# High performance PEFC electrode structures


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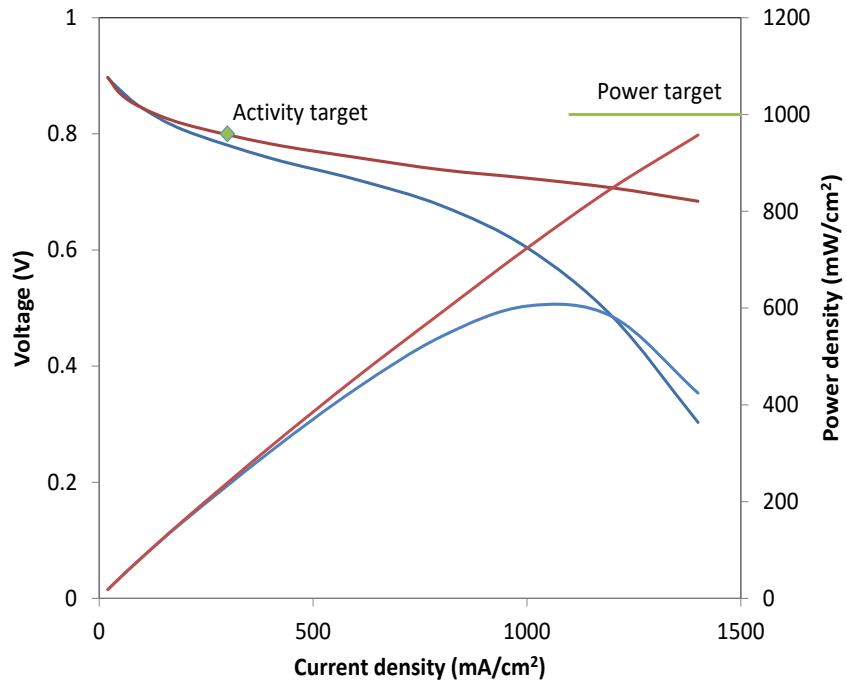
United Technologies Research Center


**FC PAD Consortia Project**

Project ID: **FC157**

DE-EE0007652

June 14, 2018




Polarization curve for an ultra-low-loaded PtNi/C cathode

- Raw in **blue**,
- Transport-corrected in **red**.


***This presentation does not contain any proprietary, confidential, or otherwise restricted information.***

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# Overview

## Timeline

| | |
|---|---|
| Project Start: | October 2016 |
| Actual Start: | Jan 2017 |
| Project Duration: | 45 months (with no-cost extensions) |
| BP-1 End Date: | June 30, 2018 |
| Project End Date: | June 30, 2020 |

## Budget

| | |
|---|---|
| Total Project Budget: | $3,019K |
| ▪ Federal Share | $2,415K |
| ▪ Cost Share (20%) | $604K |
| Total Funds Spent*: | $748K |
| Total Funds for BP-1: | $972K |

*** as of 3/31/2018**

## Key Barriers

- Achieve DOE's 2020 Targets for MEAs

| Characteristic | Units | 2015 Status | 2020 Targets |
|---|---|---|---|
| Platinum-group metal (PGM) total loading (both electrodes) | mg PGM /cm$^2$ | 0.13 | ≤ 0.125 |
| Performance @ 0.8 V | mA/cm$^2$ | 240 | 300 |
| Performance @ rated power (150 kPa$_{abs}$) | **mW/cm$^2$** | **810** | **1,000** |

## Partners

Ion Power

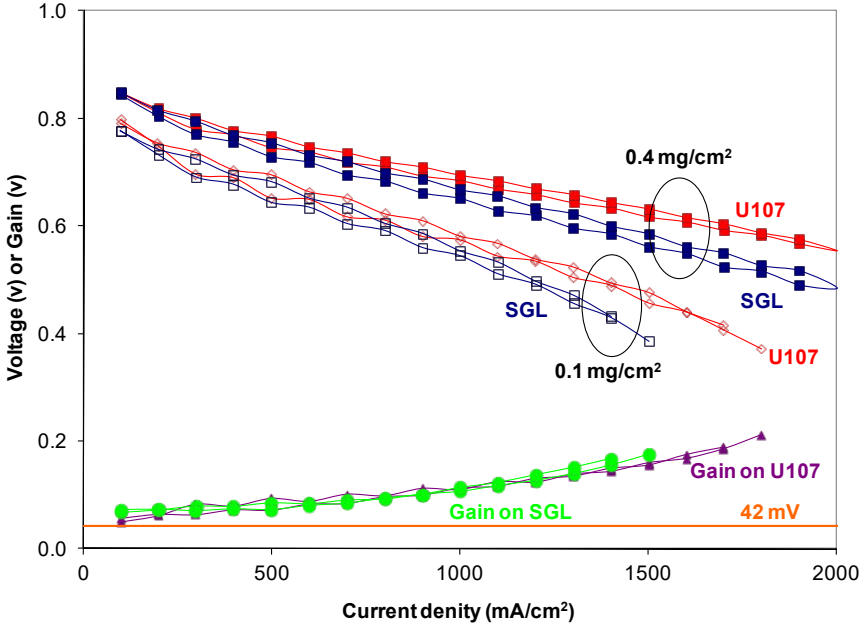
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

UALR UNIVERSITY OF ARKANSAS AT LITTLE ROCK

# Relevance

***Objective:*** Develop *improved fundamental understanding of transport limitations* in a SOA MEA and use this know-how to ***develop and demonstrate high-performance MEAs with ULCLs***

- High-activity ORR catalysts have been developed & demonstrated
  - MEAs with **ultra-low catalyst loadings (ULCLs) can meet activity targets**
  - ***Transport losses are major barrier***
    - Flux rate per catalyst site is increased
      - Transport losses increase
    - MEAs with ULCLs cannot yet meet power density (high current) targets

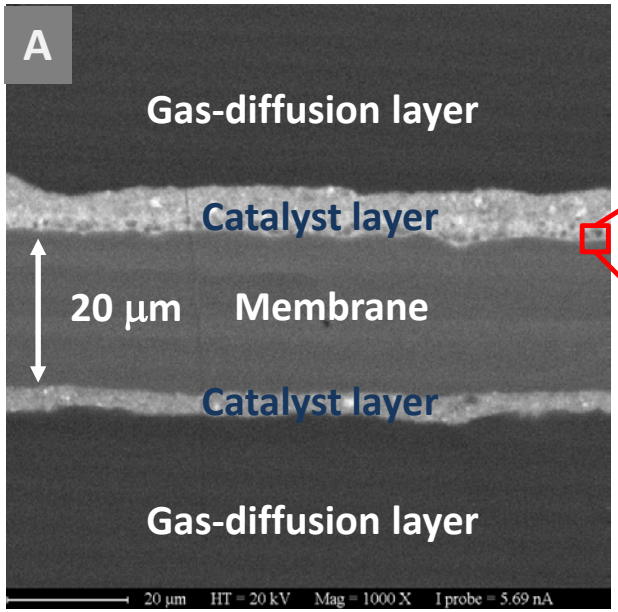


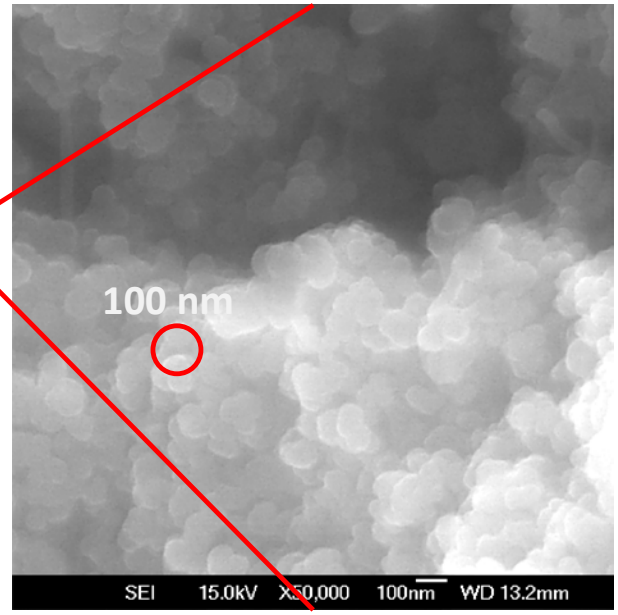

- **Need to reduce transport losses in MEAs with ULCLs**
  - ***First step is to determine actual root-cause mechanisms*** (*e.g.*, not CCL thickness)
  - Fundamental understanding lacking (***previous models did not agree w/ data***)

