
High-Performance Polymer Electrolyte Fuel Cell Electrode Structures

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Overall Objectives

- Develop improved understanding of the various transport losses in polymer electrolyte fuel cell (PEFC) cathode catalyst layers with state-of-the-art (SOA) ultra-low catalyst loadings (ULCLs) of platinum-group metals (PGMs).
- Obtain this fundamental understanding by developing and validating a detailed microstructural cathode-catalyst layer (CCL) model.
- Utilize this validated CCL 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) 2019 Objectives

- Fabricate thin-film catalysts with graded structures and incorporate these alternative catalyst materials into complete MEAs.
- Initiate the development of a microstructural CCL model for alternative catalyst structures, such as the thin-film catalysts.

- Validate UTRC's microstructural model of CCLs with conventional Pt-supported catalyst using performance of relevant MEAs; the model should reproduce key polarization metrics to within 25%.
- Demonstrate progress toward meeting DOE's 2020 MEA performance targets with carbon-supported catalyst with ULCLs; specifically, ≥ 240 mA/cm² at 0.8 V and ≥ 905 mW/cm² at rated power measured using the Fuel Cell Technologies Office's specified polarization curve protocol.

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 Plan¹:

- (A) Durability (improved understanding of initial transport losses is required to mitigate)
- (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 ULCLs. For simplicity, the team is utilizing MEAs that do not utilize SOA catalyst loadings for the anodes (e.g., ≤ 0.025 mg-PGM/cm²) because making MEAs with this extremely low catalyst loading is challenging on a lab scale (electrodes fabricated by hand), and the key remaining barrier is improving cathode performance with ULCLs. Using higher loadings on the anodes also ensures that the performance losses on the anodes are minimal, which is ideal for studying losses on the cathodes.

FY 2019 Accomplishments

- Utilized UTRC's hierarchical model of the CCL to guide the development of advanced MEAs with reduced transport losses.

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

- Demonstrated MEAs with Pt-alloy catalysts with high performance at 0.8 V and with improved transport losses and higher power densities at rated power than those demonstrated with FY 2018 MEAs.
- Completed an initial model for CCLs utilizing alternative catalysts (e.g., thin-film catalysts), which compared five major variations of possible CCL architectures.
- Completed the development of a new hierarchical model of the CCL, which was successfully validated using both the team's data and multiple data sets in literature on ULCL MEAs.
- Compared performance predictions using UTRC's hierarchical CCL model to experimental data on the impact of varying platinum mass fraction and changes in relative humidity.
- Fabricated new thin-film catalysts with a variety of unique porous microstructures by varying key catalyst-deposition parameters, such as sputtering pressures and substrate materials.

Table 1. Progress toward 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 per electrode)
MEA performance	mA/cm ² _{geo} @ 0.8 V	≥300	≥500
MEA performance	mW/cm ² _{geo} @ 0.675 V	≥1,000	≥950

INTRODUCTION

MEAs with ULCLs of highly active Pt-alloy catalysts have already been demonstrated to exceed DOE's 2020 high-efficiency target of >0.3 A/cm² at 0.8 V [1]; however, meeting the rated-power target of 1 W/cm² with these MEAs has been far more challenging because mass-transport losses in conventional PEFC CCLs increase as the amount of catalyst is decreased [2]. 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 was to improve the fundamental understanding of transport losses in PEFC cathode catalyst layers because the sources of these transport losses had historically not been sufficiently understood, as evidenced by disagreement about the key mechanisms [3]. This has been accomplished by developing and validating a new model of the CCL, which is described below. This improved fundamental understanding has also been used to help guide the design of improved MEAs that have reduced mass-transport losses. These improvements in understanding of transport losses in CCLs with ULCL should also help with the development of more advanced CCLs that utilize new and novel architectures or materials, which can ultimately enable achievement of the simultaneous requirements of high mass activity, low PGM loading, and high power densities.

APPROACH

The initial project objectives have been realized by the development and validation of a new and detailed microstructural model of the CCL. 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 [4]. 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 transport-loss mechanisms. A sufficiently detailed geometric model of the CCL has been developed to uniquely determine what components and mechanisms are major contributors to transport losses in the CCL. This model has been validated using a wide variety of CCL-characterization methods to measure and verify the key geometric details included in the model, as well as by testing of a variety of MEAs, under various operating conditions, to validate the model's performance-prediction capabilities.

The core project team includes the capability to fabricate SOA MEAs using conventional carbon-support catalysts. In addition, UALR has unique capabilities to fabricate thin-film catalyst architectures, which can be used to fabricate CCLs with alternative electrocatalyst structures. Therefore, the team has the ability to make

and test both SOA MEAs and novel catalyst materials, and these capabilities are being 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. Each CCL variant needs to be subjected to a variety of diagnostic tests that help to quantify the different overpotentials. An iterative process is used to develop high-performance MEAs, which is depicted in Figure 1. In addition to the core team, the world-class material-characterization capabilities of the Fuel Cell Performance and Durability (FC-PAD) Consortium are being used to help the team measure key geometric details of the CCLs.

