similar to Case 2, but only those catalyst sites in contact with the ionomer are active. Case 4 treats transport limitations inside the agglomerates; O_2 transport in the core of the agglomerates could occur in (a) gas with Knudsen effects, (b) ionomer, or (c) liquid water.

densities/porosities and performed cyclic voltammetry and rotating disk electrode measurements in aqueous perchloric-acid electrolyte to study their electrochemical activity and stability. Specific activity values showed that porous films have higher catalytic activity compared to that of denser films with rotating disk electrode measurements. This data will be used to design the density-modulated Pt-TF by optimizing the thickness and the density of the bottom and top layers of the film.

CONCLUSIONS AND UPCOMING ACTIVITIES

The primary focus of this project, to date, has been on developing both the advanced methods and materials required to develop the next-generation of MEAs. It is projected that these MEAs shall have significantly different CCL structures than conventional MEAs. These advanced MEAs may utilize both conventional catalyst materials (e.g., PGMs supported on carbon), as well as novel catalysts (e.g., Pt-TFs). The complete theoretical models and the fundamental understanding derived from the combination of modeling and testing of advanced MEAs with various electrode structures in this project shall eventually be published in the open literature, and this should help the entire PEFC community understand the key transport mechanisms in ultra-low-loaded MEAs, which should lead to the development of improved PEFCs that meet both the cost and performance targets established by DOE for transportation applications.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. M.L. Perry, "Polymer Electrolyte Fuel Cell Diagnostics," presented at the 2017 Spring *Electrochemical Society* Meeting (invited talk), New Orleans, LA, May 2017.

2. M.L. Perry, "High Performance PEFC electrode structures," presented at the 2017 FCTO Annual Merit Review (AMR) meeting, Project ID# FC157, Washington DC, June 2017.

REFERENCES

1. D. Myers, et. al., Rationally designed catalyst layers for PEMFC performance optimization," presented at the 2016 FCTO AMR meeting, Project ID# FC157, Washington DC, June 2016.

2. A. Weber, et al., "A Critical Review of Modeling Transport Phenomena in Polymer-Electrolyte Fuel Cells, J. Electrochem. Soc., **161**, F1254 (2014).