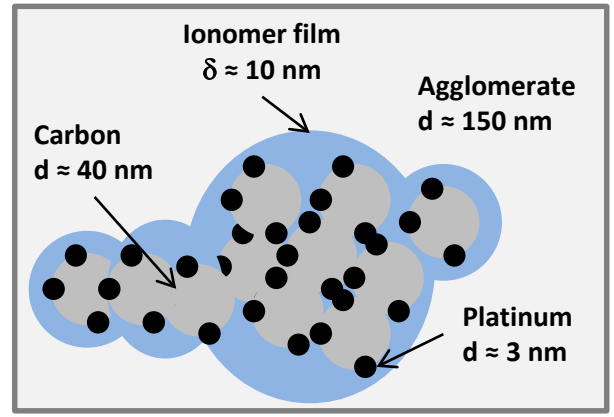
***Improved understanding of transport losses in PEMFCs with ULCLs is needed***

# Technical Approach

## Develop Detailed Geometric (*i.e.*, microstructure) Model of CCL

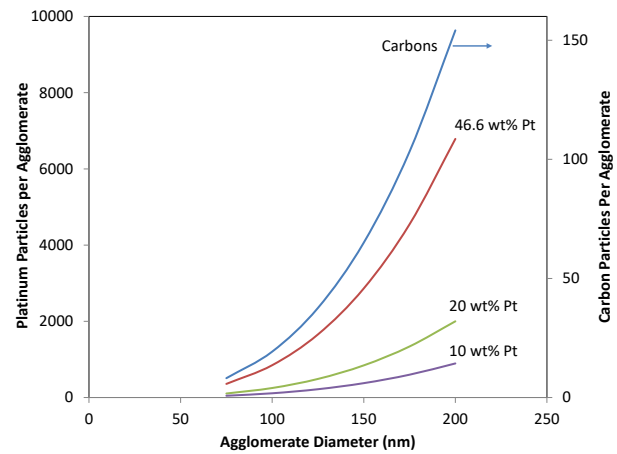



***Cathode catalyst layer (CCL)***
*contains multiple length scales*

1) Develop realistic microstructure model to help discern key mass-transport limitations in MEAs with ULCLs
2) Valid microstructure CCL model with experimental data
3) Use validated CCL model to determine how to potentially mitigate transport losses
4) Develop & demonstrate MEAs with ULCLs with reduced transport losses




***Multiple possible transport-limiting mechanisms within CCL***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# Approach & Collaborations

***With key FC-PAD Consortia roles, to date***

Ion Power

MEAs that exceed DOE's BOL Performance Targets → Durability Testing (ASTs)

Make electrodes to probe model

United Technologies Research Center

Los Alamos NATIONAL LABORATORY

Build increasingly sophisticated electrode model

- ***Core Project team has capability to lead modeling and fabricate key materials required***

Characterize electrodes

Oak Ridge National Laboratory

United Technologies Research Center

- ***FC PAD Consortia can potentially assist with every task shown here***

Non conventional catalysts

University of Arkansas at Little Rock

Improve electrode design

Cell diagnostics that highlight different losses

United Technologies Research Center

United Technologies Research Center

***Iterative process enables both improved understanding & cell performance***



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# Accomplishments & Progress

- Four major Quarterly Milestones have been successfully completed since the 2017 AMR meeting
  - Project is currently on-schedule (revised from original)
  - Subsequent slides show key results for the last 3 milestones
- ***Go/No-Go Milestone*** was validation of UTRC's new CCL Model
  - Model agrees well with in-cell performance data, using CCL geometric parameters measured by a variety of methods
    - This has been successfully completed using both the team's data AND with others' data

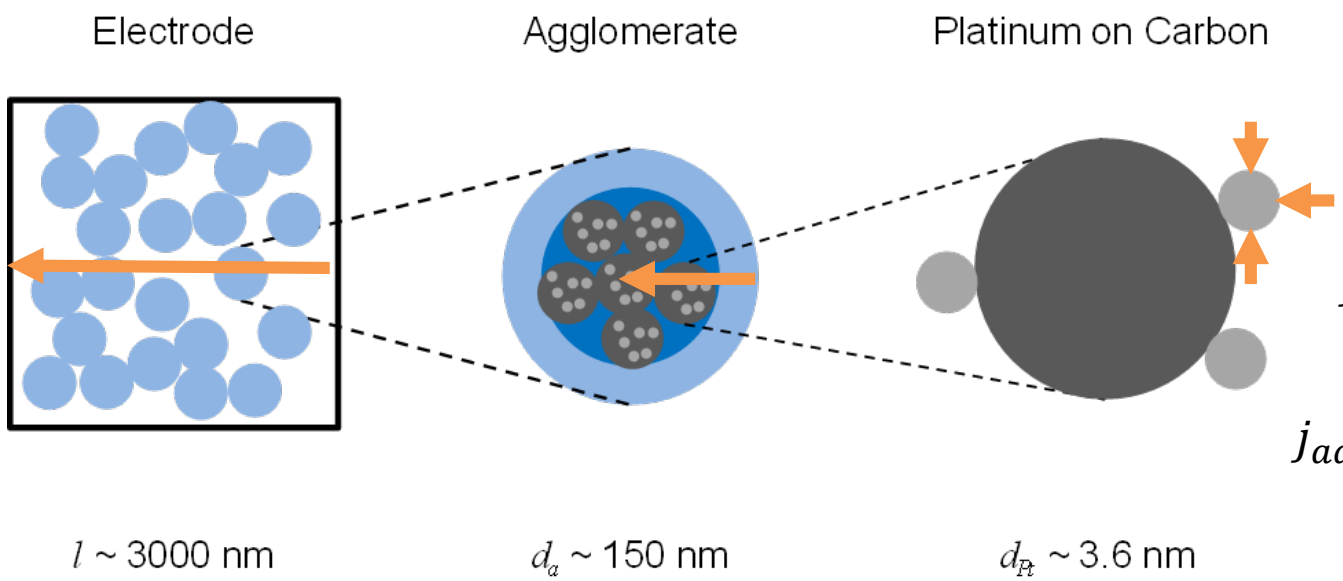
| Milestone I.D. | Tasks | Task Title | Milestone Description and Status |
|---|---|---|---|
| 2 | 3, 4 | Carbon-supported MEA Fabrication | Team has demonstrated SOA performance Pt-only catalyst (Pt loading ≈ 0.1 mg/cm$^2$) with Ion Power MEA. |
| 3 | 2 | Model development and validation | UTRC's microstructural electrode model provided to LBNL and this model has been implemented in FC-PAD's PEFC model. |
| 4 Go/No-Go | 2 | Model development and validation | UTRC's microstructural electrode model has been validated with SOA MEA data, both with Ion Power MEAs and with others' data. |
| 5 | 6 | Novel catalyst MEA Fab | Successfully fabricated a MEA (w/ 12.5-cm$^2$ cell active area) using thin-film catalyst deposited by UALR on GDL and tested by UTRC. |

# Technical Progress

## *UTRC has developed new Hierarchical Model of the CCL*

UTRC's cathode-catalyst layer (CCL) Model is differentiated from previous models by:

- Explicit treatment of diffusion at two different length scales
  1) Agglomerates, and
  2) Platinum nano-particles