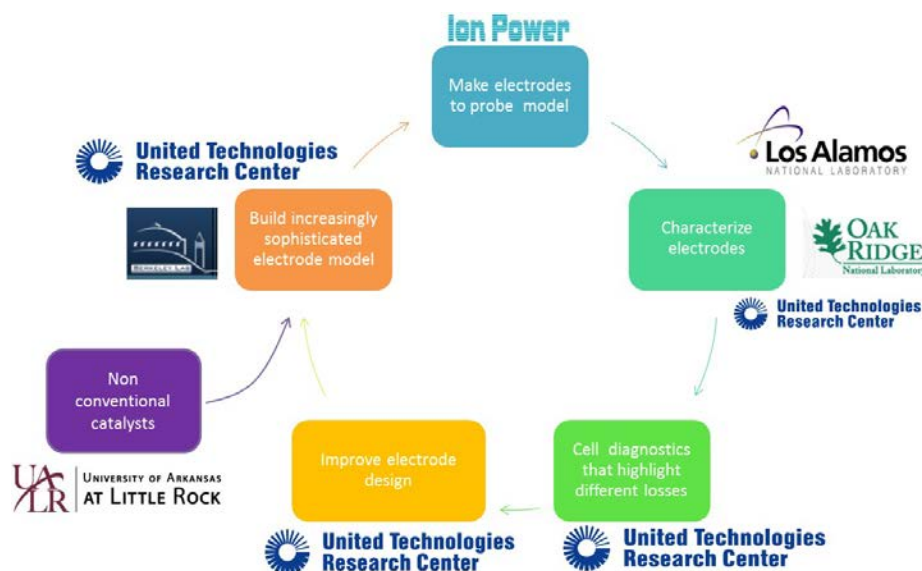


Figure 1. Simple graphical depiction of the team's iterative approach to achieving the objectives.

RESULTS

UTRC has developed and validated a new type of hierarchical CCL model [5]. Conceptually, the model treats the catalyst layer as an assembly of representative spherical volume elements (i.e., agglomerates) that contain supported catalyst particles and are flooded with electrolyte as depicted schematically in Figure 2. Uniquely, this hierarchical model includes both spherical diffusion losses at the scale of platinum particles, as well as transport processes at the scale of the agglomerates, which is the only scale normally considered in many CCL transport models. This hierarchical approach was motivated by the realization that very large fluxes occur on catalyst particles near the outer surface of agglomerates at high overpotentials. The agglomerate in Figure 2 (not to scale) contains an interior core comprising platinum (light grey) on carbon (dark grey) separated by ionomer (dark blue), and an exterior ionomer film (light blue). Relatively large pores between agglomerates, often called secondary pores, are available for gas transport. The structure is largely determined by the morphology of the carbon black support. Carbon blacks in fuel cells typically contain significant amounts of micro, meso, and macroporosity. Electrolyte occupies the mesoporosity while the macroporosity remains open for gas transport. In FY 2018, UTRC validated this new CCL model using both the team's data and results reported on ULCL MEAs in the literature. The model was also rigorously and quantitatively compared to 11 other CCL models, which was described in a published paper [6].

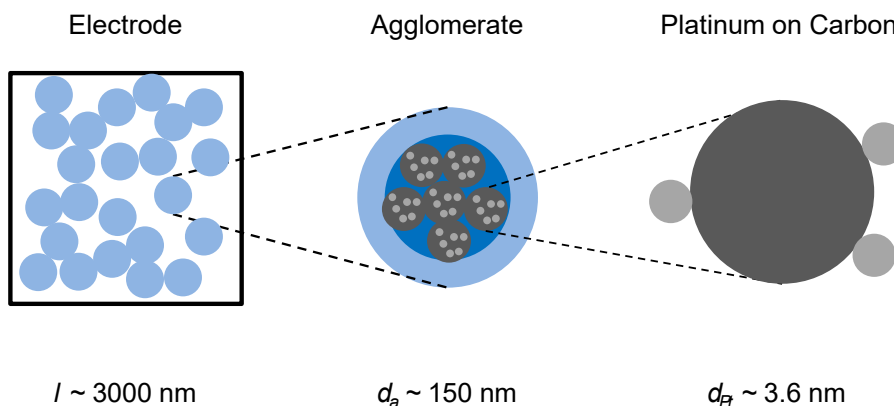


Figure 2. From left to right: schematic representations of (1) agglomerates in a gas diffusion electrode, (2) an individual agglomerate consisting of a core containing platinum, carbon, and ionomer surrounded by an ionomer film, and (3) platinum on a primary carbon particle.