$$j_d = \frac{D(c_\infty - c_s)}{r}$$

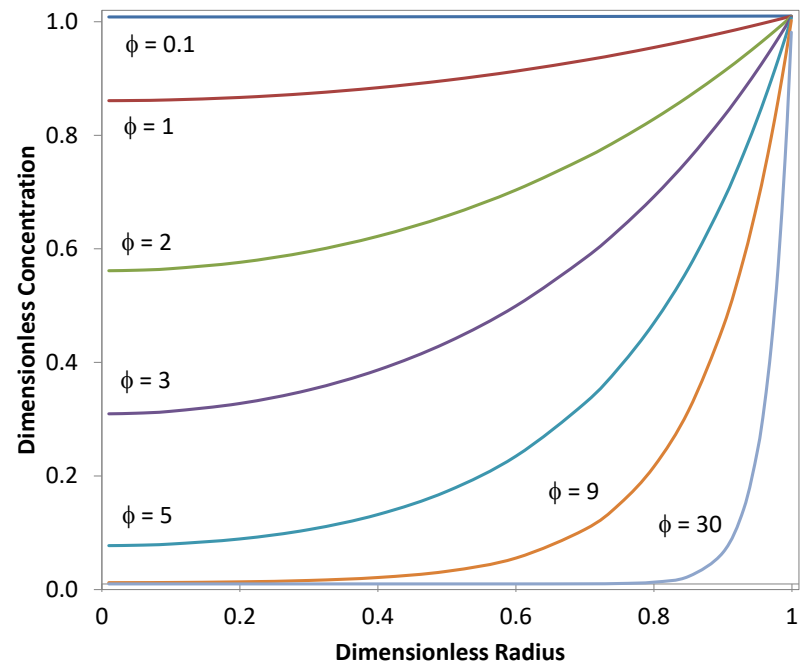
$$j_{ads} = k_{ads}(c_s - c_o)$$

***UTRC CCL model includes transport losses at three different length scales***

# Technical Progress

## *UTRC model accounts for extremely large fluxes to limited catalyst surface area in CCLs with ultra-low Pt loading*

- Model treats agglomerates with Thiele modulus-effectiveness factor approach
  - Thiele modulus, ϕ, is ratio of kinetic and diffusion rates
  - With ultra-low loadings, diffusion dominates and ϕ is large
  - At ϕ = 30, 90% of agglomerate is inactive and reaction is confined to a narrow surface region of the agglomerate
- ***Significant transport losses occur at length scales of the catalyst particles***
  - Use Modified Thiele modulus and effectiveness factor
  - Also modify the "reaction" rate constant to include slow adsorption and local diffusion at scale of Pt particles
  - Relationship between effectiveness factor, η, and ϕ remains the same because overall process is 1st order in oxygen



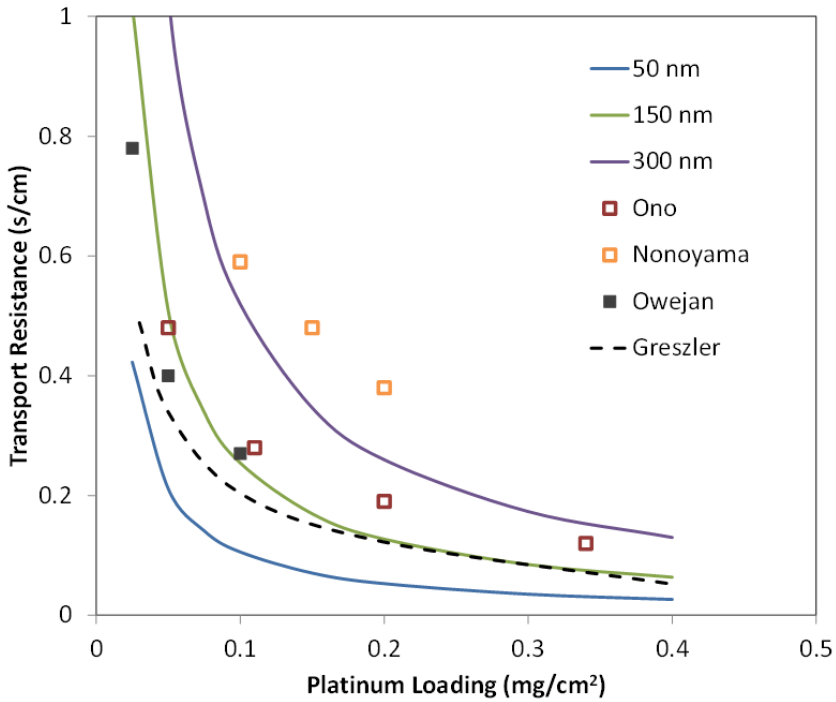

$$j_{Pt} = \frac{i_{Pt}}{n_e F} = \frac{c_\infty}{\frac{1}{k_r} + \frac{d_{Pt}}{D} + \frac{1}{k_{ads}}} = \frac{k_r c_\infty}{1 + \frac{k_r d_{Pt}}{D} + \frac{k_r}{k_{ads}}} = k_* c_\infty$$

***Including transport losses at Pt-particle length scales results in $i_{lim}$ α Pt loadings***

# Technical Progress

## *UTRC's CCL model has been validated using literature data*

- Model validated using:
  - Experimentally measured agglomerate & platinum sizes
  - CCL Transport Resistances reported by GM and TMC




- 300-nm curve is close to the result for ***E-type carbon*** from TMC
- 150-nm curve is close to the result for ***Vulcan carbon*** from GM & Nissan
- 50-nm curve is close to the result with only local losses

**Data sources:**

**Nissan:** ***Ono, Y., et al.*** *2010, ECS. Trans.* ***28****(27), p. 69*

**TMC:** **Nonoyama, N,** ***et al.***, 2011, *JECS* **158**, p. B416

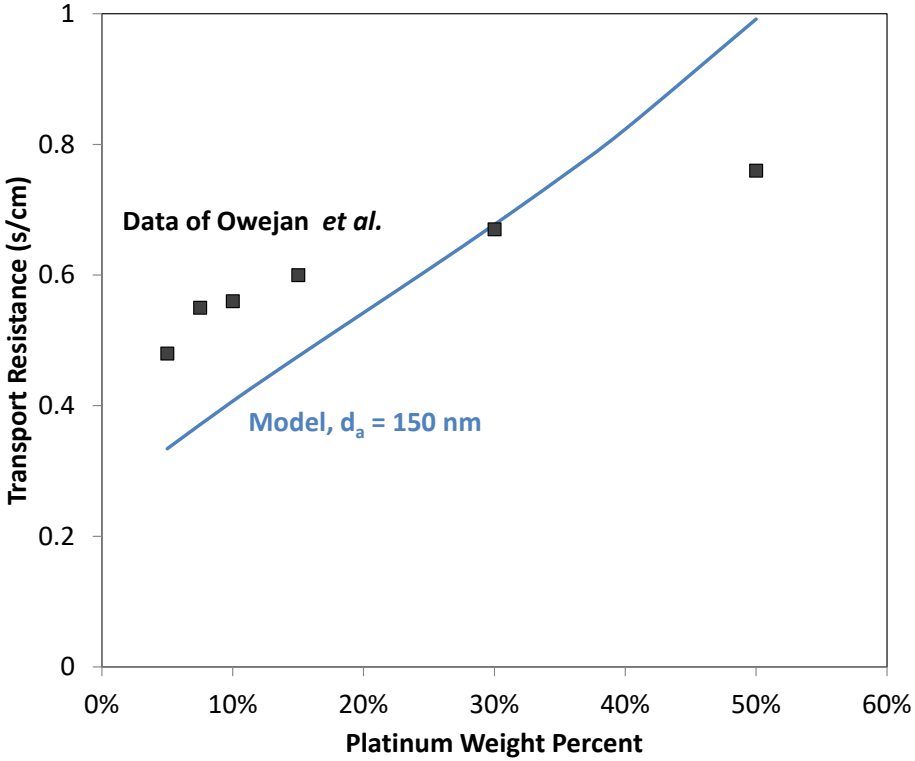
**GM:** ***Owejan, J. P., et al.,*** *2013, JECS* ***160****, p. F824.*

***UTRC model explains why $O_2$-transport resistance increases as Pt content decreases***

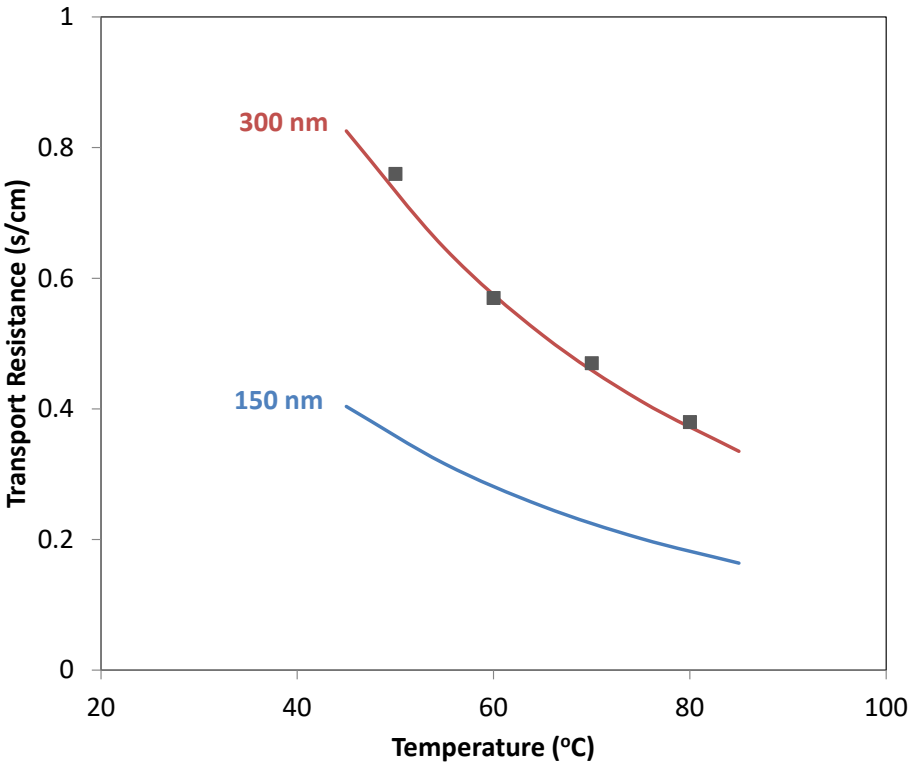
# Technical Progress

## *Model is commensurate with key operating parameters*

- Good agreement with experimental sensitivities to both Pt wt% and *T*




***Owejan, J. P., et al.,*** *2013, JECS* ***160****, p. F824*

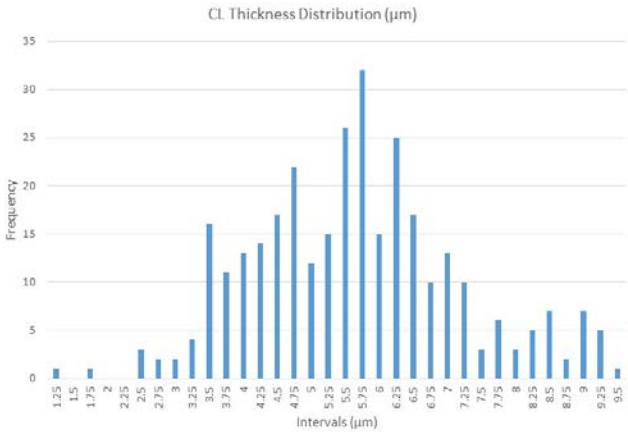


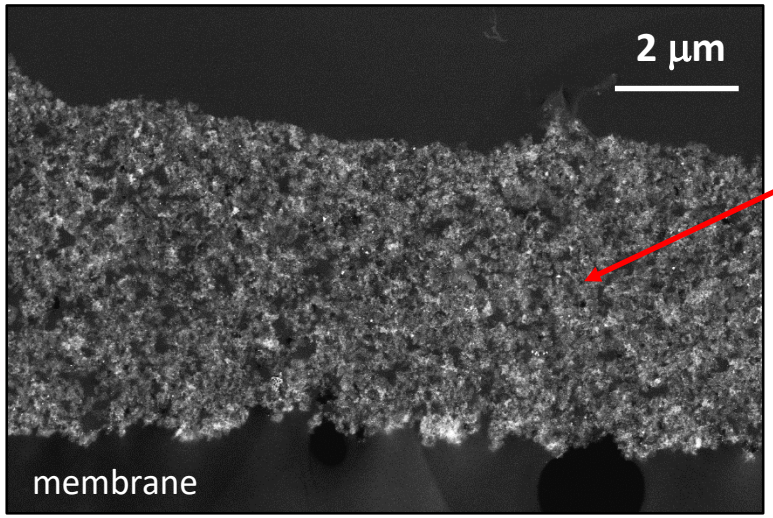

**Nonoyama, N, *et al.***, 2011, *JECS* **158**, p. B416

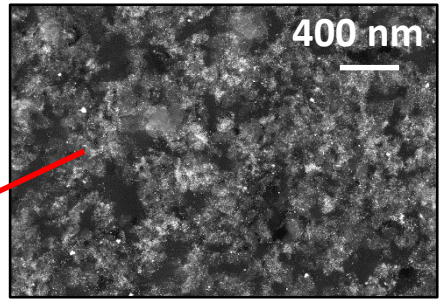
***Manuscript on UTRC's Hierarchical Model has been submitted for publication***

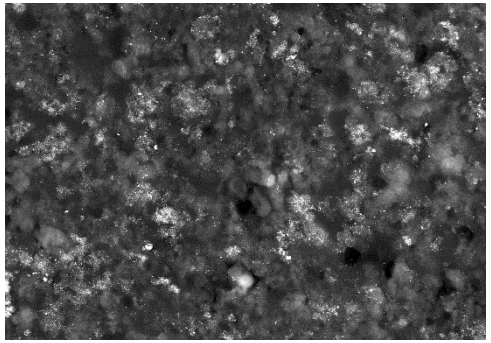
# Technical Progress

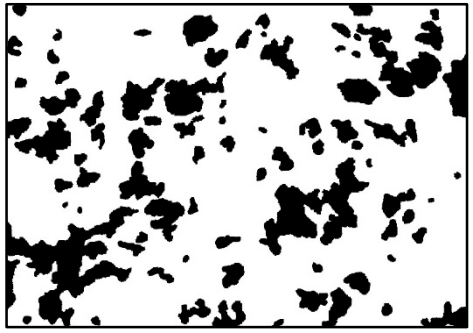
## *Ion Power MEAs characterized in collaboration with FC PAD*

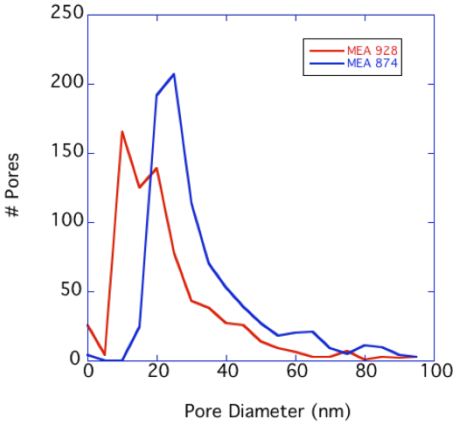




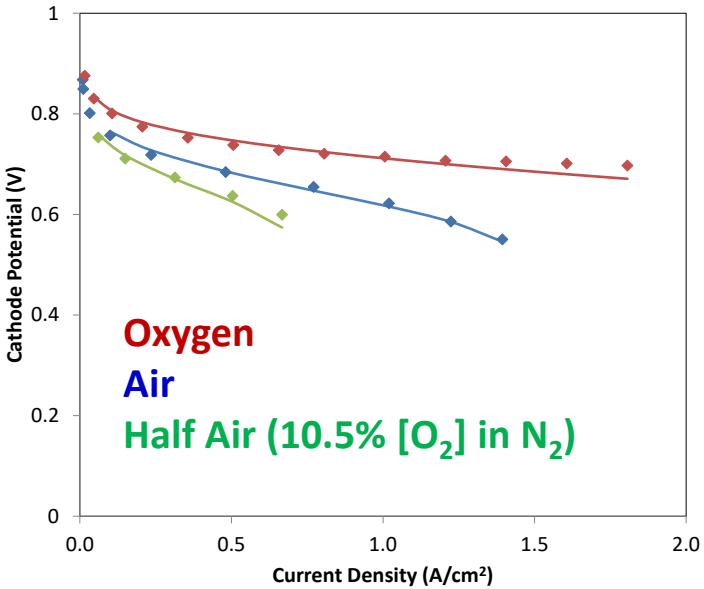



***UTRC model explains why $O_2$-transport resistance increases as Pt content decreases***

# Technical Progress

## *UTRC's CCL model has been validated using team's data*

- Model validated using:
  - Key CCL parameters measured by UTRC and FC-PAD Consortia, including (and method):
    - Pt Loading (XRF)
    - Ionomer Loading (TGA)
    - Electrode Porosity (multiple measurements)
    - Meso-porosity of Catalyst (from supplier)
    - Agglomerate Diameter (multiple measurements)
    - Ionomer Film thickness (calculated)
  - Catalyst and ionomer properties reported in the literature
  - Isolate GDL transport losses
    - Allows calculation of $[O_2]$ at the GDL-CCL interface
  - Isolate membrane resistance losses
    - *In-situ* measurements




Comparison of model to data obtained by UTRC on *Ion Power* MEA with Pt loading of approximately 0.1 mg/cm$^2$

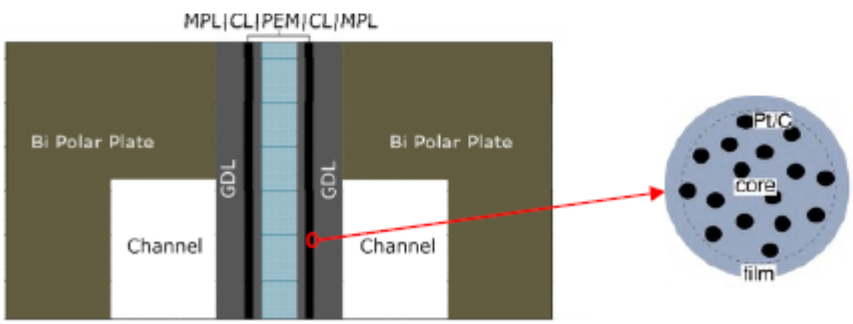
Activity on air and half air are increased 31% relative to oxygen and air, respectively, to fit low current data. No other parameters fit.