During FY 2019, UTRC published a third paper on the hierarchical CCL model, which includes a complete model for the air electrode and utilizes this to examine the impact of varying platinum mass fraction and changes in relative humidity (RH) [7]. This multiscale model, which includes transport at the nanoparticle, agglomerate, and electrode scales as well as kinetic and ohmic polarizations, was compared to a comprehensive set of data published by General Motors on MEAs with varying ULCLs and a wide range of platinum mass fractions [8]. Figures 3 and 4 illustrate some key results from this work. Figure 3 shows how the optimal Pt mass fraction (i.e., the wt % of Pt on carbon support (ω)) varies with the catalyst loading and the humidity. This optimum occurs at each catalyst loading because as ω decreases the oxygen transport losses inside the agglomerates decrease (due to the lower flux rate to each agglomerate), whereas the ohmic and gas-phase oxygen transport losses increase because the CCL becomes thicker. Lower mass fractions are favored at lower catalyst loadings because the reduced intra-agglomerate transport losses are more than offset by the increased ohmic and gas-phase losses associated with increasing the thickness of the CCL. This trade becomes less favorable under drier conditions because ohmic losses become more significant, hence the optimal ω is higher at lower RH. The relative importance of these various losses in the CCL is illustrated in Figure 4, which is a polarization breakdown for a ULCL at intermediate RH. Gas-phase transport losses in thin CCLs are small relative to oxygen transport at the agglomerate and nanoparticle scales, which is primarily diffusion in the ionomer phase. Ohmic losses are also significant and comparable in magnitude to the combined intra-agglomerate losses. Therefore, improving both oxygen and proton transport in the ionomer is key to boosting performance with these conventional CCLs.

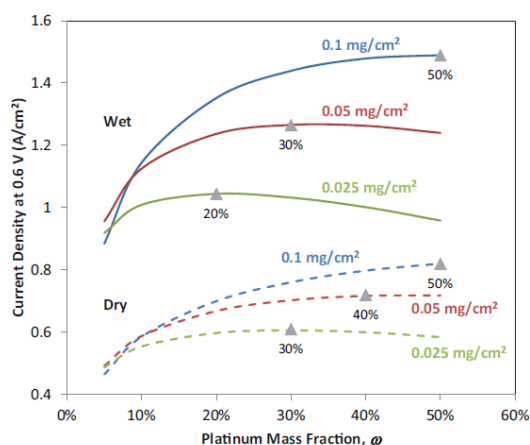


Figure 3. Predicted current densities at 0.6 V versus Pt mass fraction at the three different ULCLs and two different relative humidities: 100% RH (wet) and 65% RH (dry). The maximum current density for each line is depicted by the gray triangles.

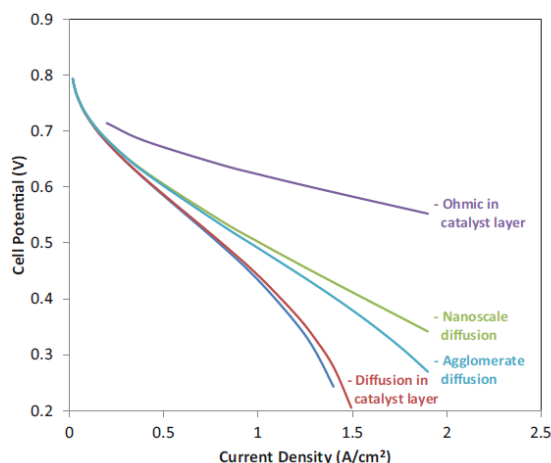


Figure 4. Sources of overpotential in a ULCL CCL with 0.025 mg/cm² of 50 wt % platinum operating on partially humidified air. The bottom dark blue line is the cell performance (i.e., all losses included).

CONCLUSIONS AND UPCOMING ACTIVITIES

UTRC's hierarchical CCL model has been successfully developed and validated. UTRC has also shown that this new model matches the experimentally observed responses of MEAs with ULCLs in a manner that is notably superior to other CCL models described in the literature. UTRC is continuing to extend this hierarchical CCL model to incorporate various types of carbon supports, such as high-surface-area carbons, and validate these various conventional CCL architectures with the appropriate ULCL MEAs. The team is also continuing to use this hierarchical CCL model to guide the development of advanced MEAs that utilize conventional carbon-supported catalysts. UTRC is also developing a microstructural model for CCLs that utilize alternative materials, such as thin-film electrocatalysts. The team has developed the capability to fabricate and test MEAs with thin-film catalysts, and these will be used to validate the models of alternative CCLs. This work should lead to the development of improved PEFCs, which can ultimately meet both the cost and performance targets established by DOE for transportation applications.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. R.M. Darling, "A Comparison of Models for Transport Resistance in Fuel-Cell Catalyst Layers," *JECS* 165 (2018): F1331–1339.
2. R.M. Darling, "Modeling Air Electrodes with Low Platinum Loading," *JECS* 166 (2019): F3058–F3064.
3. M.L. Perry, "High Performance PEFC Electrode Structures," presented at DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation (AMR) Meeting, Washington, DC, May 2019, Project ID# FC157.
4. R.M. Darling, "High Performance PEFC Electrode Structures," presented at Fuel Cell Tech Team Meeting in Detroit, MI, October 2019.

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4. A. Weber, et al., *J. Electrochem. Soc.* 161 (2014): F1254.
5. R.M. Darling, *J. Electrochem. Soc.* 165 (2018): F571.
6. R.M. Darling, *J. Electrochem. Soc.* 165 (2018): F1331.

7. R.M. Darling, *J. Electrochem. Soc.*, 166 (2019): F3058.
8. J.P. Owejan, et al., *J. Electrochem. Soc.* 160 (2013): F824.