***Model predicts performance on oxygen and air using minimal fitting parameters***

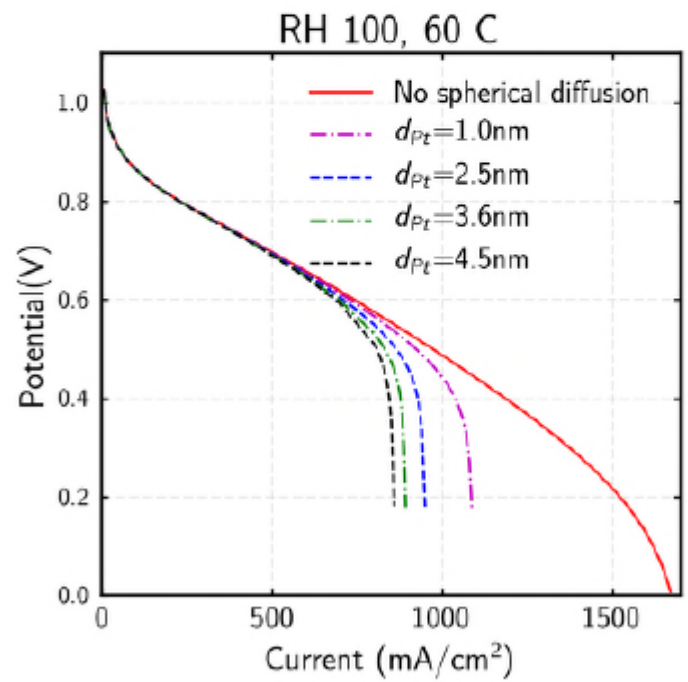
# Inclusion of Spherical Diffusion near Pt Particles in MEA Model

- Full scale 2-D MEA simulation model in COMSOL
- Multi-component diffusion, electronic conduction, protonic conduction, water transport
- Butler-Volmer kinetics for HOR in anode
- Tafel kinetics for ORR in cathode with agglomerate model

- Local spherical diffusion effects near Pt particles included
  - Modified Thiele modulus
  - Modified effectiveness factor




- Cell performance is highly sensitive to size of Pt particle
- No spherical diffusion corresponds to $d_{Pt} = 0$
- Bigger Pt particles induce stronger local diffusion effects, and therefore lower performance



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# Technical Progress: Non-Conventional Catalysts

## Pt Thin-Film (TF) electrocatalysts with different microstructures

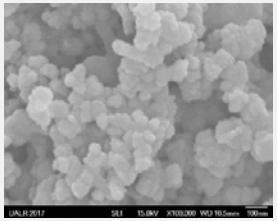
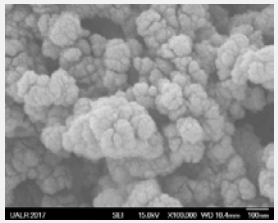
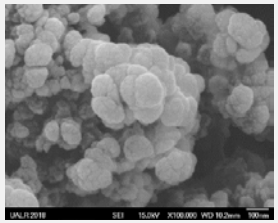
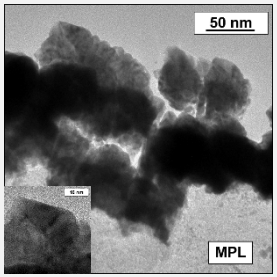
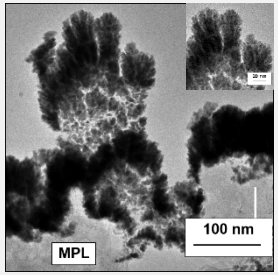
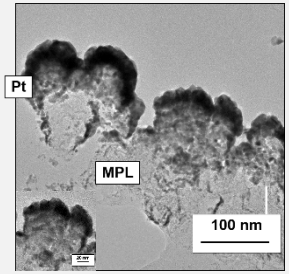
Tansel Karabacak's Group, University of Arkansas at Little Rock

Collaboration with LANL, ORNL, and ANL

Goal: Producing Pt thin film electrocatalysts with various microstructures and investigate their ORR activity and MEA performance.

Approach:

- Deposit Pt thin film catalysts onto MPL with different sputter growth approaches to control the microstructure (e.g. see SEM and TEM images below).
- Microstructure of the Pt layers deposited on a flat surface (e.g. glassy carbon) and rough surface (MPL) are quite different. Therefore, we are currently developing an in-situ method to obtain CV and RDE profiles of these GDEs, which will be more comparable with MEA tests.

| | Normal Angle Deposition (NAD) | High Pressure Sputtering (HIPS) | Glancing Angle Deposition (GLAD) |
|---|---|---|---|
| | | | |
| SEM Images (top-view) |  |  |  |
| TEM |   |   |   |
| | ▪ Densely packed fibrous structure consistent with the zone-T in structure zone model[1] of sputtered thin films<br>▪ Dense Pt layer thickness on MPL surface ~20-50nm. Weight loading ~0.1 $mg_{Pt}/cm^2$.<br>▪ Pt grain size >10 nm | ▪ Cauliflower-like fractal nanocolumnar structure formation consistent with the shadowing effect modeling work[2]<br>▪ Thickness of Pt surface layer ~20-50nm . Weight loading ~0.1 $mg_{Pt}/cm^2$.<br>▪ Pt grain size (columnars) <10 nm | ▪ Enhanced side growth and globular structure formation consistent with the shadowing growth simulation work[2]<br>▪ Thickness of Pt surface layer >~50 nm. Weight loading ~0.1 $mg_{Pt}/cm^2$.<br>▪ Pt grain size >10 nm |

1) http://draftugentbe.webhosting.be/index.php?p=124&m=82

2) Karabacak, T., J. P. Singh, Y-P. Zhao, G-C. Wang, and T-M. Lu. "Scaling during shadowing growth of isolated nanocolumns." *Physical Review B* 68, no. 12 (2003): 125408.

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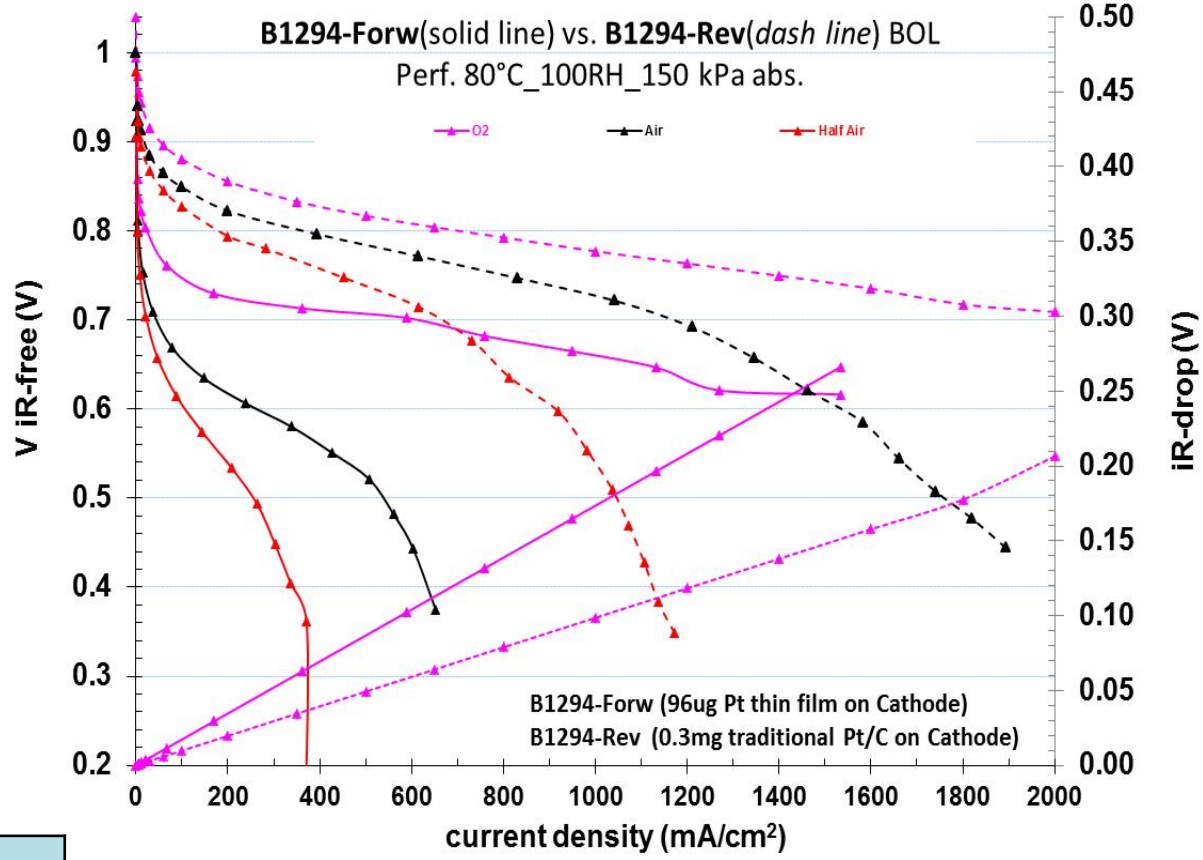
# Technical Progress: Results obtained with a *UALR-fabricated MEA*

- This cell was fabricated by:
  - UALR used GDL as substrate to deposit TF catalyst
  - UTRC built a PEMFC by integrating this UALR-catalyzed GDL with a "half MEA" (membrane with conventional Pt/C catalyst on one side), plus a non-catalyzed GDL
- UTRC ran cell in both Forward and Reverse configurations




| | Anode ("forward") | Cathode ("forward') |
|---|---|---|
| Pt Loading | 0.3 mg/cm$^2$ | 0.096 mg/cm$^2$ |
| GDL | SGL25BC | SGL25BC |
| **Membrane** = Nafion®212 | Active area = 12.25 cm$^2$ | |

- These results show that **UALR's TF-electrode makes a good Anode** with ≈ 0.1 mg Pt/cm$^2$
- Cathode performance is poor, but this is a good result for ***first-of-its-kind* MEA**

***Successfully demonstrated that MEAs can be fabricated from UALR's thin-film catalysts***

# Collaboration & Coordination Summary

*Continued collaboration with Project Partners*:

- A variety of custom MEAs, and other materials, were provided by ***I.P.*** for testing and characterization purposes
- Both UTRC and LANL have tested MEAs fabricated from **UALR** catalyst (and "½-MEAs" provided by ***Ion Power***)

***UTRC has expanded our collaborations with FC PAD Consortia***

- CCL characterization done in a collaboration with:
  - **LANL** (*e.g.*, SEM, XRF, TGA, MIP, and BET)
  - **ORNL** (*e.g.*, TEM of MEAs, CCLs, & catalyst)
- Continue to collaborate with **LBNL** on modeling work

***5 significant collaboration partners on this project, to date***

# Proposed Future Work

***Major goals for the next year of this project:***

- Use improved understanding of mass-transport loss mechanisms to improve CCLs & fabricate MEAs with improved performance
- Continue to make improvements to Pt/C-catalyst model
- Develop new microstructure-CCL model with thin-film (TF) catalysts

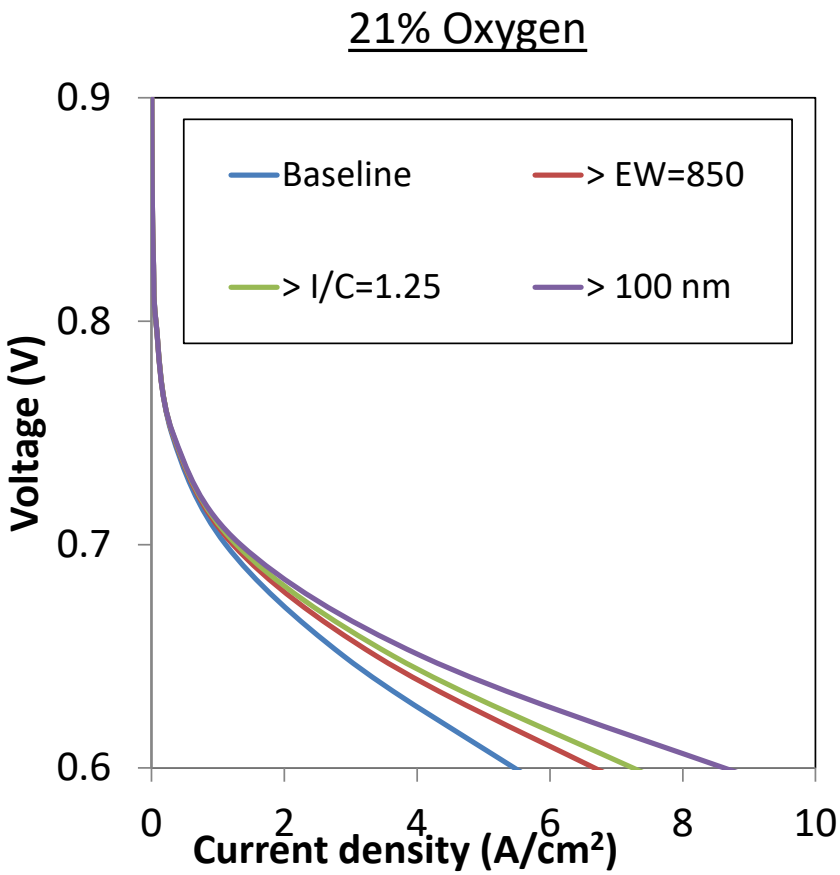
| Milestone I.D. | Tasks | Task Title | Brief Milestone Description |
|---|---|---|---|
| 6 (4Q2018) | 3, 4 | Carbon-supported MEA Fabrication | Demonstrate MEA that can meet 2020 performance targets with high stoichiometric flow rates (*e.g.*, ≥ 1 W/cm$^2$ at rated power). |
| 7 (1Q2019) | 2 | Model development and validation | Initial thin-film catalyst CCL structure model completed and incorporated into complete PEFC model that can generate polarization curves with requisite cell operating parameter inputs. |
| 8 Go/No-Go (2Q2019) | 2, 3, 4, & 5 | Model validation and C-supported MEA performance | Validate microstructural model with improved accuracy, and demonstrate MEA with significantly improved transport-limited performance (*e.g.*, ≥ 905 mW/cm$^2$ at rated power measured using the specified polarization curve protocol in FCTO's MYRDD. |

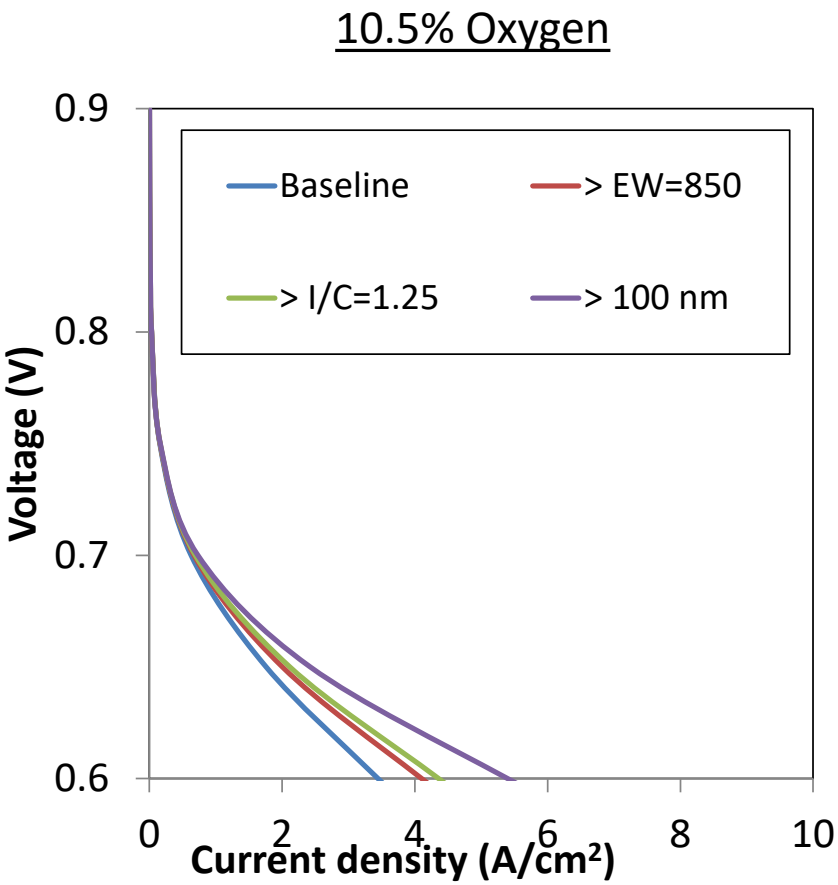
***Major focus will be on demonstrating improved MEAs/CCLs with conventional catalysts***

*Any proposed future work is subject to change based on funding levels*

# Projected Improvements with Pt/C MEAs

***Use UTRC's Hierarchal Model to predict optimal CCL composition***



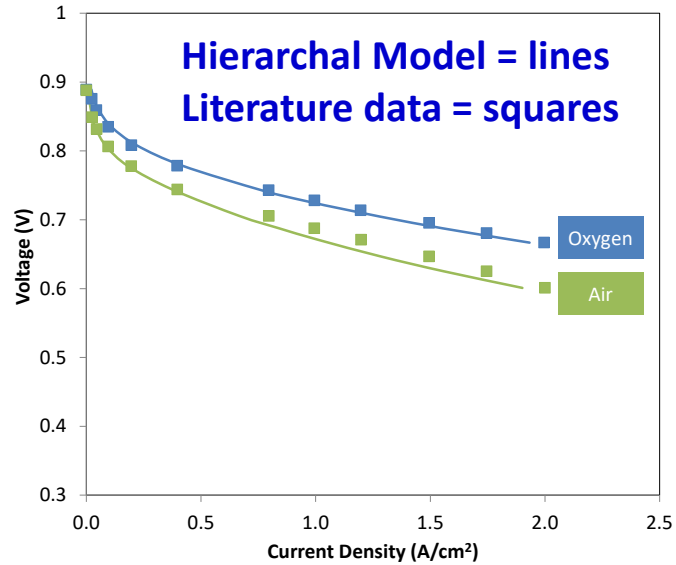

Key changes: Lower EW, slight increase in I/C, smaller agglomerates.

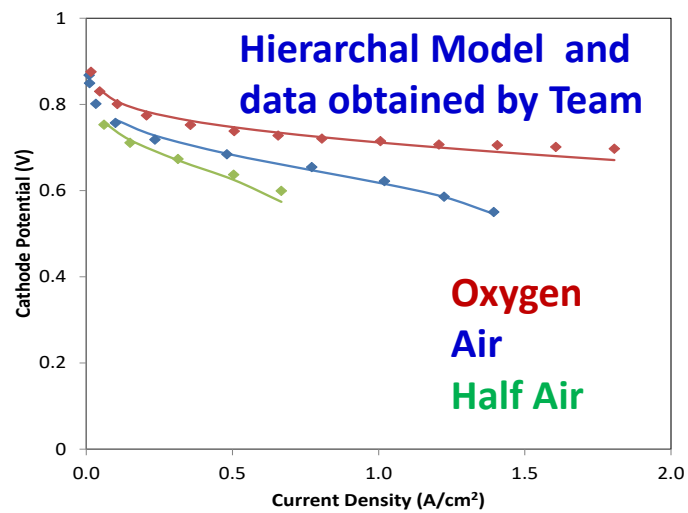
***Any proposed future work is subject to change based on funding levels.***

# Summary

United Technologies Research Center

- Major barrier to meeting *DOE's 2020 MEA Targets* are mass-transport losses in cathode-catalyst layers (CCLs)
- Hierarchal CCL Model incorporates mass transport at multiple length scales and has been validated with two data sets
- Hierarchal CCL Model accurately predicts limiting currents that are proportional to Pt loading, and other trends (*e.g.*, *T*, wt%)
- Hierarchal Model predictions shall be used to develop advanced MEAs with reduced transport losses
- Project includes both conventional (Pt/C) and thin-film (TF) catalysts
- TF-based MEAs have been successfully fabricated and tested




***Best path to MEAs with reduced transport losses is accurate CCL model***

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## Project Partners

Ion Power

- Stephen Grot

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## FC PAD Partners

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Oak Ridge National Laboratory

- Karren More

Berkeley Lab

- Adam Weber
- Lalit Pant

# TECHNICAL BACK-UP SLIDES



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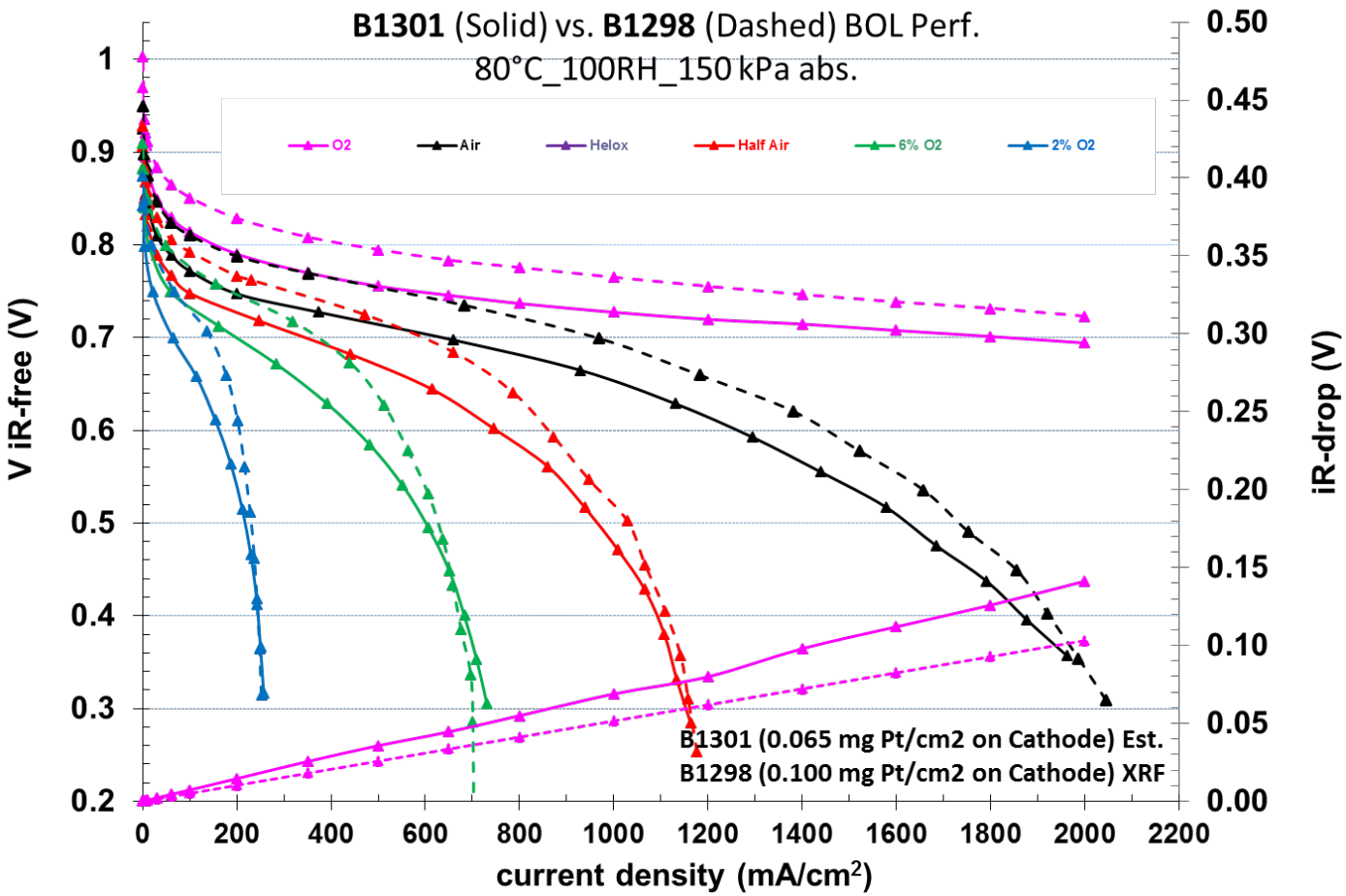
# UTRC Cell Performance with Ion Power MEAs

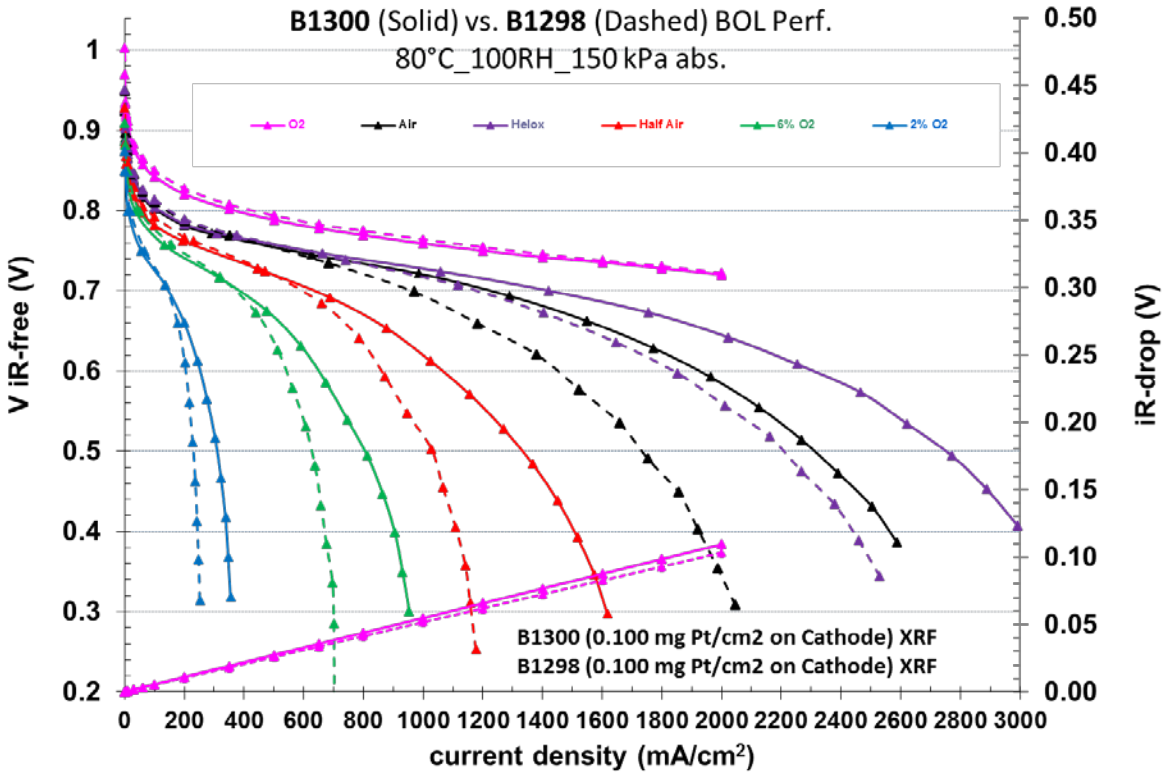
1) Cell B1298: SGL25BC/ I.P.-MEA /SGL25BC, 12.25-cm$^2$_SP-triple serpentine, co-flows.
2) Cell B1301: Same as B1298, with similar I.P.-MEA (with presumably lower Pt loading)
   - Same components, except "smooth" *vs*. "wavy" electrodes

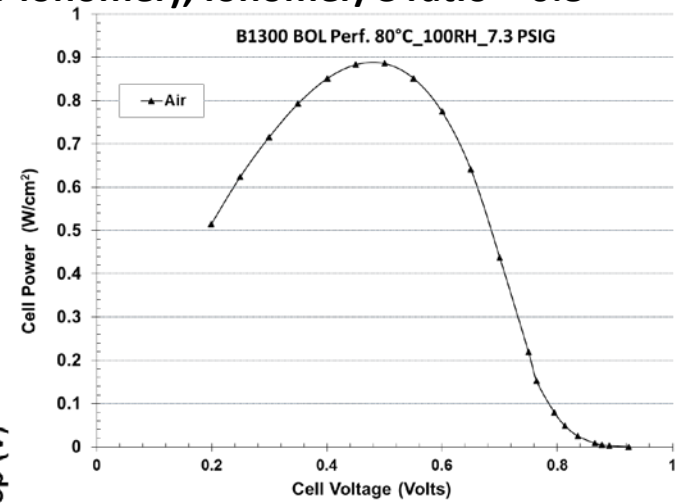



Testing conditions: 80°C_100%RH_150kPa abs

# UTRC Cell Performance with Ion Power MEAs

1) Cell B1298: SGL25BC/ I.P.-MEA /SGL25BC, 12.25-cm$^2$_SP-triple serpentine, co-flows.
2) Cell B1300: SGL25BC/ I.P.-MEA /UTRC-GDL, 12.25-cm$^2$_SP-triple serpentine, co-flows.
- Same I.P.-MEA with TEC10V20E catalyst, I.P. ink (1100 EW ionomer), Ionomer/C ratio = 0.8




| | B1300 IP MEA | B1298 IP MEA |
|---|---|---|
| Pt size & Pt Loading | 25 A<br>0.10 mg (XRF) | |
| H2-Xover | 6.9 mA/cm$^2$ | 4.6 mA/cm$^2$ |
| ECA (m$^2$/g-Pt) | 63 | |
| Mass activity A-mg Pt | 0.30 | |
| CI @ 1A_$O_2$ | 55 mV | 52 mV |
| H2-Pump | 6.0 mOhm | 6.2 mOhm |

Testing conditions: 80°C_100%RH_150kPa abs

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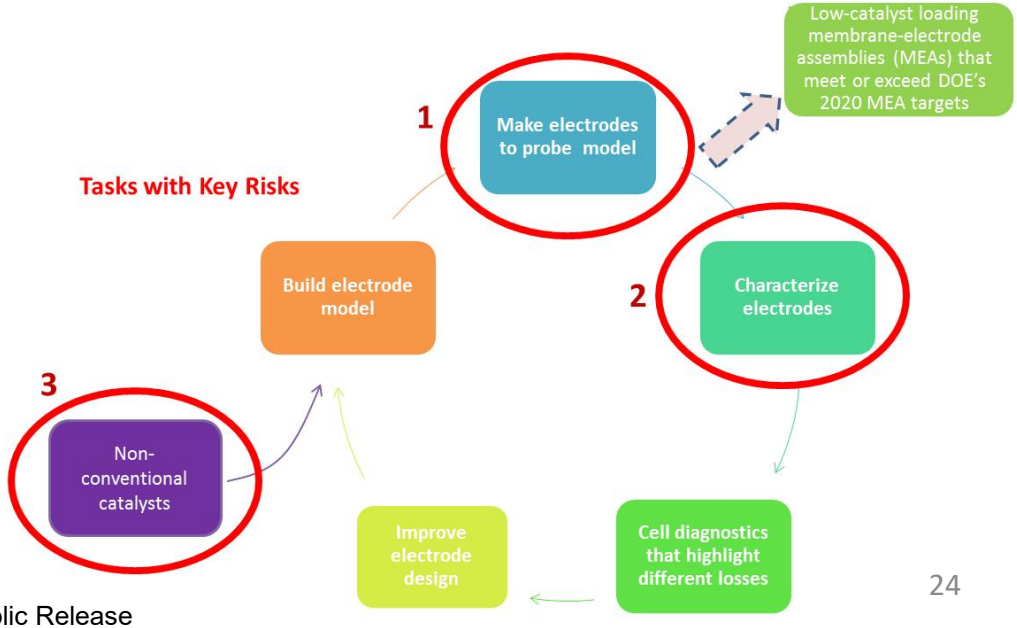
# Critical Assumptions & Potential Issues

Key **technical risks** include:

1) Fabrication of CCLs with sufficient differentiation to uniquely identify model parameters and/or sufficiently uniform ULCLs
2) Capability to adequately characterize structures to provide accurate input for the geometric models.
3) Availability of sufficient quantities of alternative catalysts (*e.g.*, thin-film and/or nanoframe structures) to support the fabrication of MEAs by conventional techniques

***Team has the capabilities, experience, and expertise to address these issues.***

***Also have FC PAD Consortia resources that can potentially help mitigate these as well.***



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# Supplementary Agglomerate Modeling Details

Normal Thiele modulus without spherical diffusion is defined as:

$$\phi_0 = \frac{r_{agg}}{3}\sqrt{\frac{k_c}{D_{O_2N}\epsilon_{agg}^{1.5}}},$$

where, $r_{agg}$-agglomerate core radius, $D_{O_2N}$ - diffusivity of oxygen in bulk ionomer, $\epsilon_{agg}$- fraction of ionomer in agglomerate, $k_c$-reaction constant.

The corrected Thiele modulus after adding spherical diffusion is defined as:

$$\phi = \frac{\phi_0}{\sqrt{1 + \varphi\, exp\left(\frac{-\alpha F}{RT}\eta\right)}},$$

where, $\varphi$ is given as:

$$\varphi = \frac{d_{pt} i_0}{4F D_{O_2N}\epsilon_{agg}^{1.5} c_{O_2}^{ref}},$$

$d_{pt}$ is the diameter of platinum particle.

Conventional effectiveness factor based on corrected Thiele modulus is given as:

$$E_r^0 = \frac{1}{\phi}\left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi}\right),$$

The updated effectiveness factor describing diminishing of total current w.r.t. kinetic current at surface is given as:

$$E_r = \frac{E_r^0}{1 + \varphi \exp\left(\frac{-\alpha F}{RT}\eta\right)}$$



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